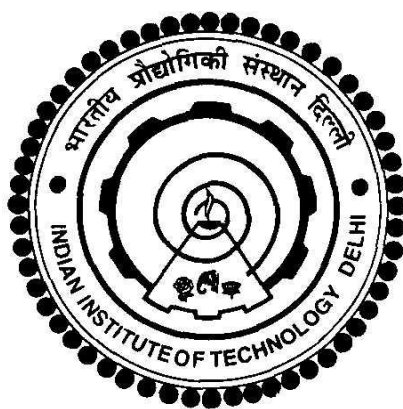


**EXPERIMENTAL AND THEORETICAL
INVESTIGATIONS ON HEAVY OIL UPGRADING**

RAJEEV KUMAR



**DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

MAY 2021

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EXPERIMENTAL AND THEORETICAL INVESTIGATIONS ON HEAVY OIL UPGRADING

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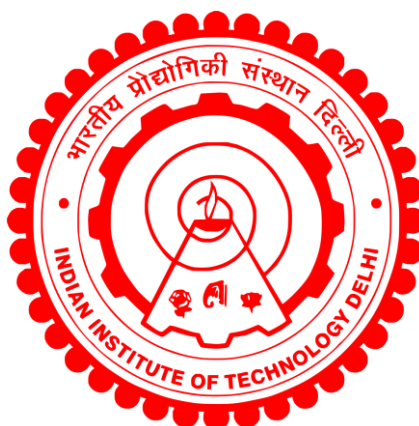
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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

MAY 2021

Dedicated to my Wife, Priyanka
for her endless love, support, and encouragement

CERTIFICATE

This is to certify that the thesis titled “**Experimental and theoretical investigations on heavy oil upgrading**” being submitted by **Mr. Rajeev Kumar** to the Indian Institute of Technology Delhi for the award of degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. Mr. Rajeev Kumar has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.



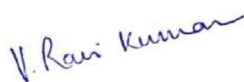
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ACKNOWLEDGMENTS

The names you would find in this acknowledgement page is the very basis of the existence of this thesis. Their support and encouragement have been incredible which helped me to focus on my research work and I thoroughly enjoyed the doctorate experience. At the onset, I would like to express my sincere gratitude to my academic supervisor **Prof. Sreedevi Upadhyayula** for her guidance, unrelenting support, and persistence throughout this journey. It has been a great pleasure and privilege for me to work under her supervision. She has given me the right advice starting from comprehensive examination, synopsis till completion of the thesis chapters. My heartfelt thanks to her for all her support during the tenure.

My special thanks to my industrial supervisor **Dr. Ravi Kumar V** for motivating me to enroll for doctoral program and motivating for research work. I thank him for the guidance, support and the conducive environment provided for innovation. I express my sincere gratitude for his help in meticulously correcting the thesis chapters.

I thank my research committee members **Prof. K. K. Pant, Dr. Ali Haider and Dr. K. A. Subramanian** for their invaluable suggestions and directions especially during my research work.

I would like to thank my lab and IITD mate **Dr. Abhijeet, Dr. Tanmoy, Dr. Gul and Mr. Shashank** for their help in completing all official duties at IIT during the entire program.

I thank my friends and colleagues at BPCL, **Ms. Sonal, Dr. Raj, Mr. Muzaffar, Mr. Prashant, Dr. Pranab, Mr. Seetaram, Mr. Bhanwar, Dr. Mathew, Dr. Chanchal, Dr. Arundhathi, Mr. Ankur, Dr. Shivanand, Dr. Kishore. Dr. Viswanathan, Mr. Bhargava and Mr. Bharat Sajjan** for their support and motivation during the program.

I am thankful to the management of Bharat Petroleum Corporation Ltd for providing me the advanced infrastructure available at Corporate R&D Centre (CRDC) to carry out my research work with freedom. Special thanks to **Mr. K. V. Seshadri** (former Executive Director – R&D) who has been instrumental behind introducing this opportunity for R&D professionals.

Finally, my words are redundant for my lovable parents (*Smt. Shail Devi & Shri S.N. Sahi*), elders, *Sulochana & Basant* and youngers, *Kritanshi, Kritika, Kartik, Rani and Mukesh*, in the family for moral support and understanding for my long time absence from home and unavailability. **Ms. Unnati Kumar**, she has been supporting since she was 2 and provided me immense energy to complete the thesis at her 9, I must thank her big.

I would like to express my sincere gratitude to all who either directly or indirectly contributed towards the successful completion of this work.

