

**MANGANESE OXIDE ON ZEOLITE CATALYSTS FOR
OXIDATIVE CRACKING OF NAPHTHA TO OLEFINS:
EVALUATION AND KINETICS**

BY

Alolaywi Ahmed Sami

A Thesis Presented to the
COLLEGE OF GRADUATE AND INTERDISCIPLINARY STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

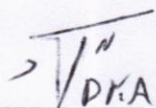
FEBRUARY-2025

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

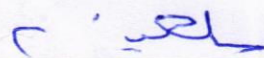
DEANSHIP OF GRADUATE STUDIES

This thesis, written by Alolaywi Ahmed Sami under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of | MASTER OF SCIENCE IN CHEMICAL ENGINEERING


Dr. Saad F. Alafnan

Dr. Saad F. Alafnan

Department Chairman

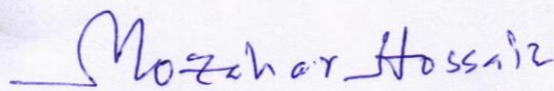


Dr. Suliman Al-Homidan

Dean of Graduate Studies

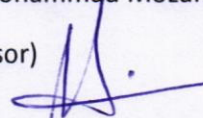
Feb - 2025

Date


Dr. Mohammad Mozahar Hossain

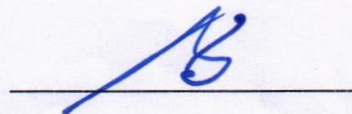
Dr. Mohammad Mozahar Hossain

(Advisor)



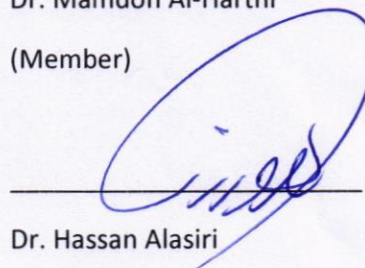
Dr. Yahya Gambo

(Member)



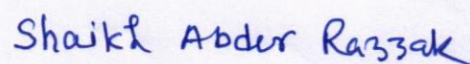
Dr. Mamdoh Al-Harathi

(Member)



Dr. Hassan Alasiri

(Member)


Dr. Shaikh Abdurrazzak

Dr. Shaikh Abdurrazzak

(Member)



© ALOLAYWI AHMED SAMI

2025

*To Almighty Allah, my parents, my colleagues and my teachers
greatly appreciated for your all efforts to improve me personally and professionally.*

ACKNOWLEDGMENTS

Blessings and gratitude to Almighty Allah, the Creator of the universe, whose creation is unparalleled. I am profoundly thankful for the health and strength He has granted me, enabling the completion of my work and daily responsibilities.

I extend special thanks to my parents for their unwavering support throughout my studies; without their guidance, I would not have reached this significant milestone in my life. My sincere appreciation goes to my supervisor, Dr. Mohammad Mozahar Hossain, for his invaluable time and motivation throughout this research project. I would also like to express my gratitude to my co-advisor, Dr. Yahya Gambo, and my committee members, Dr. Hassan Saeed Alasiri, Dr. Shaikh Abdur Razzak and Dr. Mamdouh Al-Harthi. Their dedication and support, along with that of the entire faculty in the Chemical Engineering Department, have been instrumental in equipping me with the knowledge to face future challenges.

I would like to acknowledge the contributions of my mentors, Mr. Akolade Idris Bakare and Dr. Sagir Adamu, who have been exceptionally supportive and friendly. Their wealth of experience has greatly enriched my learning journey. I also extend my gratitude to Dr. Abdullah Aitani, Dr. Emad N Shafei, Dr. Abdulkadir Tanimu, Mr. Abdulbari Siddiqui, Mr. Ramzi H. Al-Shugaih, Mr. Mohammed Faisal AlHawaj, Mr. Mian Rahat Saeed, Mr. Abdualah Alsulaiman, and Mr. Roy Cuba Villarmino. I pray that Almighty Allah rewards them abundantly for their contributions to my research success. I wish to express my heartfelt appreciation to King Fahd University for providing me the opportunity to further my studies.

•

I am particularly grateful to Mr. Ahmed Alshushan and Mr. Abdulmuhsin Alshaer for their support in securing my sponsorship.

Finally, I extend my gratitude to all the special individuals, colleagues, family members, and friends who have contributed in various ways to my journey. Your support has been invaluable, and I am truly grateful.

•

Contents

ACKNOWLEDGMENTS	v
List of Tables	ix
List of Figures	x
List of Abbreviations	xi
ABSTRACT	xiii
ملخص الرسالة	xiv
Chapter 1: Introduction	1
1.1. Background	1
1.2. Olefins Production from Naphtha	5
1.3. Problem Statement	6
Chapter 2: Literature Review	7
2.1 Steam Cracking to Produce Olefins	8
2.2. Catalytic Cracking to Produce Olefins	8
2.3. Oxidative Dehydrogenation (ODH) to Produce Olefins	10
2.4. Oxidative Cracking Process Description	11
2.5. Naphtha Global Market; Chemical and Physical Composition	12
2.6. Prospects of Oxidative Cracking	19
2.7. Oxidative Cracking Catalyst and Chemistry	21
2.8. Olefins Production by dehydrogenation of C₅/C₆ to Alkanes	26
2.9. Reaction Mechanism	27
2.10. Kinetics of Oxidative Cracking	33
2.11. Conclusion of Literature Review	38
Chapter 3: Objectives	40
Chapter 4: Methodology	41
4.1. Materials and Catalyst Synthesis	41
4.1.1 Synthesis of Montmorillonite Supported Manganese Oxide	41
4.1.2. Synthesis of Zeolites/Montmorillonite Manganese Oxid Matrices	41
4.2 Catalyst Characterization	42
4.2.1 Temperature-Programmed Reduction (TPR) Test	42
4.2.2. X-ray diffraction (XRD) Test	43
4.2.3. Temperature-Programmed Desorption (TPD) Test	44
4.2.4. Fourier Transform Infrared Analysis (FTIR) TEST	44

4.2.5. Scanning Electron Microscopy (SEM) Test	45
4.2.6. Brunauer-Emmett-Teller (BET) Surface Area Analysis Test	45
3.3. Oxidative Cracking Experiment	45
Chapter 5: Results and Discussion	50
5.1. Catalyst Characterization	50
5.1.1. Scanning Electron Microscopy (SEM)	50
5.1.2. X-ray diffraction (XRD)	51
5.1.3. Fourier Transform Infrared Analysis (FTIR)	52
5.1.4. Temperature-Programmed Desorption (NH ₃ -TPD)	53
5.1.5. Temperature-Programmed Reduction (H ₂ -TPR)	55
5.1.6 Nitrogen Adsorption Isotherms Analysis	57
5.2. Oxidative Cracking of Naphtha on MnO _x /ZSM-5	58
Chapter 6: Kinetic Modelling	66
6.1. Introduction to Kinetic Modelling of Light Straight Run Naphtha	66
6.2. Modelling Approach and Assumptions:	68
6.3. Lumped Kinetic Data for Model Development	69
6.4. Reaction Networks Development and Order Rate of Reaction Determination	75
6.5. Kinetic Models Explanation	78
6.6. Kinetic Model Results and Recommendation:	79
Chapter 7: Conclusion	87
7.1. Conclusions	87
7.2. Recommendations	88
Reference	90
VITAE	98

List of Tables

Table 1: Comparison between Naphtha and Ethane as feedstock for Steam Cracker [17].	5
Table 2: Overview of Factors in Global Naphtha Market	19
Table 3: Obtained Properties and Values from PIONA for LSRN Feed	47
Table 4: Product distribution of oxidative cracking of LSRN using MnO _x /ZSM-5	60
Table 5: Propene Yield (%) for MnO _x /ZSM-5 at Different Temperatures and C/O	62
Table 6: Lumped Data of Temperature 550 °C to Construct Kinetic Model	71
Table 7: Lumped Data of Temperature 600 °C to Construct Kinetic Mode	73
Table 8: Lumped Data of Temperature 625 °C to Construct Kinetic Model	74
Table 9: Kinetic Parameters Estimation for Proposed Model 1 st order of LSRN Conversion	86

List of Figures

Figure 1: Naphtha to Olefins Production Processes [11].	3
Figure 2: Propene Production in Tons Global Demand [15].	4
Figure 3: Refining Catalyst Market Behavior[32]	13
Figure 4:Market Summary of Naphtha CAGR 4% [22].	15
Figure 5: Global Refined Products Consumption in Mbd between 2017-2021[35].	18
Figure 6: Oxidative Cracking with Catalyst Regeneration proposed Process [20].	20
Figure 7: Propane Feed Aactivity for Various Catalyst [38].	25
Figure 8: Reaction Mechanism for Oxidative Cracking of n-hexane [39].	28
Figure 9: Proposed Reaction Mechanism for Oxidative Cracking of Boron Nitride [40].	32
Figure 10: Reaction Network for Oxidative Cracking of n-Hexane [38].	33
Figure 11: Micro-activity Test Unit (MAT) Real Picture labelled with part	48
Figure 12: Schematic Diagram of MAT (Fixed Batch Reactor).	49
Figure 13: SEM micrograph Screened Catalyst and EDS of ZMn-5.	51
Figure 14: XRD of Zeolite and Catalysts with Manganese Loadings.	52
Figure 15: FTIR of ZMn-5, Zmn-10 and Zmn-15 Catalyst.	53
Figure 16: NH ₃ Temperature-programmed desorption (NH ₃ -TPD) of ZMn catalyst matrices	55
Figure 17: TPR Profile of the MnO _x /ZSM-5 Catalysts with Loadings of 5%, 10% and 15%.	57
Figure 18:(a). Nitrogen adsorption/desorption isotherm of MnO _x /ZSM-5 (ZMn5)	58
Figure 19: (a) LSRN Conversion and Propene Selectivity of Screened Catalyst	61
Figure 20: Conversion and Olefins Yield for LSRN over MnO _x /ZSM-5	62
Figure 21: Yields of (a) Propene, (b) Ethene	63
Figure 22: Yields of (a) 1,3 Butadiene, (b) Hydrogen.	64
Figure 23: Yields of (a) C1-C2 alkane, (b) Paraffins.	65
Figure 24: Yields of (c) coke, (d) LCO and HCO	65
Figure 25: Reaction Network Developed for Oxidative Cracking of n-Hexane[62].	66
Figure 26: Reaction Network Developed for Catalytic Crackling of Naphtha[64].	67
Figure 27: Lumped Kinetic Data and LSRN Conversion for 550 ° C and Various C/O	72
Figure 28: Lumped Kinetic Data and LSRN Conversion for 600 ° C and Various C/O	74
Figure 29: Lumped Kinetic Data and LSRN Conversion for 625 ° C and Various C/O	75
Figure 30: Reaction Network Diagram for Oxidative Cracking of LSRN	76
Figure 31: Reaction Network Diagram for Oxidative Cracking of LSRN	77
Figure 32: Parity Plot of Experimental Vs Predicted for LSRN Oxidative Cracking.	81
Figure 33: Experimental Data for LSRN Conversion Vs Predicated by Model.	82
Figure 34: Experimental Data for LSRN Conversion Vs Predicated by Model.	83
Figure 35: Experimental Data for LSRN Conversion Vs Predicated by Model.	84

