CONVERSION OF DI-AROMATICS TO MONO-AROMATICS OVER Y-ZEOLITE AT FCC CONDITIONS

SATHEESH V K

DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY DELHI
JULY 2024

CONVERSION OF DI-AROMATICS TO MONO-AROMATICS OVER Y-ZEOLITE AT FCC CONDITIONS

by

SATHEESH V K

Department of Chemical Engineering

Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

to the

Indian Institute of Technology Delhi

July, 2024

Dedicated to my family
for the endless love, support, and encouragement

CERTIFICATE

This is to certify that the thesis entitled "Conversion of di-aromatics to mono-aromatics over Y-zeolite at FCC conditions", being submitted by Satheesh V K to the Indian Institute of Technology, Delhi, is worthy of consideration for the award of the degree of Doctor of Philosophy and is a record of the original bonafide research work carried out by him under our guidance and supervision. The results contained 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. We certify that he has pursued the prescribed course of research.

Date: 15th July, 2024

Dr. Kamal K. Pant
Professor
Department of Chemical Engineering
Indian Institute of Technology, Delhi
Hauz Khas, New Delhi -110016

Dr. Divesh Bhatia
Associate Professor
Department of Chemical Engineering
Indian Institute of Technology, Delhi
Hauz Khas, New Delhi -110016

ACKNOWLEDGMENTS

My praises and thanks to the **Almighty** and my **Parents** for the blessings throughout my research work and completing the research successfully.

I am highly indebted to my supervisors, **Prof Kamal K Pant** and **Prof Divesh Bhatia**, for their insightful feedback, unwavering guidance, and continuous encouragement. Your mentorship and expertise have been irreplaceable in formulizing my research work.

I express my sincere thanks to the members of my SRC, **Prof. Sreedevi Upadhyayula, Prof. Manoj Ramteke** and **Prof. M. R. Ravi** for their valuable insights, constructive criticism, and dedicated time spent reviewing and evaluating my work. Your suggestions have significantly improved the quality of my research work.

I am extremely grateful to the management of R&D Centre, Indian Oil Corporation Ltd for allowing me to carry out the research activities effectively and sparing me the resources, experimental facilities and characterization / analysis support for the research and learning.

This endeavour would not have been possible without the support, inspiration and cooperation by **Sh. Debasis Bhattacharyya**, Executive Director, R&D Centre, IOCL. I express my deepest gratitude to him.

I am grateful to **Dr. Alex C. Pulikottil** and **Dr. A.V. Karthikeyani** for providing me the space to conduct the experiments and guidance. Also, my thanks to **Mr. Sandup Bhutia, Dr. C. Chidambaram, Dr. Vatsala Sukumaran, Dr. K B Srinivas** and **Mr. A Vignesh** for the support provided in carrying my research work.

I extremely thankful to **Dr. K.O. Xavier** for his insightful suggestion and invaluable inputs to develop and refine my thoughts.

I am forever thankful to my father-in-law, **Mr. T.K. Sivaraman**, for his continuous and unwavering support and constant impel in successful completion of my research work.

Completion of this research work would not have been accomplished without the unconditional support, understanding and patience of my wife - **Ajita**, my daughter - **Nikita** and my son - **Nihal**. Your profound belief in me has been a constant source of motivation. I am always indebted to you all.

Last but not the least, I would like to thank all who directly or indirectly has encouraged and supported me in completing this research work. Thank you from the bottom of my heart.

Date: 15th July, 2024

Satheesh V K

ABSTRACT

Due to the increasing demand of chemicals/petrochemicals and global plans on reduction of fossil fuels in view of reduction of CO_2 emissions, there is a thrust in refining sector to convert the various hydrocarbon streams into value-added chemicals/petrochemicals for improving the refining margin. Light Cycle Oil (LCO) from Fluid Catalytic Cracking (FCC) unit is normally blended in diesel pool after improving its cetane number in the hydrotreating unit. Therefore, opportunity exists for the conversion of LCO to predominantly chemicals/petrochemicals feedstock in FCC unit itself through the selection of proper Y zeolite catalyst. Upon detailed characterization of LCO used in the current study, it was found that LCO consists of more than 60% di-aromatic molecules.