May 2021



Rajeev Kumar

ABSTRACT

In a refinery operation, the profitability margin is increased when heavy /opportunity crudes diet are increased in refining process without affecting its processability. High asphaltene content in heavy oils can affect the desalter operation by forming strong water emulsions with asphaltene, leading to fouling in heat exchangers means excess fuel firing and thus, increased CO₂ emissions, and/or coking issues due to incompatibility. If this happens, refineries can lose more than the advantage of purchasing the heavy crudes. Thus the accurate prediction of crude oil blend compatibility can be a robust tool which refinery operators would like to use before starting any refinery process. Current benchmark processes to determine crude compatibility is done experimentally and takes minimum weeks' time to complete.

In the present work, a quick and accurate crude oil blend compatibility (K Model) is developed by coefficients obtained by regression analysis between the ratios of physical parameters of known crude oils and composite compatibility measure determined from multiple compatibility test results of the known crude oils. To get the in-depth understanding and to develop simple analytical tool, CP-MAS ¹³C-NMR analysis is used along with other analytical techniques such as FT-IR, TLC-FID, CHNS, TGA and XRD for characterizing asphaltenes. CP-MAS ¹³C-NMR data in correlation with other characterization data revealed that with increase of aliphatic-carbon with respect to aromatic-carbon in an asphaltenic structure would lead to incompatibility. This finding was substantiated through desalting and fouling experiments.

A method (s) and system (s) has been attempted for predicting detailed characterization of unknown crudes based on few physical parameters within minutes otherwise standard laboratory based testing takes 3-4 weeks' time. In addition to this, investigation of physical parameters of crudes and their impact on kinematic viscosity of residue and heavy products has been carried out to increase heavy oil processing.

For upgrading heavy oils, a two stage solvent deasphalting dearomatization (SD-A²) process has been conceptualized for upgrading heavy oils. In the first stage, pentane, heptane and refinery untreated/ treated naphtha streams were investigated for deasphalting performance. To enhance the deasphalting, spent catalyst from Fluid Catalytic Cracking Unit (FCCU) is used in the first stage which showed increase in pitch yields up to 2 wt%. In the second stage, six polar solvents viz. sulfolane, N-methylpyrrolidone (NMP), tri-ethylene glycol, tetra-ethylene glycol, furfural and N-formylmorpholine (NFM) have been analyzed for dearomatization. The phase equilibria behaviour of these six potential polar solvents was investigated, including the interaction behaviour of their components with heavy oil components using ternary phase diagrams at ambient conditions, before selecting the most suitable solvent for dearomatization. Based on the phase equilibria data, distribution coefficient, selectivity, and performance index (PI) of the solvents was also estimated. For the oils which have C₆–C₁₅ carbon range, the universal quasi-chemical UNIQUAC model was used to predict the liquid–liquid equilibria (LLE) and solvent NMP gave highest PI for the high carbon number feedstock. The effects of solvent types and solvent to feed ratio on the deasphalting performance was also investigated. Finally, the DAO obtained at each stage was fed to a FCC bench-scale unit and the results showed significant improvement in gasoline yields up to 5 wt% and the coke was also lowered to 2 wt%.

संक्षेप

रिफाइनरी संचालन में, लाभप्रदता मार्जिन तब बढ़ जाता है जब रिफाइनिंग प्रक्रिया में इसकी प्रक्रिया क्षमता को प्रभावित किए बिना भारी / अवसरपूर्ण कूड की मात्रा बढ़ा दी जाए। भारी तेलों में ज्यादा अस्फाल्टीन होने से पानी के साथ मजबूत इमल्शन बनाकर डिसाल्टर ऑपरेशन को प्रभावित कर सकती है, अस्फाल्टीन के कारण हीट एक्सचेंजर्स में फाउलिंग होता है, इसका मतलब है अतिरिक्त ईंधन की खपत और इस प्रकार, असंगतता के कारण कार्बन डाइऑक्साइड उत्सर्जन में वृद्धि, और / या कोकिंग होने की संभावना है। यदि ऐसा होता है, तो रिफाइनरियों को भारी कूड खरीदने के लाभ से अधिक नुकसान हो सकता है। इस प्रकार कच्चे तेल के मिश्रण की अनुकूलता की सटीक भविष्यवाणी के लिए एक मजबूत उपकरण जरूरी है जिसे रिफाइनरी संचालक किसी भी रिफाइनरी प्रक्रिया को शुरू करने से पहले उपयोग करना चाहेंगे। कूड संगतता निर्धारित करने के लिए वर्तमान बेंचमार्क प्रक्रियाएं सिर्फ प्रयोगात्मक रूप से ही की जाती हैं और इसे पूरा करने में न्यूनतम एक सप्ताह या उससे ज्यादा का समय लगता है।