List of Abbreviations

LSRN	:	Light Straight Run Naphtha
NGL:	:	Natural Gas Liquid
VGO:	:	Vacuum Gas Oil
Wt. %:	:	Weight Percentage
C/O:	:	Catalyst to Oil Ratio
Mnt:	:	Montmorillonite
Mn	:	Manganese
ZSM	:	Zeolite
MnO _x	:	Manganese Oxide
MAT	:	Micro Activity Test Unit
ACE	:	Advanced Catalytic Evaluation
T	:	Temperature
FCC	:	Fluid Catalytic Cracking
ODH	:	Oxidative Dehydrogenation
DH	:	Dehydrogenation
MTPA	:	Million Tons Per Annum
C ₃ =	:	Propene

、
XRD : X-ray Diffraction

FTIR : Fourier-transform infrared spectroscopy

TPD : Temperature Programmed Desorption

TPR : Temperature Programmed Reduction

TCD : Thermal Conductivity Detector

FID : Flame Ionization Detector

GC : Gas Chromatography

ABSTRACT

Full Name : [Alolaywi Ahmed Sami]
Thesis Title : [MANGANESE OXIDE ON ZEOLITE CATALYSTS FOR OXIDATIVE CRACKING OF NAPHTHA TO OLEFINS: EVALUATION AND KINETICS]
Major Field : Chemical Engineering Department
Date of Degree : FEB 2025

Global olefin production such as propene is projected to grow by 160 million tons in 2027, driven by increasing demand in various industries such as plastics, chemicals, and textiles. However, traditional production methods like thermal and fluid catalytic cracking are energy-intensive endothermic processes, with limited olefin yields as gasoline is the primary product. Oxidative cracking presents a promising alternative, being exothermic in nature and generating lower carbon emissions. To efficiently explore this process in a laboratory setting, requiring less operation costs and initial investments, a robust kinetic model is needed. This model will help determine the optimal reaction conditions, catalyst activity, and product selectivity, paving the way for the development of a sustainable and efficient olefin production technology. This study investigates the effect of Metal oxide supported on Zeolites as catalyst to convert LSRN to olefins for example MnOx/ZSM5, MnOx/ZSM10 and MnOx/ZSM15 to assess the performance under controlled conditions. The finding includes highest propene yield (14.69%) obtained for MnOx/ZSM5 at catalyst to oil ratio of 6 and 625 °C. This study also explores the reaction mechanism and the role of free lattice oxygen to facilitate oxidative cracking. Based on experimental results a robust kinetic model was developed based on certain assumptions to develop empirical formulas based on equations of rate reaction equations for a first order reaction of naphtha cracking. The results suggest addition of metals to promote oxidative dehydrogenation under regeneration conditions and conducting the kinetic modelling for this step by Langmuir-Hinshelwood mechanism.

ملخص الرسالة

الاسم الكامل: أحمد سامي صالح العليوي

عنوان الرسالة: الأكسدة التأكسيرية عن طريق عنصر المنغنيس المدعوم على الزيوليت لتحويل النافثا إلى أوليفينات: النمذجة للمحفز مع تقييم المحفز

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: فبراير 2025

من المتوقع أن ينمو الإنتاج العالمي للأوليفينات مثل البروبين بمقدار 160 مليون طن في عام 2027، مدفوعًا بزيادة الطلب في مختلف الصناعات مثل البلاستيك والكيماويات والمنسوجات. ومع ذلك، فإن طرق الإنتاج التقليدية مثل التأكسير التحفيزي الحراري والسوائل هي عمليات ماصة للحرارة كثيفة الاستهلاك للطاقة، مع إنتاج محدود من الأوليفينات حيث أن البنزين هو المنتج الأساسي. يمثل التأكسير التأكسدي بديلاً واعدًا، حيث أنه طارد للحرارة بطبيعته ويولد انبعاثات كربون أقل. توفر البيئة المعملية ظروف مناسبة من أجل البحث والتطوير مع تكاليف أقل وذلك من أجل التوصل إلى نموذج مبني على ظروف تفاعل معينة لتحديد نشاط المحفز ومقدار المنتج وذلك من أجل تطوير تكنولوجيا مستدامة وفعالة لإنتاج الأوليفينات. تبحث هذه الدراسة في تأثير أكسيد معدن المنغنيس المدعوم على الزيوليتات كمحفز لتحويل النافثا الخفيفة إلى أوليفينات وذلك لتقييم الأداء تحت ظروف محكمة. تتضمن النتيجة أعلى إنتاجية من البروبين (14.69%) تم الحصول عليها عند نسبة المحفز إلى الزيت البالغة 6 و 625 درجة مئوية. تستكشف هذه الدراسة أيضًا آلية التفاعل ودور الأكسجين لتسهيل التأكسير التأكسدي. تم من خلال استعمال نتائج التجارب تطوير نموذج حركي بناء على فرضيات وعمل معادلات مبنية على معادلات رياضية توضح تفسير النافثا كونه مبني على تفاعل من الدرجة الأولى.

Chapter 1: Introduction

1.1. Background

The petrochemical industry heavily relies on light olefins like ethylene and propylene, primarily produced through established methods like steam cracking. However, these methods have limitations – significant coke formation, high energy consumption, and limited olefin yields[1]. A promising alternative is oxidative cracking, which offers an exothermic process with potentially reduced coke formation and enhanced efficiency at lower temperatures[2]. However, challenges like carbon loss remain. To address these challenges and compete with established methods, research focuses on two types of catalysts: transition metal oxides and alkali/alkaline earth oxides[3]. These catalysts operate at lower temperatures and initiate cracking reactions followed by thermal cracking. Furthermore, optimizing reactor design can further enhance efficiency and product selectivity. Advancements in catalyst and reactor design hold the potential for oxidative cracking to revolutionize olefin production, offering a more sustainable and efficient alternative to traditional methods[4], [5], [6], [7]. The oxidative cracking goes through heterogenous and homogenous phase reactions with selective formation to light alkenes or in case of carrying the reaction without catalyst presence formation of more alkanes and aromatics is common[8], [9]. The present study will be based on kinetics data obtained using a micro-activity test unit (MAT) in order to obtain conversion and selectivity at various temperatures and catalyst to oil ratio for the determination of reaction mechanism and most optimum conditions resulting in light olefins production[10].

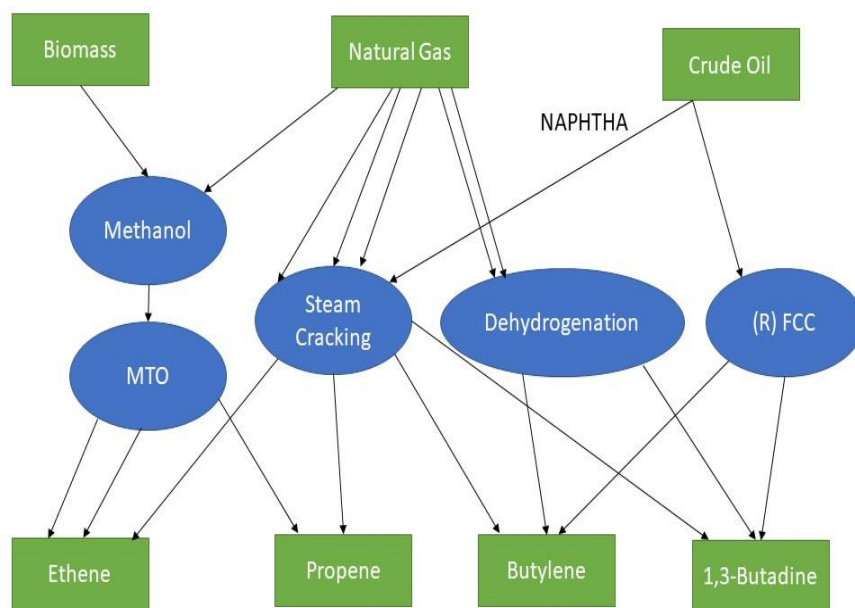


Figure 1: Naphtha to Olefins Production Processes [11].

Propene, an example of light olefins product with its unique three-carbon structure and reactive double bond, is a key building block for numerous materials[12]. This versatility stems from its combined allylic methyl group and olefinic bond, allowing for diverse chemical transformations. Polypropylene, accounting for a staggering 68% of the market share in 2018, exemplifies its impact, finding applications from packaging to medical equipment. But propene's potential extends far beyond[13]. Processes like epoxidation, halogen addition, and alkylation unlock a treasure trove of valuable derivatives such as propylene oxide, styrene, iso-butanol, cumene, and acrylonitrile, each contributing significantly to various industries. The impact of the COVID-19 pandemic on propene derivative demand was complicated. While industries for example aviation confronted with travel restrictions and decreased demand for related chemicals, the medical and packaging

sectors experienced a surge, ensuring that polypropylene remained largely unaffected[14]. Looking ahead, the future of propene is bright. Production is estimated to reach 191.8 million tons per annum (MTPA) by 2030, highlighting its continuous demand from various industries.

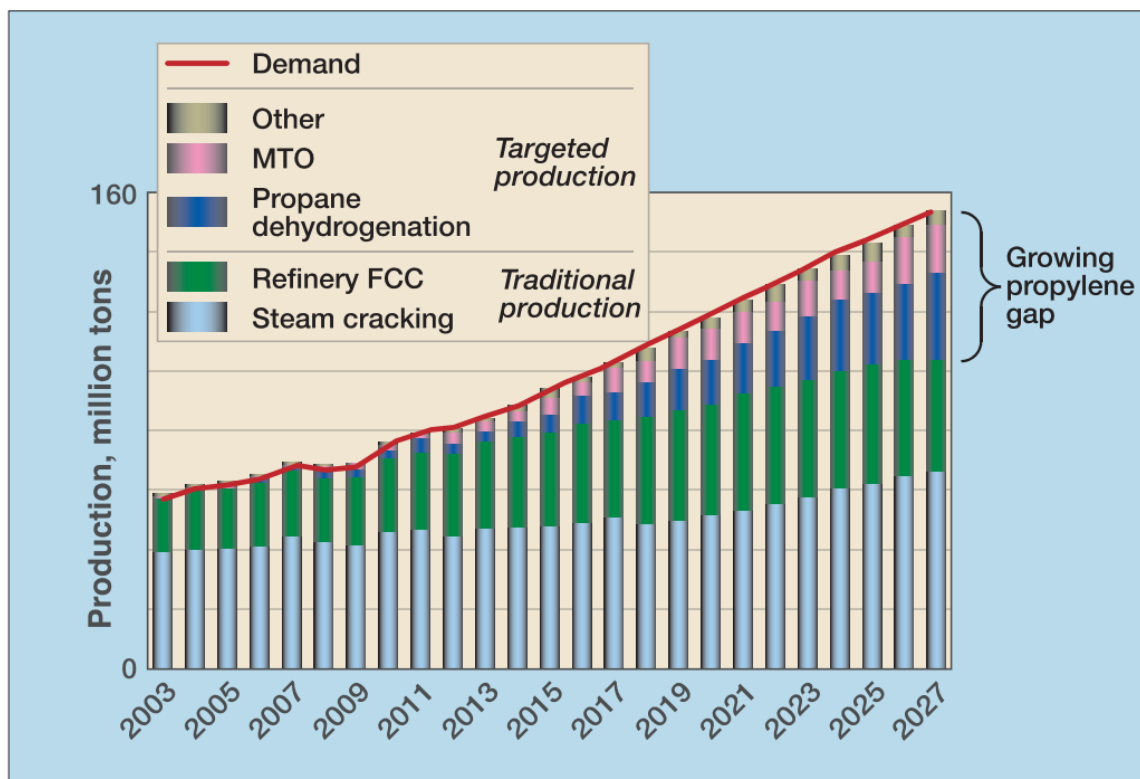


Figure 2: Propene Production in Tons Global Demand [15].

The ability to meet this demand growth of propene requires innovation in design and discovery of catalyst to increase propene production while maintain regulations of environment and also better reactors design. The ability to meet this demand growth of propene requires innovation in design and discovery of catalyst to increase propene production while maintain regulations of environment and also better reactors design [16].