In the current research work, experimental cracking was carried out in fixed and fluidized bed micro reactors using a two-ring naphthenic compound (Decalin), di-aromatic compound [2-methyl naphthalene (2MN)], and Y zeolite based catalyst to assess the formation of mono-aromatics. The gas and liquid products were analysed in Refinery Gas Analyser and Mass Spectroscopy equipped with Gas Chromatography to identify the individual molecules formed during cracking. For ease of analysis, the product molecules were lumped together based on the type of molecules as Gas, paraffin + naphthene (PN), mono-aromatics (MA), naphtheno-aromatics (NA), di-aromatics(DA), tri-aromatics (TA), and Coke.

The cracking pathways were studied using Decalin and 2MN separately over Y zeolite. It was noted that Coke and Gas was found increased with increase in conversion while all other products were decreased. While analysing the products formed based on various classes of reactions such as cracking, alkylation, hydrogen transfer, ring opening and ring contraction, it was found that cracking and hydrogen transfer reactions predominates over others at higher

conversion. This can be explained based on higher acidity of Y zeolite. The extent of such reaction was much lower in case of 2MN due to its higher stability as compared to Decalin.

Cracking study was further extended for 2MN using a catalyst derived from Y zeolite. Experiments were conducted at various reaction temperatures and catalyst-to-oil ratios pertaining to FCC unit operation. Based on the analysis of products, it was found that the alkylation and cracking reactions were predominant in this case. The reaction pathways indicate that the coke was predominantly formed through poly-aromatics by disproportionation reactions. Hydrogen was also formed during this reaction, which will be consumed in the hydrogen transfer and ring opening/cracking reactions. The major pathway for the mono-aromatics formation was the hydrogen transfer followed by cracking and ring opening reactions. Estimation of kinetic parameters was also carried out for the reaction network considered. Model prediction showed a good match with the experimental data.

The effect of hydrogen donor (Decalin) concentration and rare earth content of catalyst on improving the yield of mono-aromatics was also studied. It was found that both hydrogen donor and high rare earth content catalyst were increasing the conversion of 2MN to mono-aromatics. Finally, LCO was also cracked over the catalyst to identify the feasibility of increasing the mono-aromatics yield in FCC unit. Overall, the current research will provide a systematic insight that will help in designing the optimized catalyst and the hydrogen rich stream to be used for maximizing the conversion of LCO to mono-aromatics in FCC unit.

सार

रसायनों/पेट्रोकेमिकल्स की बढ़ती मांग और CO_2 उत्सर्जन में कमी के मद्देनजर जीवाश्म ईंधन में कमी की वैश्विक योजनाओं के कारण, रिफाइनिंग मार्जिन में सुधार के लिए विभिन्न हाइड्रोकार्बन धाराओं को मूल्य वर्धित रसायनों/पेट्रोकेमिकल्स में परिवर्तित करने के लिए रिफाइनिंग क्षेत्र में जोर दिया जा रहा है। एफसीसी यूनिट से लाइट साइकिल ऑयल (एलसीओ) को हाइड्रोट्रीटिंग यूनिट में सीटेन संख्या में सुधार के बाद आम तौर पर डीजल पूल में मिश्रित किया जाता है। इसलिए, उचित वाई जिओलाइट उत्प्रेरक के चयन के माध्यम से एफसीसी इकाई में ही एलसीओ को मुख्य रूप से रसायनों/पेट्रोकेमिकल्स फीडस्टॉक में बदलने का अवसर मौजूद है। एलसीओ के विस्तृत लक्षण वर्णन पर, यह पाया गया कि एलसीओ में 60% से अधिक डाय-एरोमैटिक अणु होते हैं।