वर्तमान कार्य में, ज्ञात कच्चे तेल के भौतिक मापदंडों के अनुपात और ज्ञात कच्चे तेल के कई संगतता परीक्षण परिणामों से निर्धारित समग्र संगतता माप के बीच प्रतिगमन विश्लेषण द्वारा प्राप्त गुणांक द्वारा एक त्वरित और सटीक कच्चे तेल मिश्रण संगतता (के मॉडल) विकसित किया गया है। गहन समझ प्राप्त करने और सरल विश्लेषणात्मक उपकरण विकसित करने के लिए, सीपी-एमएस ¹³सी-एनएमआर विश्लेषण का उपयोग के साथ साथ अन्य विश्लेषणात्मक तकनीकों जैसे एफ़टी-आईआर, टीएलसी-एफ़आईडी, सीएचएनएस, टीजीए एवम एक्सआरडी का उपयोग अस्फाल्टीन को चिह्नित करने के लिए किया जाता है। अन्य लक्षण वर्णन डाटा के साथ सहसंबंध में सीपी-एमएस ¹³सी-एनएमआर डाटा से पता चला है कि एक अस्फाल्टीन संरचना में ऐलिफटिक-कार्बन के संबंध में ऐरोमाटिक्स-कार्बन की वृद्धि से असंगति हो जाएगी। इस खोज को डिसाल्टीङ्ग और फाउलिंग प्रयोगों के माध्यम से प्रमाणित किया गया।

कुछ भौतिक मापदंडों के आधार पर अज्ञात कूड के विस्तृत लक्षण वर्णन की भविष्यवाणी के लिए मिनटों के भीतर ही एक विधि(ओं) और प्रणाली(ओं) का प्रयास किया गया है, अन्यथा मानक प्रयोगशाला आधारित परीक्षण में

3-4 सप्ताह का समय लगता है। इसके अलावा, भारी तेल प्रसंस्करण को बढ़ाने के लिए कच्चे तेल के भौतिक मापदंडों और अवशेषों और भारी उत्पादों की विस्कोसिटी पर उनके प्रभाव की जांच की गई है।

भारी तेलों के उन्नयन के लिए, भारी तेलों के उन्नयन के लिए एक दो-चरण विलायक डिअस्फाल्टिंग डियरोमैटाइजेशन (एसडी-ए²) प्रक्रिया की अवधारणा की गई है। पहले चरण में, पेटेन, हेप्टेन और रिफाइनरी अनुपचारित/उपचारित नेफ्था धाराओं की डिअस्फाल्टिंग प्रदर्शन के लिए जांच की गई है। डिअस्फाल्टिंग को बढ़ाने के लिए, पहले चरण में फ्लुइड कैटेलेटिक क्रैकिंग यूनिट (एफसीसीयू) से उपयोग किए गए उत्प्रेरक का इस्तेमाल किया है, जिससे पिच की पैदावार में 2 भार% तक की वृद्धि देखी गई। दूसरे चरण में, छह ध्रुवीय सॉल्वेंट्स जैसे कि सल्फोलेन, एन-मिथाइलपाइरोलिडोन (एनएमपी), ट्राई-एथिलीन ग्लाइकॉल, टेट्रा-एथिलीन ग्लाइकॉल, फुरफुरल और एन-फॉर्मिलमॉर्फोलिन (एनएफएम) का विश्लेषण डिओमैटाइजेशन के लिए किया गया है। इन छह संभावित ध्रुवीय सॉल्वेंट्स के चरण संतुलन व्यवहार की जांच की गई, जिसमें डिओमैटाइजेशन के लिए सबसे उपयुक्त विलायक का चयन करने से पहले परिवेशी परिस्थितियों में टर्नरी चरण आरेखों का उपयोग करते हुए भारी तेल घटकों के साथ उनके घटकों के अंतःक्रियात्मक व्यवहार शामिल किए गए। चरण संतुलन डेटा के आधार पर, सॉल्वेंट्स के वितरण गुणांक, चयनात्मकता और प्रदर्शन सूचकांक (पीआई) का भी अनुमान लगाया गया सी₆-सी₁₅ कार्बन रेंज वाले तेलों के लिए, तरल-तरल संतुलन (एलएलई) की भविष्यवाणी करने के लिए सार्वभौमिक अर्ध-रासायनिक यूएनआईक्यूएसी मॉडल का उपयोग किया गया और विलायक एनएमपी ने उच्च कार्बन संख्या फीडस्टॉक के लिए उच्चतम पीआई देखा गया। डिअस्फाल्टिंग प्रदर्शन पर विलायक के प्रकार और फ़ीड अनुपात के लिए विलायक के प्रभावों की भी जांच की गई। अंत में, प्रत्येक चरण में प्राप्त डीएओ को एफसीसी बेंच-स्केल यूनिट में टेस्ट किया गया और परिणामों ने 5 भार% तक गैसोलीन की पैदावार में महत्वपूर्ण बढ़ावा देखा गया और साथ में कोक को भी 2 भार% तक कम पाया गया।