1.2. Olefins Production from Naphtha

For various feedstocks such as naphtha or ethane processed in catalytic crackers and other types of technologies employed will result in olefins production in ranges of percentage. Two examples of technologies to produce olefins are catalytic cracking of naphtha and hydro-pyrolysis of naphtha. Depending on the feedstock a comparison between Naphtha and Ethane is listed in the table below for a steam cracker [17].

Table 1: Comparison between Naphtha and Ethane as feedstock for Steam Cracker [17].

Product Name	Naphtha	Ethane
Ethylene yield (wt.%)	29-34	80-84
Propylene yield (wt.%)	13-16	1-1.6
Aromatics and C4+ yield (wt.%)	10-16	2-3
Butadiene yield (wt.%)	4-5	1-1.4
Methane yield(wt.%)	13-14	4.2
Hydrogen yield(wt.%)	1	4.3

Table 1 shows that steam cracking of naphtha yields more propylene compared to using ethane as the feedstock. However, since the steam cracker uses ethane as the feed, it is expected to produce a higher yield of ethylene compared to naphtha steam cracking. The weight percentage yield of propylene from steam cracking of naphtha was around 13-16%, and this was achieved at higher temperatures. In contrast, catalytic cracking of naphtha produced a higher propylene yield of 18-31 weight percentage, but at a lower temperature of 550°C. The catalyst used in the catalytic cracking experiment was composed of Al-MFI zeolites, which had a combination of two types of heteroatoms (Fe, Ga) and metal oxides, such as aluminum oxide, and was tested with n-hexane as the feedstock[18]. For catalytic

oxidative cracking, Boyadjian et al. achieved a 16.8% yield of light olefins using a Li/MgO catalyst, but this also resulted in a relatively high 24.6% yield of CO_x, which is undesirable. Their experiments were conducted at a reaction temperature of 575°C.

1.3. Problem Statement

The global demand for light olefins, such as propylene and ethylene, is on the rise. However, the current production methods, like steam cracking and fluid catalytic cracking, are more expensive than simply using hydrocarbon feedstocks like naphtha or propane. These conventional processes are also highly energy-intensive, as they require high temperatures to operate. To address this challenge, oxidative cracking presents a promising alternative. In this process, alkanes are first cracked to produce other alkanes, which are then subjected to an oxidative hydrogenation reaction to yield the desired alkenes. The key advantage of oxidative cracking is that it can be conducted at a lower temperature range, typically between 575-615 degrees Celsius. Operating in this exothermic temperature range helps reduce the overall energy requirements. Additionally, the carbon produced during this process can be minimized by carefully selecting an effective catalyst system that inhibits the formation of Co. The main focus of this investigation is to explore the oxidative cracking of naphtha, with the following objectives:

1. Developing highly active and stable catalysts for the process and ensure lower formation of CO_x byproducts.
2. Elucidating the reaction mechanism and optimizing propylene selectivity.
3. Establishing a kinetic model to estimate the relevant parameters for the oxidative cracking of naphtha.

Chapter 2: Literature Review

There are several established routes for producing olefins from naphtha feedstock:

1. Thermal Cracking: This process involves the thermal decomposition of naphtha at high temperatures to yield olefins and other hydrocarbon products[19].
2. Steam Cracking: In this method, naphtha is cracked in the presence of steam at elevated temperatures, typically between 750-900°C, to maximize the production of ethylene and other light olefins[20].
3. Catalytic Cracking: Naphtha is cracked over a heterogeneous catalyst, such as zeolites, to produce a range of olefins, including propylene, which can be the primary product[21].
4. Catalytic Oxidative Cracking: Naphtha is cracked in the presence of oxygen over a catalyst, resulting in the selective formation of light olefins through a combination of cracking and oxidative dehydrogenation reactions[22].
5. Redox Oxidative Cracking: This process utilizes a redox catalyst system to crack naphtha and produce olefins, with the catalyst undergoing cyclic reduction and oxidation steps[23].
6. Oxidative Dehydrogenation Cracking: Naphtha is subjected to oxidative dehydrogenation reactions, typically over metal oxide-based catalysts, to selectively convert the feedstock into desired olefin products[24].

Each of these routes has its own advantages, challenges, and product selectivity profiles. The choice of the most suitable approach depends on factors such as feedstock availability, desired product mix, energy efficiency, and environmental considerations.

2.1 Steam Cracking to Produce Olefins

The primary route for producing olefins from naphtha is steam cracking, which is an energy-intensive process. For instance, producing 1 ton of ethylene via steam cracking of naphtha requires 28.5 GJ of thermal energy and results in 1.9 tons of carbon dioxide emissions. In this process, the yield of ethylene is maximized, while propylene is a secondary product[25]. However, the high demand for propylene makes this process less attractive in the industry. As an alternative, catalytic cracking has emerged as a more viable option. The light olefins produced through steam cracking utilize feedstocks such as LPG, ethane, and naphtha. The process employs a tubular-type reactor, where the hydrocarbon feedstock is mixed with steam at elevated temperatures ranging from 750 to 900°C, to meet the highly endothermic and energy-intensive requirements of the process[26]. Heavier hydrocarbons tend to yield more propene during steam cracking. It is important to consider the availability and profitability of the feedstock. However, the propene yields are minimized in modern steam crackers, which have shifted towards using ethane-based feeds.

2.2. Catalytic Cracking to Produce Olefins

The catalytic cracking of naphtha is aided by heterogeneous catalysts, such as zeolites, which help reduce the cracking reaction temperature. However, the process still requires heat for the vaporization and pyrolysis of naphtha. One of the major products obtained from fluid catalytic cracking of light naphtha is propylene. The selectivity towards propylene can be enhanced by minimizing hydrogen transfer reactions. There are three main methods to increase propylene selectivity in fluid catalytic cracking:

- Increasing the reaction temperature.
- Utilizing coked catalysts.
- Employing shape-selective catalysts.

Compared to steam cracking, catalytic cracking offers better economic sustainability. In fluid catalytic cracking, the focus has shifted towards maximizing diesel and gasoline yields to meet the demands of the transportation industry, rather than prioritizing propylene production. Various reactor types are employed to evaluate the catalyst and feedstock in fluid catalytic cracking, including riser reactors and high severity downer reactors. Each reactor type is used for specific applications related to propylene production. However, the results are more promising for the downer reactor compared to the riser reactor, due to differences in residence time and back-mixing. These reactors are used at the laboratory scale and allow processing larger amounts of feed and catalyst compared to the Advanced Catalytic Evaluation (ACE) unit. The ACE unit enables the evaluation of six different catalyst types and various injection times[27]. When designing heterogeneous catalysts for fluid catalytic cracking, several key parameters must be considered:

1. Activity: The catalyst must exhibit high activity to facilitate the cracking reactions.
2. Attrition Resistance: The catalyst particles must have sufficient attrition resistance to withstand the mechanical stresses during circulation in the reactor.
3. Stability: The catalyst must maintain its structural and chemical integrity under the high-temperature and steam-rich conditions.
4. Metal Tolerance: The catalyst should be able to handle feedstocks containing metal impurities without significant deactivation.

5. Coke Selectivity: The catalyst should minimize the formation of coke, which can deactivate the active sites.
6. Fluidizability: The catalyst particles must have appropriate physical properties to ensure efficient fluidization in the reactor.

Attrition resistance is particularly important, as the catalyst particles need to withstand the mechanical stresses during circulation and maintain their structural integrity. When coke is formed during the reaction, it must be effectively burned off in the regenerator, which requires the catalyst particles to sustain high temperatures and steam partial pressures. Heavy feedstocks can also introduce poisoning issues and coke formation challenges. To overcome these problems, the catalyst must have good metal tolerance and high coke selectivity. Y-zeolite is a commonly used catalyst for fluid catalytic cracking, as its porous structure contains acid sites that facilitate the conversion of larger hydrocarbon molecules into the desired range of gasoline-range products. Clay is often added as a filler to provide additional heat capacity requirements. The catalyst system also includes other components, such as different alumina and silica sources, as well as metal traps. These components are mixed in an aqueous slurry and spray-dried to form spherical catalyst particles with meso- and macro-porous structures. The trapped metals typically include nickel and vanadium[28]

2.3. Oxidative Dehydrogenation (ODH) to Produce Olefins

Oxidative cracking of alkanes, such as hexane and pentane, is a process that produces alkenes and water instead of hydrogen. This reaction is catalyzed by metal oxide catalysts and aided by gas phase oxygen or lattice oxygen. Conducting the reaction at lower

temperatures is desirable, provided that the thermodynamic driving force exists. To limit undesired complete oxidation reactions and products (CO_x), the process can be carried out under anaerobic conditions. Studies have shown that the selectivity to olefins in the oxidative dehydrogenation of propane can be enhanced by using specific catalysts. For example, depositing 0.2 wt.% Au on La₂O₃ creates nanosized gold particles that aid the impregnation of sulphate groups on bare and sulphated supports, resulting in improved lattice oxygen mobility. In the oxidative cracking of naphtha, using n-hexane as the feed, higher yields of propylene and butylene can be achieved while maintaining a low cracking temperature. This has been studied using the Li/MgO catalyst system, which exhibits similar behavior to propane oxidative cracking, where a homogeneous reaction initiates the heterogeneous reaction[29]. Hexane is more reactive than ethane and propane, allowing the operation temperature to be reduced to around 575 °C, which helps to lower energy requirements.

2.4. Oxidative Cracking Process Description

For both types of oxidative cracking reactions, the schematic diagram of the process based on the fixed-bed reactor that has oxygen supply to it and the free environment of oxygen using lattice oxygen is represented in Figure 24. The difference between each process is the type of reactor as fixed bed is usually used when oxygen is supplied and fluidized bed serve for the purpose of free oxygen environment and a regenerator is also connected to the fluidized bed to burn the coke on the catalyst to recycle it back to the reactor[30]. This process for oxidative cracking is distinguished from other cracking processes by the following:

- 1- The presence and the type of the catalyst used for oxidative cracking for example using rare earth metals and product yields.
- 2- The feed in oxidative cracking is mixed with oxygen in free oxygen environment or with the aid of an oxygen supply source.
- 3- The operation temperature of oxidative cracking is low in compared with other processes and ranges from 550°C.
- 4- In other processes for example steam cracking external heating sources is used to crack but for oxidative cracking heat is generated within the reaction itself through auto-thermal means.

2.5. Naphtha Global Market; Chemical and Physical Composition

Naphtha is a high-value and expensive chemical in the petroleum industry, comprising a complex mixture of paraffins, naphthenes, and aromatics in the range of C₅-C₁₂. It is a versatile feedstock with various applications. For example, paraffins can be hydrocracked to produce ethylene, while naphthenes can be reformed to produce aromatics. Naphtha cracking products include ethylene, which had a global market of 148 million tons in 2014 and is projected to increase by 400% by 2050. Currently, 55% of steam cracking is completed using naphtha, making it the leading technology for ethylene production. However, this process results in high energy consumption and carbon dioxide emissions [31]. The market demand for propylene from naphtha is also expanding at an average rate of 5.7% annually. Propene demand exceeds that of ethene, making it crucial to achieve higher selectivity for propene over ethene during cracking reactions. This can be achieved

by selecting suitable catalysts, such as acid cracking catalysts such as ZSM-5 in fluid catalytic cracking. Approximately 60% of global naphtha feedstock is processed in fluid catalytic cracking refineries, while the remaining 40% is used in steam cracking for ethylene plants[32]. However, only half of the global propylene is produced by steam cracking, compared to ethylene.