वर्तमान शोध कार्य में, मूल्यांकन के लिए दो-रिंग नैफ्थेनिक यौगिक (डेकालिन), डाय-एरोमैटिक यौगिक (2-मिथाइल नेफ्थलीन (2MN)) और वाई जिओलाइट आधारित उत्प्रेरक का उपयोग करके स्थिर और द्रवीकृत बिस्तर माइक्रो रिएक्टरों में प्रायोगिक क्रैकिंग अध्ययन आयोजित किया गया था। मोनो-एरोमैटिक्स का निर्माण. क्रैकिंग अध्ययन में गठित व्यक्तिगत अणुओं की पहचान करने के लिए गैस और तरल उत्पादों का क्रमशः गैस क्रोमैटोग्राफी से सुसज्जित रिफाइनरी गैस विश्लेषक और मास स्पेक्ट्रोस्कोपी में विश्लेषण किया गया था। विश्लेषण में आसानी के लिए, उत्पाद अणुओं को गैस, पैराफिन + नेफ्थीन (पीएन), मोनो-एरोमैटिक्स (एमए), नेफ्थेनो-एरोमैटिक्स (एनए), डी-एरोमैटिक्स (डीए), ट्राई- जैसे अणुओं के प्रकार के आधार पर एक साथ जोड़ा गया था। एरोमेटिक्स (टीए) और कोक।

क्रैकिंग पथों का अध्ययन वाई जिओलाइट पर अलग-अलग डेकलिन और 2 एमएन का उपयोग करके किया गया था। यह देखा गया है कि रूपांतरण में वृद्धि के साथ कोक और गैस में वृद्धि देखी गई जबकि अन्य सभी उत्पाद घट रहे हैं। क्रैकिंग, एल्केलेशन, हाइड्रोजन ट्रांसफर, रिंग ओपनिंग और रिंग संकुचन जैसी प्रतिक्रियाओं के विभिन्न वर्गों के आधार पर गठित उत्पादों का विश्लेषण करते समय, यह पाया गया कि क्रैकिंग और हाइड्रोजन ट्रांसफर प्रतिक्रियाएं उच्च रूपांतरण पर दूसरों पर हावी होती हैं। इसे वाई जिओलाइट की उच्च अम्लता के आधार पर समझाया जा सकता है। डेकालिन की तुलना में इसकी उच्च स्थिरता के कारण 2MN के मामले में ऐसी प्रतिक्रिया की सीमा बहुत कम है।

वाई जिओलाइट से प्राप्त उत्प्रेरक का उपयोग करके क्रैकिंग अध्ययन को 2MN के लिए आगे बढ़ाया गया था। एफसीसी इकाई संचालन से संबंधित विभिन्न प्रतिक्रिया तापमान और तेल उत्प्रेरक अनुपात पर प्रयोग किए गए। उत्पादों के विश्लेषण के आधार पर, यह पाया गया है कि इस मामले में एल्किलेशन और क्रैकिंग प्रतिक्रियाएं प्रमुख हैं। प्रतिक्रिया पथ से संकेत मिलता है कि कोक मुख्य रूप से पॉली-एरोमैटिक्स के माध्यम से असंगत प्रतिक्रियाओं द्वारा बनता है। इस प्रतिक्रिया के दौरान हाइड्रोजन भी बनता है, जो हाइड्रोजन स्थानांतरण और रिंग ओपनिंग/क्रैकिंग प्रतिक्रियाओं में खर्च हो जाएगा। मोनो-एरोमैटिक्स के गठन का प्रमुख मार्ग हाइड्रोजन स्थानांतरण है जिसके बाद क्रैकिंग और रिंग ओपनिंग प्रतिक्रियाएं होती हैं। काइनेटिक मॉडलिंग भी किया गया और प्रतिक्रिया नेटवर्क के लिए गतिज मापदंडों का अनुमान लगाया गया। मॉडल पूर्वानुमान ने प्रयोगात्मक डेटा के साथ अच्छा मेल दिखाया।