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NOMENCLATURE

AEL	Arab Extra Light
AH	Arab Heavy
AL	Arab Light
AM	Arab Mix
API	American Petroleum Institute
AR	Atmospheric residue
Ar	Aromatics
As	Asphaltene
AVU	Atmospheric Vacuum Unit
BL	Belayim
BPMARRK	Bharat, Prashant, Muzaffar Ahsan, Ravi, Rajeev Kumar
C	Concentration of oil in aromatic solvent
CCR	Conradson Carbon Residue
CCRU	Continuous Catalytic Reformer Unit
CCU	Catalytic Cracking Unit
CDU	Crude Distillation Unit
CHNS	Carbon, Hydrogen, Nitrogen, Sulphur
CII	Colloidal Instability Index
CLO	Clarified Oil
CP-MAS	Cross Polarization Magic Angle Spinning
CS	Cutter Stock
CSI	Colloidal Stability Index
CRDC	Corporate R&D Centre
C ₅	Pentane
C ₇	Heptane
DAO	Deasphalted Oil
DCU	Delayed Coker Unit
DHA	Detailed Hydrocarbon Analysis
DHDS	Diesel Hydro-Desulphurization
D1	Differential in crude price
D2	Differential in processing cost
FBP	Final Boiling Point
FCCU	Fluid Catalytic Cracking Unit
FID	Flame Ionization Detector
FO	Fuel Oil
FP	Flash Point
FR	Flocculation Ratio
FT-IR	Fourier Transform Infrared Spectroscopy
GC	Gas-Chromatography
GO	Gas Oil
HCU	Hydrocracker
H _D	Heptane Dilution
HN	Heavy Naphtha
IBP	Initial Boiling Point

IN	Insolubility Number
IPR	Intellectual Property Rights
IR	Infrared (IR)
K	Compatibility (Kompatibility)
Kero	Kerosene
KR	Kochi Refinery
KV	Kinematic Viscosity
KW	Kuwait
KV-VR	Kinematic Viscosity of Vacuum Residue
LCO	Light Cycle Oil
LEDA	Low Energy Deasphalting
LLE	Liquid-Liquid-Extraction
LN	Light Naphtha
LPG	Liquefied Petroleum Gas
LSFO	Low Sulphur Fuel Oil
LSHS	Low Sulphur Heavy Stock
MCR	Micro Carbon Residue
MH	Mumbai High
ML	Marib Light
MR	Mumbai Refinery
MS	Mass Spectroscopy
MW	Molecular weight
N	Nitrogen
NB	Nile Blend
NFM	N-formylmorpholine
Ni	Nickel
NMP	N-methylpyrrolidone
NMR	Nuclear Magnetic Resonance
OAP	Onset asphaltene precipitation
OCM	Oil Compatibility Model
P	Heithaus Parameter
P _a	Solubility of asphaltene in oil
PI	Performance Index
P _o	Solubility power of maltenes in oil
PP	Pour Point
QQA	Qualitative-Quantitative Analysis
R	Resins
RCR	Ramsbottom Carbon Residue
RG	Ras Gharib
RGA	Refinery Gas Analyzer
RGP	Refinery Gate Price
RJ	Rajasthan
RMSE	Root Mean Square Error
RN	Raffinate Naphtha

ROSE	Residuum Oil Supercritical Extraction
RPC	Refinery processing cost
S	Sulphur
SARA	Saturates, Aromatics, Resins, Asphaltene
Sat	Saturates
SB	Saharan Blend
S _{BN}	Solubility Number
SCP	Stability Cross Plot
SDA	Solvent Deasphalting
SD-A ²	Solvent Deasphalting Dearomatization
SG	Specific Gravity
SimDist	Simulated Distillation
SP	Stankiewicz Plot
TBP	True Boiling Point
TE	Toluene Equivalence
TETRA	Tetra-ethylene glycol
TGA	Thermo gravimetric analysis
TLC	Thin Layer Chromatography
TMS	Sulfolane
TRI	Tri-ethylene glycol
UCO	Unconverted Oil
UNQUAC	Universal quasi-chemical
UV	Ultraviolet
UZ	Upper Zakum
V	Vanadium
VDU	Vacuum Distillation
VGO	Vacuum Gas Oil
VR	Vacuum residue
V _s	Volume of solvent
V _T	Titration volume
W _A	mass of oil sample
W _C	West Canadian
XRD	X-Ray Diffraction