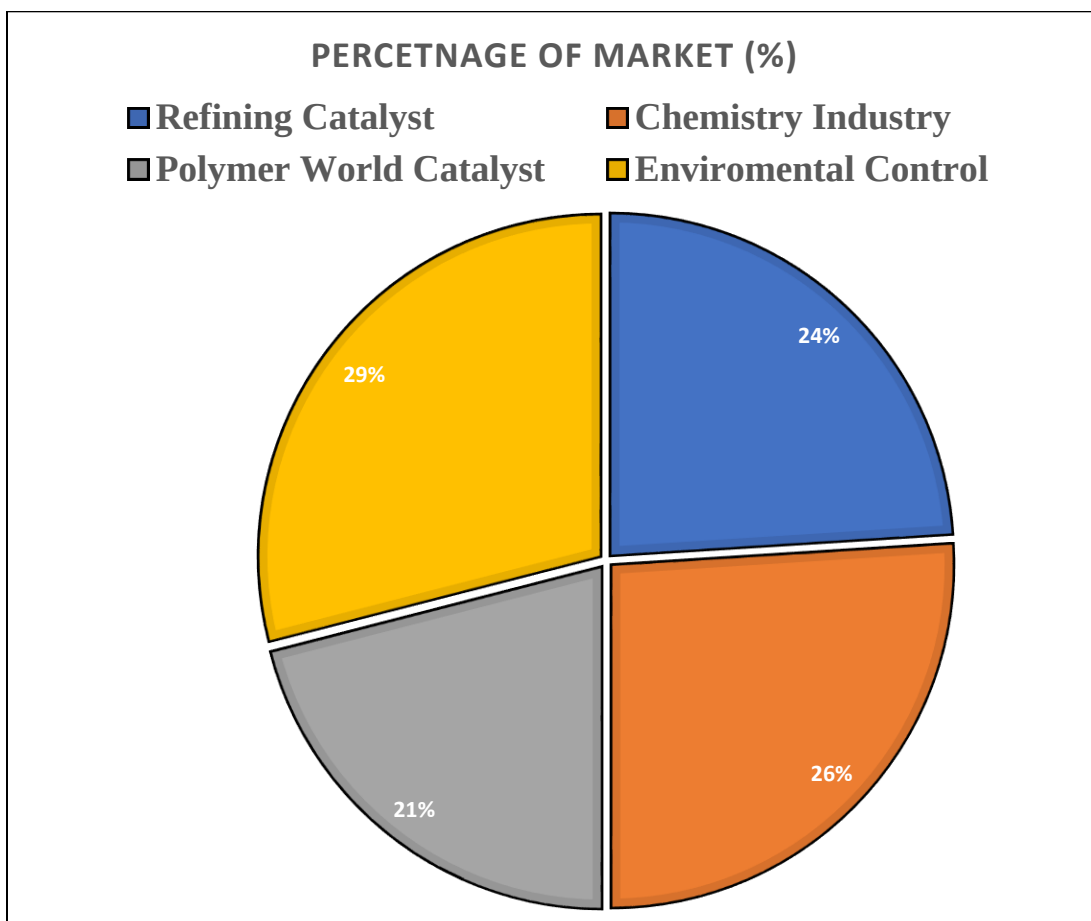


Figure 3: Refining Catalyst Market Behavior[32]

The remaining half of global propylene is produced via conventional fluid catalytic cracking of naphtha, while around a tenth of global propylene production comes from specific methods such as metathesis of 2-butene and ethylene, as well as propane dehydrogenation [33]. The world market for chemicals, environment, and the chemical

industry is around \$10.5 billion, and the refining catalyst market accounts for approximately 24% of this market. Refining catalysts, such as zeolites, are used in various processes for naphtha feed, for instance, catalytic naphtha reforming and light naphtha hydro-isomerization[34]. The valuation of the naphtha market is estimated to reach \$244.61 billion by 2021, according to the US Energy Administration. The compound annual growth rate of the naphtha market for the years between 2022-2028 is expected to increase by 4%, with 2022 as the base year for this forecast. The Asia-Pacific region is the fastest and largest growing market, with major players including Saudi Aramco, LG Chem, ExxonMobil, Formosa Petrochemical Corporation, and Reliance Industries Limited. There are several reasons for the high growth rate in the Asia-Pacific region:

- A- Rapid industrialization and urbanization
- B- Increasing demand for transportation fuels and petrochemicals
- C- Favorable government policies and incentives for the petrochemical industry
- D- Availability of abundant and cost-effective feedstock, such as naphtha
- E- Presence of major petrochemical hubs and refining centers

The domination of the naphtha market by the Asia-Pacific region is due to these factors, which have contributed to the region's significant share in global naphtha production and consumption. Other factors contributing to the spread of naphtha in this market are as follows:

1. End-users' growth for different industries such as petrochemical, fertilizers, paints, and coatings, leading to a rise in naphtha demand in India, Japan, and China.

2. Manufacturers in Japan are looking to the aerospace industry, and they require aircraft components that depend on naphtha for commercial and defence aircraft. This production has increased further in recent years due to an increase in cargo demands.
3. The South Korean Defence Acquisition Program Administration will invest USD 2.1 billion in plans for working on light aircraft, with Hyundai Heavy Industries participating in the manufacturing at a cost of USD 210 million for annual maintenance.



Figure 4:Market Summary of Naphtha CAGR 4% [22].

4. Australia's share of the world's airspace is around 10%, and this has a significant contribution of 2% to its gross domestic product. The aerospace industry in Australia generates a revenue of four billion dollars yearly, with one thousand firms, and Europe, the United States, China, and ASEAN countries account for 45%

of the profit generated. This growth process of the market is highly probable will continue in the coming years.

Naphtha plays a crucial role in the growth of various markets, primarily as a fuel that is sometimes blended with other chemicals like kerosene for the aviation industry. It is mainly used for military jet fuels due to its low freezing point. The COVID-19 pandemic had a significant impact on many industries, such as construction, resulting in less demand for materials like paints and coatings. However, the naphtha market has started to recover and grow post-pandemic, thanks to government support for various industries. The following trends in the naphtha market have been observed:

- Increased demand for naphtha in the petrochemical industry, driven by the growing need for plastics, synthetic fibers and other petrochemical products.
- Rising demand for naphtha as a feedstock in the fertilizer industry, particularly in regions with a strong agricultural sector.
- Growing use of naphtha in the production of paints, coatings, and solvents, as the construction and manufacturing sectors rebound from the pandemic's effects.
- Increased blending of naphtha with other fuels, such as gasoline, to meet the demand for cleaner and more efficient transportation fuels.
- Ongoing research and development efforts to explore alternative uses for naphtha, such as in the production of biofuels and renewable chemicals, to reduce the industry's environmental impact.

- The petrochemical industry will lead the growth of naphtha market over the medium term and as an example of this is the Indian market for fertilizers will have an increase demand.
- The growth of population and expansion of industrialization will increase the demand for naphtha in transportation sector in countries such as Japan and India and an increase of demand for natural gas in United State is likely to reduce the demand for it.

By the year 2022, the naphtha market size was estimated at \$244.61 billion. It is forecasted to grow to \$336.26 billion by 2030. The rising demand for naphtha from the petrochemical industry is due to the following reasons:

1. Naphtha market classification by process is divided into naphtha reforming, steam cracking, gasoline blending, and others. These processes are used for the manufacturing of chemicals such as olefins and aromatics, for instance propene, benzene, and toluene. The market of these chemicals is continuously growing. By application naphtha market plays an important role for energy, chemicals, and fuels. Cost-effective high-octane diesel are processed by using olefin-rich naphtha as feedstock.
2. Two joint ventures have been established by Saudi Aramco and the Malaysian national oil and gas company, Petronas, for the Refinery and Petrochemicals Integrated Development (RAPID) project in Johor, Malaysia. The project is worth around seven billion dollars and is designed to process approximately 300,000 barrels of crude oil per day.

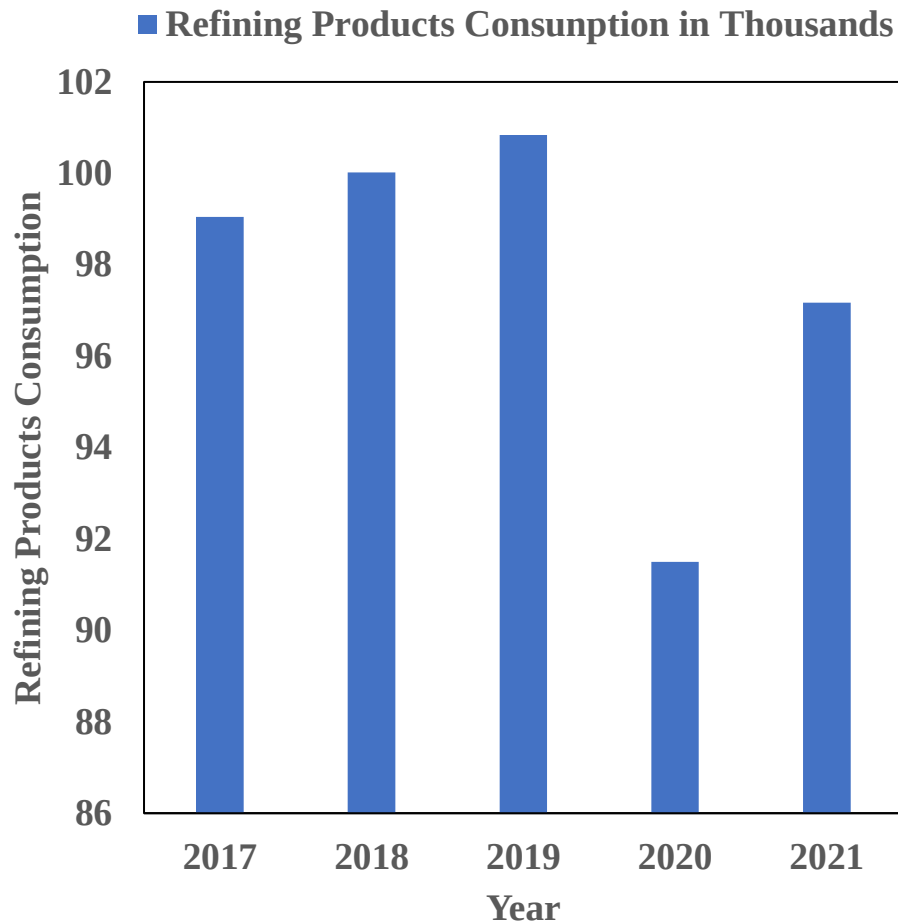


Figure 5: Global Refined Products Consumption in Mbd between 2017-2021[35].

3. This will also include around six petrochemical plants for the production of an annual output of more than 3.5 million metric tons. By the year 2025, the United Kingdom is planning to launch 111 oil and gas industry projects, comprising 83 upstream projects, 23 midstream projects, and 5 petrochemical projects. The United Kingdom is expected to lead the upcoming projects in the European region's oil and gas sector, accounting for 25% of the pipelined projects which are likely to commence by 2025. The country shall be boasting 111 oil and gas industry projects in the near term, out of which 83 will be midstream alongside with refinery and petrochemical plants.