मोनो-एरोमैटिक्स की उपज में सुधार पर हाइड्रोजन दाता (डेकालिन) सांद्रता और उत्प्रेरक की दुर्लभ पृथ्वी सामग्री के प्रभाव का भी अध्ययन किया गया। यह पाया गया कि हाइड्रोजन दाता और उच्च दुर्लभ

पृथ्वी सामग्री उत्प्रेरक दोनों 2MN के मोनो-एरोमैटिक्स में रूपांतरण बढ़ा रहे थे। अंत में, एफसीसी इकाई में मोनो-एरोमैटिक्स उपज बढ़ाने की व्यवहार्यता की पहचान करने के लिए उत्प्रेरक पर एलसीओ को भी क्रैक किया गया। कुल मिलाकर, वर्तमान शोध एक व्यवस्थित अंतर्दृष्टि प्रदान करेगा जो एफसीसी इकाई में एलसीओ के मोनो-एरोमैटिक्स में रूपांतरण को अधिकतम करने के लिए उपयोग किए जाने वाले अनुकूलित उत्प्रेरक और हाइड्रोजन समृद्ध धारा को डिजाइन करने में मदद करेगा।

Contents

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

A	Cross-sectional area of catalyst bed (m^2)
C^{exp}	Experimental value of molar concentration
C^{cal}	Calculated value of molar concentration
d	Diameter of reactor (m)
dz	Differential length of catalyst bed in the reactor(m)
E_i	Activation energy as per Arrhenius equation (kJ/mole)
$F_{i(feed)}$	Weight of i^{th} component of feed (g)
$F_{i(product)}$	Weight of i^{th} component of unconverted feed in product (g)
Gas	H_2 and C_1 to C_4 hydrocarbons
h	Height of the catalyst bed (m)
k_{0i}	Frequency factor as per Arrhenius equation (1/s)
N_{exp}	number of experiments
$P_{i(product)}$	Weight of i^{th} component of product (g)
r_i	Rate of reaction of i molecule
t	Time of injection of feed (s)
W_F	Weight of feed injected (g)
Wc	Weight of catalyst loaded into the reactor (g)

2D GC	2 dimensional Gas Chromatography
2MN	2-methyl naphthalene
ABD	Apparent Bulk Density
BDE	Bond Dissociation Energy
BET	Brunauer–Emmett–Teller

BYLP	Becke's three-parameter exchange functional combined with the Lee-Yang-Parr correlation functional
CLO	Clarified Oil
C/O	Catalyst to oil ratio
COTC	Crude to chemicals
DA	Di-aromatics (two ring aromatics including any side chain),
FCC	Fluid Catalytic Cracking
FCCG	FCC Gasoline
GC-MS	Gas Chromatograph with mass spectrometer
GGA	Generalized Gradient Approximation
HCN	Heavy Cracked Naphtha
LCO	Light Cycle Oil
LCN	Light Cracked Naphtha
MA	Mono-aromatics (Benzene & its derivatives)
NA	Naphtheno-aromatics (all aromatics with naphthenic ring)
OF	Objective function
PBU	Primary Building Units
PN	All paraffin products having C no > 4 and all Naphthenes
PONA	Paraffins, Olefins, Naphthenes & Aromatics
RGA	Refinery Gas Analyzer
SBU	Secondary Building Units
TA	Tri-aromatics (all aromatics having three rings or more)
TPD	Temperature-Programmed Desorption
USY	Ultra Stable zeolite Y
UCS	Unit Cell Size

WHSV	Weight Hourly Space Velocity
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

Subscripts

i	Index used for referring components
j	Index used for referring experiments

Greek letters

τ	Residence time, s
ϵ	Porosity of catalyst bed
ϑ_T	Volumetric flow rate at reaction conditions (m^3/s)