Table 2: Overview of Factors in Global Naphtha Market

Naphtha Chemical Processes	Naphtha End User Industries	Naphtha Market Region
Naphtha Reforming	Petrochemical	Europe
Steam Cracking	Aerospace	North America
Catalytic Cracking	Paints	Asia Pacific
Gasoline Blending	Coatings	Middle East
Oxidative Dehydrogenation	Agriculture	Latin America

2.6. Prospects of Oxidative Cracking

The feed for oxidative cracking can be light naphtha as hexane and pentane and heavy naphtha for example dodecane. Moreover, there were studies reported for a feed of propane for oxidative cracking to produce olefins or another feedstock for example cyclohexane as an alternative to steam cracking. For fixed bed reactor the oxidative cracking of n-hexane was test by catalysts such as lithium-based catalyst and in order to obtain enhanced selection of olefins. Conducting oxidative cracking through oxygen supply to the reactor will result release of CO₂ due to complete oxidation of the feed which is unfavorable. Hence, employing lattice oxygen catalyst such as VO_x / Ce-Al₂O₃ catalyst where experimental work conducted in fluidized bed as shown in the schematic diagram will result in reducing the coke formation.

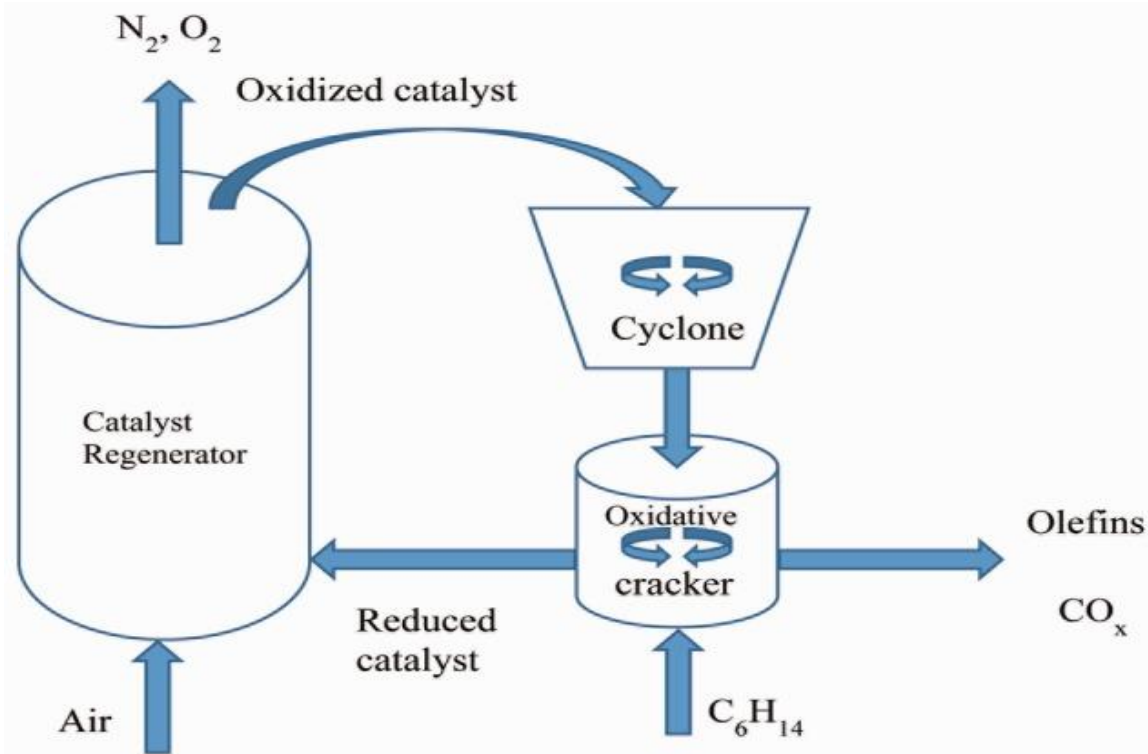


Figure 6: Oxidative Cracking with Catalyst Regeneration proposed Process [20].

As shown in the figure above, there are two fluidized-bed reactors connected to each other, each serving a distinct purpose. One reactor is responsible for cracking by oxidation, while the second is dedicated to catalyst regeneration. The circulation of catalyst occurs between the two reactors, facilitating the transfer of solid gas phase oxygen. This reaction offers several advantages, which include:

- A- The selectivity of olefins is higher.
- B- Less energy is consumed and reaction is conducted at lower temperatures.

The advantages are achieved due to reasons such as temperature control of the reaction. However, the challenges to this process lie in designing a catalyst that possesses the necessary features, including being fluidizable, having a stable structure, and exhibiting favourable kinetics.

2.7. Oxidative Cracking Catalyst and Chemistry

Metal oxide catalysts are employed for the oxidative cracking process, including rare earth oxide catalysts and crystalline metal oxide catalysts [37]. Another classification of catalyst used for oxidative cracking includes redox catalysts and non-redox catalysts. Studies have mainly focused on magnesia-supported Vanadia (VMgO) catalysts for redox types and non-redox types include rare-earth oxides. One example is an alumina-based vanadium catalyst, which has good features such as a high surface area and uniform size distribution, leading to good conversion for oxidative cracking reactions. An alternative type of catalyst for the oxidative cracking of n-hexane to olefins is vanadium oxide (VOx) supported on SrO- γ -Al₂O₃. Following a surfactant-free method, various ratios of supports containing SrO/ γ -Al₂O₃ were synthesized, and the incorporation of VOx was done via impregnation. The effect of increasing SrO is to decrease catalyst acidity, which was shown by NH₃-TPD, and allowed for catalyst modification for the reducibility noticed through H₂-TPR. Other types of analysis, including XRD, Raman, and FTIR, were conducted. These analyses have shown the appearance of VOx to be amorphous polymeric species like on the support. A one-to-one ratio of this catalyst resulted in 88% olefin selectivity with 84% conversion of n-hexane, indicating a balance between the acidity of the catalyst and the interaction between VOx and the support. The reaction was conducted in a fluidized CREC riser simulator in a free oxygen environment. In contrast, the alumina-based vanadium types of catalyst yielded lower olefins and produced coke due to the acidity of alumina, resulting in excessive cracking of the hydrocarbon. Moreover, the vanadium-alumina catalyst exhibited high selectivity for deep oxidation because of the strong interaction between them. The next catalyst highlighted is Li/MgO for the oxidative cracking of

naphtha, which has shown promising results. However, it also has drawbacks, as it is not highly active and suffers from slight deactivation. One catalyst system tested for n-hexane oxidative cracking is based on Li/MgO modified using sol-gel MoO_3 to increase the yield of light olefins. The test results have shown the best yields of light olefins ($\text{C}_2\text{-C}_4$) when promoted with a minimum amount of 0.5 weight percentage of MoO_3 , which acts on the stability of the catalyst after it has been calcined at a temperature greater than 500°C to reduce the carbonate surface formation. The efficient catalyst system should be selective by having an important feature to achieve this target. There are reactive olefins and paraffins that should be activated for the inhibition of olefins from being deeply and consecutively oxidized. For a range of naphtha hydrocarbons and to catalytically crack them, three classes of catalysts are considered: acidic, basic, and transition metal oxide catalyst. Examples of metal oxide catalysts include Cr_2O_3 , V-oxides, and Al_2O_3 . To inhibit the formation of CO_x , alkali metals such as Lithium are used for modifying rare earth oxide catalysts like CeO_2 . The Li/MgO catalyst has shown good selectivity of olefins, approximately 60 mol%, achieved at very low temperatures of around 575°C . The chemistry of this catalyst is explained by activating hexane on the Li^+O^- sites, following which a mixture of $\text{C}_1\text{-C}_5$ products is formed, composed of paraffins, olefins, and combustion products resulting from complex radical reactions in the gas phase with the existence of molecular oxygen through oxygen supply or lattice oxygen. An important factor to consider for this type of system is the effect of MoO_3 on C-H bond scission in the hexane compound and the role of this compound in minimizing the surface carbonate concentration. The fourth catalyst for the oxidative cracking of hexane to light olefins such as ethylene and propylene is perovskite oxides. The yield of olefins from this type of

catalyst was high due to good selectivity, high activity, and stability for hydrogen combustion selectivity (SHC) when a redox mode is used for the reaction. $\text{Na}_2\text{WO}_4/\text{CaMnO}_3$ accomplished a higher olefin yield of 55-58%, which is more than the 34% achieved by thermal cracking. The other catalyst, $\text{Na}_2\text{WO}_4/\text{SrMnO}_3$, obtained an olefin yield of 41%. Since oxygen is released from CaMnO_3 , a test was conducted to see the effect of Na_2WO_4 on oxygen release, and the result by O_2 -TPD (oxygen-temperature-programmed desorption) showed that this chemical has slowed down and limited the oxygen release. Other tests conducted include low-energy ion scattering (LEIS) and X-ray photoelectron spectroscopy (XPS), which showed that Na_2WO_4 covers the outer surface layer of the perovskite, resulting in eliminating the effect of near-surface Mn and alkaline earth metal cations, as well as inhibiting the formation of non-selective oxygen species. Similarly, for Sr species in SrMnO_3 , when conducting XPS analysis, Na_2WO_4 was responsible for suppressing 90% of them, as observed for CaMnO_3 . For these reasons, the studies indicate these two catalysts being promoted by Na_2WO_4 as selective redox catalysts for the efficient production of light olefins by redox oxidative cracking. The last example of a catalyst type used for oxidative cracking is Fe-substituted barium hexa-aluminates ($\text{BaFe}_x\text{Al}_{12-x}\text{O}_{19}$). Oxidative cracking is characterized by running the reaction in autothermal mode, and here, the Fe-substituted hexa-aluminates allows this to happen and yields higher olefins in comparison to the steam cracking process, where the governing reaction is endothermic. By promoting this catalyst with Na_2WO_4 , the formation of CO_x will be inhibited. In the study for this reaction, the percentage of coke dropped from 8.4-55.2% to 0.6-1.2%. The temperatures tested were in the range of 600 to 700°C, and the gas hourly space velocity was nine thousand per hour. All the hydrogen produced during the

reaction was fully oxidized. The chemistry of this catalyst is explained by lattice oxygen donating, and 20-NaW/BaFe₆ was found to double the olefins yield in comparison with the thermal cracking value recorded for it at 12.8%, while using the catalyst for oxidative cracking yielded 26%. A decreased gas hourly space velocity, for example, from nine thousand to two thousand per hour, showed an increase of approximately nine percentage points for the conversion of hexane and no significant change in olefins selectivity. The number of cycles tested for the long-term stability of the oxygen carrier NaW/BaFe₆ was 30, based on a temperature of 700°C and a gas hourly space velocity of 2,250 per hour. The range of olefins produced was 31.3-32.4%, along with a low yield of CO_x, approximately 0.6-0.7%. The suppression of non-selective oxidation reactions was determined through XPS analysis tests, which showed a shift in favour of near-surface Ba enrichment during the redox cycle, leading to the suppression of near-surface Ba content by applying the feed of n-hexane for redox oxidation as a result of using Na₂WO₄. These examples of catalysts are used for the oxidative cracking of n-hexane. Many published articles exist on the oxidative cracking of propane, and one catalyst system used for this feed is boron-based catalysts, such as boron nitride catalysis for selectivity towards propene. In comparison with V-SiO₂, boron nitride nanotubes yielded higher olefins and showed higher productivity. This catalyst system is very attractive for industrial applications due to reasons such as high thermal conductivity because of the 2-D structure of h-BN transmitting enough phonons across the BN sheets, as well as controlled selectivity. This catalyst system is relatively new, and historically, the use of this type was based on hexagonal boron nitride (h-BN) as it was used for dilution because of its ability to withstand high thermal conditions and, during oxidative cracking, has shown stability.

In 2016, the first discovery of oxidative dehydrogenation for propane dehydrogenation was reported by Eon et al. They used h-BN as a catalyst support for vanadium oxide (V₂O₅) and found that the catalyst exhibited high selectivity towards propene at temperatures between 550-650°C.

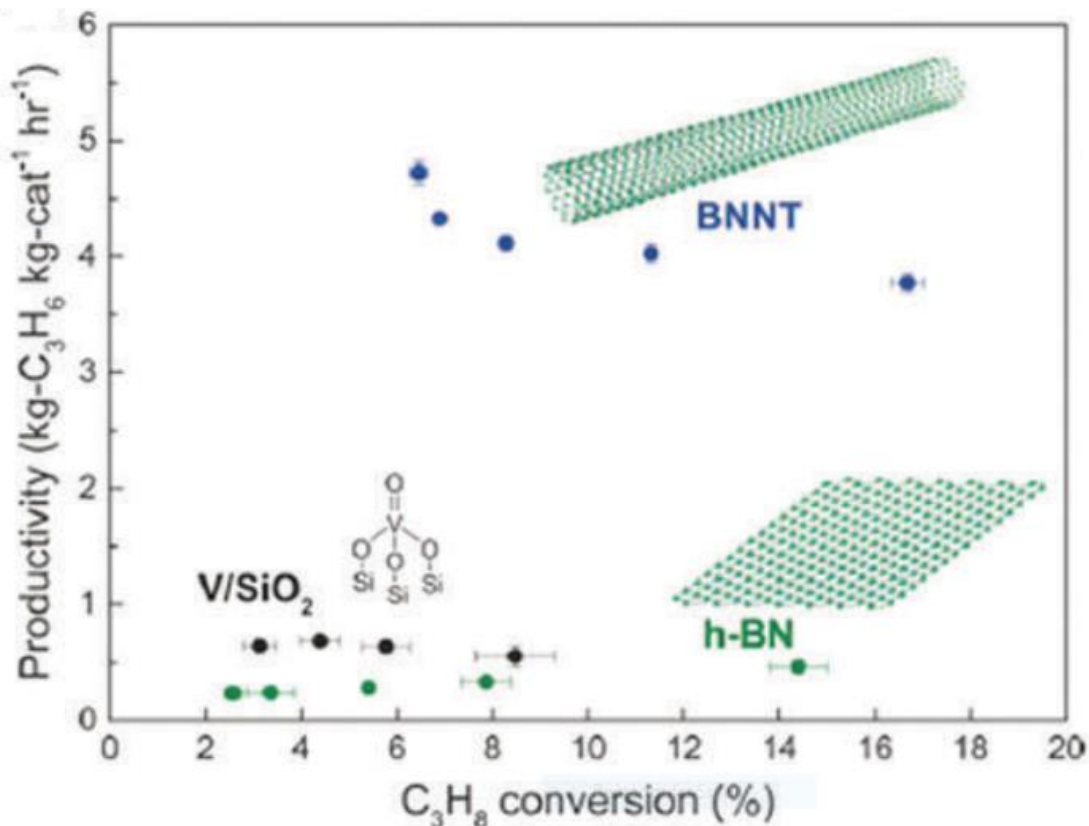


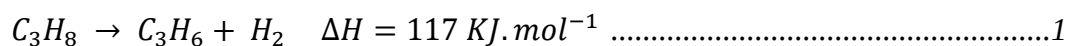
Figure 7: Propane Feed Activity for Various Catalyst [38].

Since these results were reported, further developments for the reaction mechanism and active centers of the catalyst have been ongoing. Initially, the results of the investigation have shown similar activity of h-BN to the V/SiO₂ catalyst in terms of oxidative dehydrogenation of oxygen (ODH-O₂). The promising results are from boron nitride

nanotubes (BNNTs) as a catalyst, due to their high productivity and selectivity, resulting in a higher yield of olefins than the conventional V-SiO₂ catalyst, as shown in Figure 7.

2.8. Olefins Production by dehydrogenation of C₅/C₆ to Alkanes

While many studies on propane and butane have been reported and published, there are limited studies on non-catalytic and catalytic oxidative dehydrogenation of long-chain alkanes such as n-hexane. This is due to reasons related to the non-polar C-H bond, resulting in limiting reactions to combustion and cracking, as well as the formation of radicals leading to hydrogen abstraction and substitution reactions facilitated by cracking during propagation steps. Understanding olefin production by dehydrogenation is the key to being familiar with oxidative dehydrogenation. The trend towards the production of olefins rather than crude oil is due to the economic value of alkanes, as they are cheaper than crude oil. The reaction below is an example of the dehydrogenation of an alkane to an alkene with the same carbon number:



These processes date back to 1980 for the production of light olefins, but the commercial production using them has not achieved a breakthrough due to the yield produced, which is limited by thermodynamic equilibrium. Moreover, these processes tend to produce coke, leading to the deactivation of the catalyst.

For oxidative catalytic dehydrogenation to produce olefins from hydrocarbons, there are various benefits over conventional methods, such as the reduction of coke production and catalyst deactivation. For the catalytic oxidative cracking of n-hexane, the literature reports favorable conditions to produce olefins, including lower temperatures and oxygen-rich

conditions. These conditions enhance the selectivity of hydrogen abstraction from the C-H bond over the cleavage of the C-C bond. The high conversion of alkanes by oxidative cracking to produce olefins typically indicates that most catalysts studied strongly adsorb the olefins, and the production of carbon dioxide results in limiting the yield of the olefins. This is a key challenge that researchers are working to overcome.

2.9. Reaction Mechanism

The oxidative cracking dehydrogenation of alkanes to olefins can be explained by the Mars & Van Krevelen mechanism. In this mechanism, the first step involves the hydrocarbon acting as a reducing agent for the transition metal, while the next step is the re-oxidation of the metal by oxygen. In this type of conversion of alkanes to olefins, the rate-determining step is the carbon-hydrogen splitting step. Through the literature, there are two types of reactions for oxidative cracking. Both these reactions are represented by the below equations:



To explain these equations during the experiment, the feed of hydrocarbon, such as n-hexane or pentane, is injected into the reactor from the top for a fixed-bed experiment, while the catalyst is fixed inside the reactor. The reactor is then heated to the required temperature, resulting in the activation of the feed on the surface of the oxide metal catalyst. This will result in the formation of an alkyl radical that is further dehydrogenated either by a heterogeneous type of reaction on the surface of the catalyst or a homogeneous type of reaction in the gas phase. Hence, hydrogen is formed, which reacts with lattice oxygen or

gas phase to produce a stable water molecule, and alkene is produced as well. These are the desired products for the oxidative dehydrogenation reaction. However, there are also undesired reactions that could happen, leading to the formation of CO_x. The reason behind this is non-selectivity or further oxidation if it occurs. For the catalyst system composed of lattice oxygen of VO_x/Ce-Al₂O₃, a reaction mechanism is proposed as a hypothesis and shown in Figure 8:

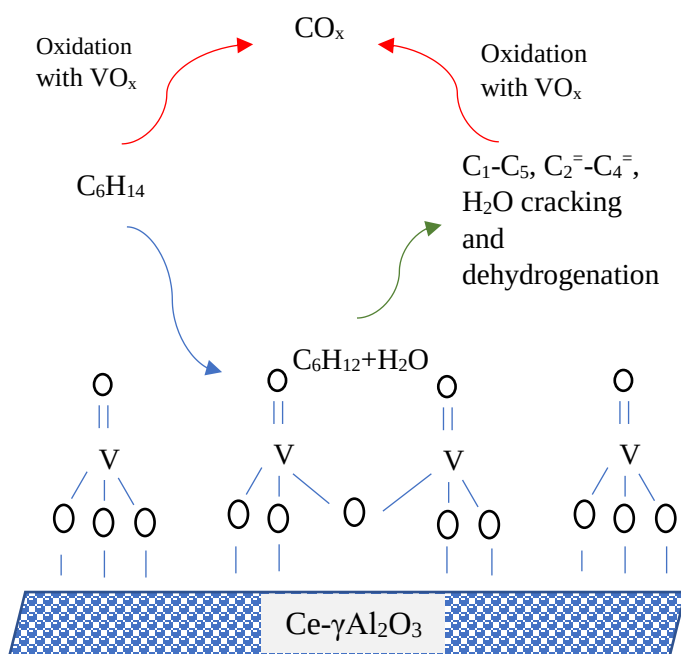


Figure 8: Reaction Mechanism for Oxidative Cracking of n-hexane [39].

The production of olefins by oxidative cracking of n-hexane via lattice oxygen of VO_x/Ce-Al₂O₃ catalysts is shown in two alternative routes, both of which produce desired products. The cracking step involves the cracking of n-hexane to produce alkanes. In the second route, the oxidative dehydrogenation of alkanes produced during the cracking step occurs, resulting in the formation of carbon dioxide due to the complete oxidation of the hydrocarbon. The alkyl radicals are created due to the mechanism of cracking, in which

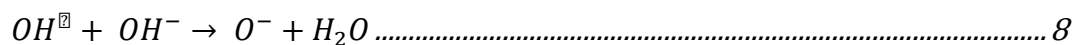
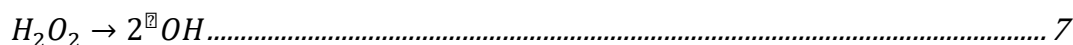
lattice oxygen aids the promotion of homolytic C-H bond abstraction from the alkane. In the gas phase, a homogeneous radical chain reaction occurs subsequently for the alkyl radicals, resulting in the formation of hydroxyl groups on the surface of the catalyst, which are released to the gas phase as water. This process leads to a reduction of the catalyst. Regeneration of the catalyst is the completion of the cracking cycle and occurs through the oxygen effect, which re-oxidizes the catalyst or combustion reactions by lattice oxygen, performing the same purpose as an alternative option. The most important aspect for the oxidative cracking reaction mechanism is the minimization of the sorption of olefins and any further oxidation. The proposed mechanism highlights the key steps involved in the oxidative cracking reaction, including the formation of alkyl radicals, their subsequent reaction in the gas phase, and the regeneration of the catalyst. Understanding and optimizing this mechanism is crucial for improving the selectivity towards the desired olefin products while minimizing the formation of undesirable byproducts. The catalyst system of Li/MgO reaction mechanism follows the equation below:



The formed products from the first step of oxidative cracking by the Li/MgO catalyst are the surface hydroxyl [OH⁻] group and alkyl radicals, as a result of the homolytic scission of C-H bonds. These products are yielded due to the release of radicals from the catalyst surface, causing the initiation of the propagated gas-phase reaction. Hence, the reaction mechanism for the production of olefins from alkanes is initiated by a homogenous gas-phase reaction, leading to a heterogeneous reaction on the catalyst surface. The two phases involved are:

- Homogenous gas-phase reaction: This involves the propagation of radical chain reactions in the gas phase, resulting in the formation of various hydrocarbon products.
- Heterogeneous catalyst cracking: The catalyst surface, in this case, Li/MgO, facilitates the initial homolytic cleavage of C-H bonds, releasing the alkyl radicals that can then undergo further reactions in the gas phase.

The combination of these two reaction pathways, the homogenous gas-phase reactions and the heterogeneous catalyst cracking, is crucial for the efficient production of olefins from alkane feedstocks. The catalyst plays a key role in initiating the radical formation, while the gas-phase reactions allow for the propagation and selective formation of the desired olefin products. Understanding and optimizing this reaction mechanism, including the interplay between the homogenous and heterogeneous steps, is essential for the development of effective catalysts and processes for the oxidative cracking of alkanes to produce valuable olefins. The reaction mechanism for the regeneration of the catalyst is shown in the below equations as proposed by Siney.



Once there is an interaction between the catalyst and the product of carbon dioxide, deactivation of the catalyst is likely to occur due to the poisoning of the active Li+O- sites.

A reported study by Lunsford et al. on the oxidative cracking of methane and propane, which are major components of natural gas liquids (NGL), found that the Li+O- sites were poisoned by carbon dioxide, presenting a drawback for applying this type of catalyst for oxidative cracking. The poisoning of the active Li+O- sites by carbon dioxide is a significant challenge that needs to be addressed for the effective use of Li-based catalysts in oxidative cracking processes. Strategies to mitigate this issue may include:

- A- Developing catalyst formulations that are more resistant to carbon dioxide poisoning, such as by incorporating additional promoters or modifiers.
- B- Optimizing the reaction conditions, such as temperature and pressure, to minimize the formation of carbon dioxide and its interaction with the active sites.
- C- Integrating in-situ catalyst regeneration or periodic reactivation steps to remove the deposited carbon species and restore the catalyst's activity.
- D- Exploring alternative catalyst systems that are less susceptible to deactivation by carbon dioxide or other byproducts.

Addressing the catalyst deactivation issue is crucial for the successful commercialization of oxidative cracking processes, as it will ensure the long-term stability and performance of the catalysts, leading to more efficient and economical production of valuable olefins from alkane feedstocks.

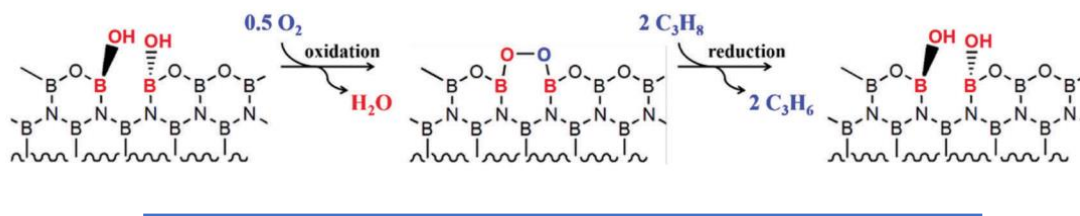


Figure 9: Proposed Reaction Mechanism for Oxidative Cracking of Boron Nitride [40].

The main by-product of oxidative cracking by V/SiO₂ is carbon dioxide, but for boron nitride nanotubes (BNNTs) catalyst, the major by-product is ethene, which is of higher value than carbon dioxide. This variation in product distribution is an indication of a distinctive reaction mechanism route. This route is not similar in mechanism to other metal oxide oxidative dehydrogenation catalysts or lattice oxygen. The investigation of this route for the reaction mechanism shows a first-order and second-order dependency for oxygen partial pressure and partial pressure of propane for the latter, as noted by Grant et al. (196). The other suggestion is related to the bond between B and N and the oxygen molecule, forming an armchair resulting in the formation of B-O-O-N active sites at the platelet edges between B-N. The activity was also tested without nitrogen existing and was at a high value. Further studies concluded that the highest compound for productivity, especially used for oxidative dehydrogenation, is (BN-OH), which is hydroxylated boron nitride. Another difference between boron-based catalysts and other metal oxide catalysts in reaction mechanism is the functionality of non-oxidation. For example, there is no record of any non-oxidative propane dehydrogenation using h-BN catalyst. The functionality of

other catalysts initially does not demand an induction period. However, boron nitride catalysts are capable of forming the required sites for activity, serving as precursors to phase activation. The Mars-Van Krevelen mechanism in metal oxide catalysts cannot be applied to boron nitride catalysts, for example, h-BN, due to the lack of lattice oxygen. Further understanding of the mechanism is necessary for the optimization of this catalyst system.

2.10. Kinetics of Oxidative Cracking

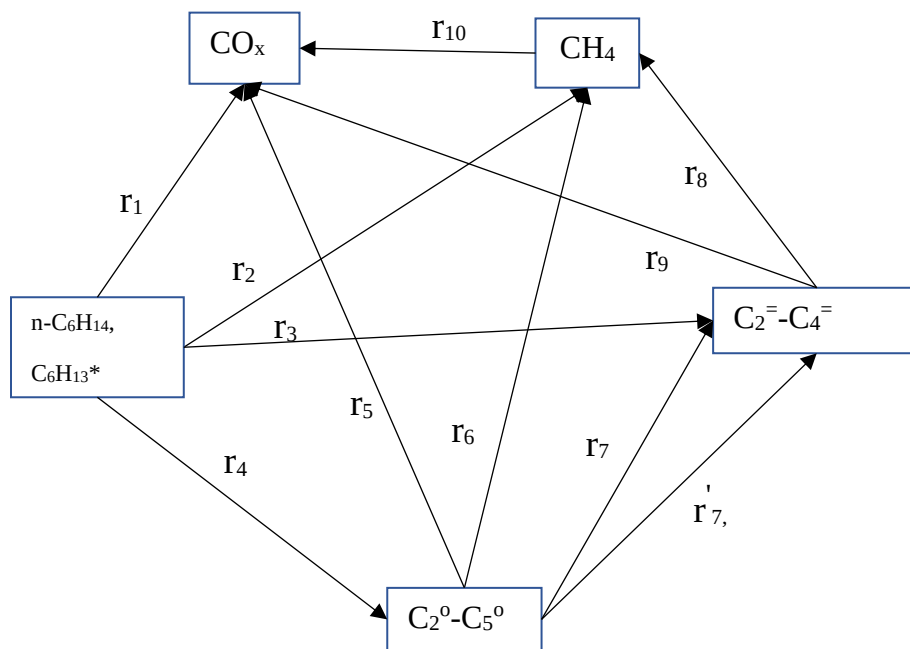


Figure 10: Reaction Network for Oxidative Cracking of n-Hexane [38].

The reaction network in the Figure 10 illustrates the basis for developing the kinetic model.

- A- Olefins and lighter alkanes are produced via cracking of n-hexane.
- B- Production of olefins and carbon oxides by oxidative dehydrogenation.
- C- Formation of coke and lattice oxygen degeneration leading to catalyst deactivation.

For each step mentioned above there are equations developed and explained in further details starting with cracking to oxidative dehydrogenation and finally deactivation.

The carbonium-ion mechanism is dominating for the cracking step explained simply for this reaction involving two steps transfer of hydrogen observed first then C-C bond fission.

The set of reactions below explain this mechanism:

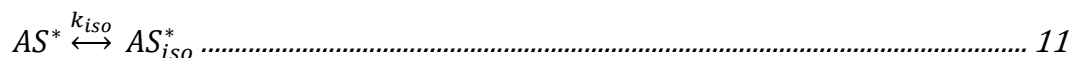
- 1- The molecule A is adsorbed on the active centre (S).



- 2- The adsorbed species then form reactive species that are short-lived.



- 3- The reactive species will transform reversibly, and this reaction is known as skeleton isomerization reaction. The primary products of isomerization can also appear because of adsorption of isomerized molecules.



- 4- The reactive species will transform irreversibly by cracking through the mechanism of carbon-carbon bond fission.



- 5- The molecules on the catalyst active sites will cracking by reversibly desorption.



- 6- The major step is postulated by reactions of cracking is chain mechanism.



Following the development of elementary reaction steps above the progress is to use these equations for coming up with equations of rate. Hence, for reaction intermediates it is possible to be written below following the pseudo steady state hypothesis (PSSH). These reaction intermediates are AS, AS^* , PS^* and R.

$$r_{AS} = k_{ad} - k_{des}C_{AS} = 0 \dots\dots\dots 15$$

$$r_{AS^*} = k_{reac}C_{AS} - k_{iso}C_{AS^*}C_{AS} - k_{fission}C_{AS^*} = 0 \dots\dots\dots 16$$

$$r_{AS^*} = k_{reac}C_{AS} - k_{iso}C_{AS^*}C_{AS} - k_{fission}C_{AS^*} = 0 \dots\dots\dots 17$$

$$r_{PS^*} = k_{fission}C_{AS^*} - k_{des}C_{PS^*} \dots\dots\dots 18$$

$$r_P = k_{des}C_{PS^*} \dots\dots\dots 19$$

The rate determined step is slowest step and as a result of high catalyst acidity this step is the product desorption step and hence the below equations are developed.

$$C_{AS} = \frac{k_{ad}C_S C_A}{k_{des}} \dots\dots\dots 20$$

$$C_{AS^*} = \frac{k_{reac}C_S C_A}{k_{fiss} + C_S k_{iso}} \dots\dots\dots 21$$

$$C_{PS^*} = \frac{k_{fiss}k_{reac}k_{ad}C_S C_A}{k_{des}^2 (k_{fiss} + C_S k_{iso})} \dots\dots\dots 22$$

From these equations and re-arranging and substituting it is possible to obtain the rate expression equation for cracking of species $I = 1, 2, 3 \dots 10$.

$$r_i = \frac{k_{fiss,i}k_{reac,i}k_{ad,i}C_S C_A}{k_{des,i}(k_{fiss,i} + C_{S,i}k_{iso,i})} \dots\dots\dots 23$$

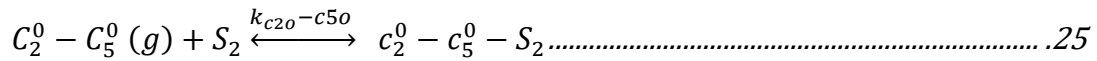
The equation above can also be obtained for any product or reactant for instance A, n-hexane, paraffins or any related chemical specie.

$$r_A = \frac{k_{fiss,A} k_{reac,A} k_{ad,A} C_{S,A} C_A}{k_{des,A} (k_{fiss,A} + C_{S,A} k_{iso,A})} \dots\dots\dots 24$$

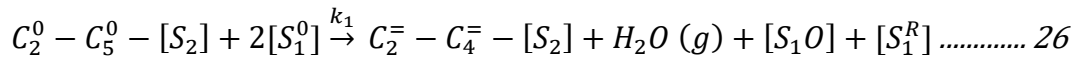
The development of kinetic model scheme for the cracking reaction is followed by establishing the model for oxidative dehydrogenation (ODH). This reaction in which olefins are produced by the reaction between hydrocarbons and the lattice oxygen catalyst .

The mechanism for these reactions is based on the Lang-muir-Hinshelwood and for understanding these reactions the six steps below clearly explain each reaction and species involved. For lattice oxygen in an oxidized site the representation is by S_1^0 and the surface oxygen vacancy in a reduced site is represented by S_1^R and the symbol S_2 is for alumina-based sites [16].

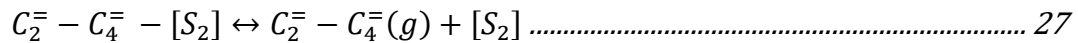
A- The catalyst surface contains S_2 which adsorbs alkanes C_2^0 - C_5^0 .



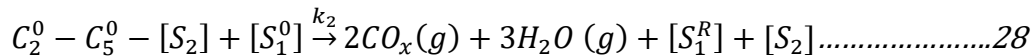
B- Through H-abstraction the oxidized site medium for S_1^0 formed from lattice oxygen having a surface reaction (r_7) will result in forming C_2^- - C_4^- .



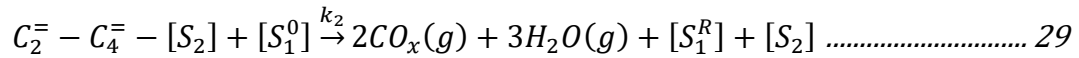
C- The reduced site has adsorbed olefins which desorption occur for.



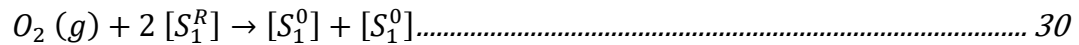
D- C_2^0 - C_5^0 will react with adsorbed lattice oxygen to form CO_x from propane r_2 and this occurs in the site of oxidization for $[S_1^0]$.



E- The oxidization site $[S_1^0]$ a further reaction will occur between lattice oxygen and adsorbed ethylene forming CO_x by ethylene (r_3).



F- Oxygen Molecule will re-oxidize the reduced metallic center.



To conclude these reaction steps the rate expression for oxidative dehydrogenation is obtained:

$$r_7' = \frac{k_{11}P_{C_2^0-C_5^0}}{1+K_{12}P_{C_2^0-C_5^0}+K_{13}P_{C_2^- - C_4^-}+K_{14}P_{CO_X}+K_{15}P_{CH_4}} \dots\dots\dots 31$$

For catalyst deactivation two major reasons the cracking reaction causing coke to deposit on the catalyst or due to oxidative dehydrogenation reaction reducing VO_x leading to the depletion of oxygen and losing activity. These two majors for catalyst deactivation are represented by the following two activity function.

$$\phi(T, t) = \alpha(T)\psi(t) \dots\dots\dots 32$$

Each term in the equation above is a function of time for $\psi(t)$ the deactivation of catalyst because of coke formation based on time on stream function and $\alpha(T)$ is function of oxygen depletion from oxidative dehydrogenation. Expression equation for each function is shown below:

$$\psi(t) = \exp(-\lambda t) \dots\dots\dots 33$$

$$\alpha(T) = \frac{\int_0^t a+b \exp\left[\frac{-(T-T_m)^2}{2c^2}\right]}{\int_0^{1000} a+b \exp\left[\frac{-(T-T_m)^2}{2c^2}\right]} \dots\dots\dots 34$$

2.11. Conclusion of Literature Review

To conclude, this review has thoroughly explained various catalyst systems for oxidative cracking reactions to produce olefins. Two types of feedstock were used for these reactions: hexane and propane. Each system has produced a certain yield of olefins, such as propene, depending on the reaction conditions and the conversion percentage. Following the detailed explanations of these catalyst systems, the reaction mechanisms for some of the systems were discussed, concluding the pathways for the desired production of olefins. The key steps involved in these mechanisms, such as the formation of alkyl radicals, heterogeneous and homogeneous reactions, and the role of lattice oxygen, were highlighted. Finally, a detailed kinetic study was reviewed for the oxidative cracking of n-hexane using a lattice oxygen catalyst. Understanding the kinetics of these reactions is crucial for optimizing the process conditions and catalyst performance to achieve higher yields of the desired olefin products. The comprehensive review of the various catalyst systems, reaction mechanisms, and kinetic studies provides valuable insights into the state-of-the-art research and development in the field of oxidative cracking for the production of light olefins. These insights can guide future research efforts to further improve the efficiency, selectivity, and scalability of these processes, ultimately contributing to the advancement of the petrochemical industry. The scope of this research study is to characterize and evaluate zeolite-based catalyst supported on metal oxide for free lattice oxygen release in a fixed batch reactor to screen best catalyst and determine optimum olefins production reaction conditions.

The research involves tests under catalyst to oil ratio range 3-6 and temperature range 550°C -625°C. Furthermore, a robust kinetic model is developed based on lumping methods clearly explaining the reaction mechanism in which the olefins are produced.

Chapter 3: Objectives

This study involves the development of highly active and stable catalyst(s) suitable for fluidized bed oxidative cracking of lighter liquid hydrocarbons for example naphtha under gas-phase oxygen-free conditions to produce light olefins – mainly butenes, propylene and ethylene. In this approach, the metal supported catalysts acts as a source of lattice oxygen, in addition to its catalytic role. In this regard, MnO_x modified zeolite-based catalysts have been investigated. The following are the specific objectives of this work:

- i. To study the effects of MnO_x on the activity (naphtha conversion) and olefins selectivity/yields.
- ii. To develop the phenomenological based kinetics model(s) representing the conversion of naphtha over $\text{MnO}_x/\text{ZSM-5}$ catalysts.

Chapter 4: Methodology

4.1. Materials and Catalyst Synthesis

Chemicals used for catalyst synthesis include Montmorillonite (Mnt) supported on manganese oxide (MnOx), ZSM zeolite and Y-Zeolite. For feed both Light Straight Run Naphtha (LSRN).

4.1.1 Synthesis of Montmorillonite Supported Manganese Oxide

Montmorillonite supported manganese oxide nanoparticles were prepared using a simple wet grinding approach. In a typical synthesis protocol, the required amount of manganese oxide salt, corresponding to the desired weight percentage (wt.%) of Mn, was added to a mortar and pestle. This mixture was properly grinded for several minutes. Thereafter, an amount of water corresponding to 75 wt.% of the total weight of the supported material was added, and the mixture was further grinded. The mixture was then dried at 70 °C for 12 h, followed by calcination at 550 °C for 6 h with a heating rate of 5 °C/min. For this study, 5, 10, and 15 wt.% Mn on montmorillonite (40 g basis) were prepared. The resulting samples are labeled Mn5, Mn10, and Mn15, corresponding to 5, 10, and 15 wt.% Mn loading on montmorillonite, respectively.

4.1.2. Synthesis of Zeolites/Montmorillonite Manganese Oxid Matrices

A mixture of zeolite Y and ZSM-5 is prepared for the purpose of this study. It is well-known that zeolites have different Si, Al, and O connections and orientations, resulting in variations in pore size and functionality. The essence of employing this mixture is to exploit the synergistic effect of these two different zeolite structures. Zeolite Y possesses large pores that can easily facilitate the exit of reactants and products. ZSM-5, on the other hand,

offers pores that can be tailored for the selective production of desired products like lighter olefins, due to its shape selectivity, and is also known for its thermal stability and coke resistance. A simple approach was employed to synthesize the zeolite/montmorillonite manganese oxide matrices. Zeolites and pre-synthesized montmorillonite manganese oxide were mixed using a blender. Afterwards, the resulting mixture was pelletized to a size range of 300 microns. The total zeolite content in the final zeolite/montmorillonite manganese oxide matrices was 70%, with a 50:50 weight ratio of zeolite Y to ZSM-5. It is important to note that all zeolites were used in their acidic (H-form). For ZSM-5, the as-received ammonium form was converted to the H-form by calcination at 550 °C for 6 h with a heating rate of 5 °C/min. Therefore, the final composition of the zeolite/montmorillonite manganese oxide matrices was 35% zeolite Y, 35% ZSM-5, and 30% montmorillonite manganese oxide (which could be Mn5, Mn10, or Mn15). During this study, three matrices were prepared by fixing the zeolite composition (50:50 Y and ZSM-5) and varying the Mn loading on the montmorillonite. The synthesized catalysts are now labeled ZMn5, ZMn10, and ZMn15.

3.2. Catalyst Characterization

4.2.1 Temperature-Programmed Reduction (TPR) Test

To understand the reduction behavior and potential activity of the freshly prepared catalysts, TPR analysis was conducted in a Microtrac MRB Belcat II catalyst analyzer. The samples, weighing 200 mg each, were loaded into a quartz tube and heated to 500 °C for three hours under an argon atmosphere. The samples were then cooled to 30 °C using argon. The TPR analysis was conducted to reduce the fresh catalysts in the temperature range of 25 to 950 °C. A gas mixture containing 10% hydrogen and balanced with argon

was used. The system was heated at a rate of 10 °C/min. During the TPR experiment, a thermal conductivity detector (TCD) was used to analyze and record the consumption of hydrogen, indicating the reduction behavior of the catalyst. The TPR analysis provides valuable information about the reducibility of the catalyst, which is directly related to the catalytic activity. The reduction peaks observed in the TPR profile correspond to the reduction of different metal oxide species present in the catalyst. By analyzing the TPR profile, the peak reduction temperatures and the extent of reduction were determined, which helps in understanding the catalyst's redox properties and its potential performance in the oxidative dehydrogenation reaction.

4.2.2. X-ray diffraction (XRD) Test

The crystal structure of the fresh and spent ZMn catalyst samples was analyzed using X-ray diffraction (XRD) techniques. The XRD patterns were recorded using a Rigaku Mini-Flex diffractometer, which employed monochromatic Cu K α radiation with a wavelength (λ) of 0.15418 nm. The operating conditions for the XRD analysis were set at 30 kV and 15 mA. The XRD measurement was conducted with a normal scan rate of 2°/min, and the 2 θ scanning range was set between 10-80°, with a step size of 0.005°. The X-ray beam was collimated using a divergent slit of 1.25° and a receiving slit with dimensions of 0.13 mm. This setup allowed for the collection of high-resolution XRD patterns, which were used to identify the crystal structure of the fresh and spent catalyst samples.

4.2.3. Temperature-Programmed Desorption (TPD) Test

The fresh catalyst samples were also subjected to temperature-programmed desorption (TPD) of ammonia (NH_3) to determine their acidity. The TPD experiments were conducted using a mixture of 5% NH_3 in helium, with a total flow rate of 50 mL/min. The catalyst samples were heated from 100 °C to 600 °C at a ramp rate of 10 °C/min, and the experiment was carried out for a duration of one hour. During the TPD analysis, the concentration of desorbed NH_3 was measured at the outlet of the reactor using a thermal conductivity detector (TCD). The TCD signal provided information about the amount and strength of the acid sites present on the catalyst surface. The TPD technique is a valuable characterization method for determining the acidity of solid catalysts. By analyzing the TPD profile, it is possible to identify the number, strength, and distribution of acid sites on the catalyst, which are crucial parameters in understanding the catalyst's performance in various reactions, such as cracking, isomerization, and dehydrogenation. The combination of TPD and other characterization techniques, such as XRD and BET surface area analysis, provides a comprehensive understanding of physicochemical properties of the catalyst and their relationship with the catalytic activity and selectivity.

4.2.4. Fourier Transform Infrared Analysis (FTIR) TEST

The molecular structure of the fresh ZMn catalyst sample, weighing 200 mg, was analyzed using Fourier-Transform Infrared (FTIR) spectroscopy. The FTIR spectra were obtained using a Thermo Scientific ATR/IR instrument.

4.2.5. Scanning Electron Microscopy (SEM) Test

The morphological properties of the synthesized MnO_x/ZSM-5 catalyst was analyzed using a JEOL JSM-6460LV scanning electron microscope running at an acceleration voltage of 20 kV. Additionally, energy-dispersive X-ray spectroscopy (EDS) was employed to provide elemental mapping and composition analysis of the catalyst.

4.2.6. Brunauer-Emmett-Teller (BET) Surface Area Analysis Test

Nitrogen adsorption isotherm analysis data was used to determine the BET (Brunauer–Emmett–Teller) surface area and the textural characteristics of the synthesized material using an ASAP 2010 analyzer from Micromeritics ASAP analyzer. Prior to the nitrogen physisorption experiment, about 0.3 g of the catalyst was placed in the sample tube and degassed under vacuum for three hours at 350 °C. The N₂ physisorption was carried out in a liquid nitrogen bath operating between 10⁻⁶ and 1 relative pressure and 77 K temperature. The Barret–Joyner–Halenda (BJH) method was used to determine the pore volume and pore diameter while BET method was employed to determine the specific surface area of the catalyst.

3.3. Oxidative Cracking Experiment

The catalytic performance of the ZMn catalyst systems was evaluated using a fixed-bed Micro Activity Test Unit (MAT). The feed, consisting of light straight-run naphtha (LSRN), was precisely injected into the reactor using a syringe pump at a rate of 0.85 g per 30 seconds. The systematic variation of operating parameters, such as temperature and catalyst-to-oil ratio, enabled the researchers to gain valuable insights into the catalyst's activity, selectivity, and potential for industrial applications. In this regard, temperature

was varied at 550, 575, 600 and 625 °C, and the catalyst-to-oil ratio was set at 3, 4, 5 and 6. For each experimental run, 4 g of the oxidized catalyst sample was loaded into the reactor bed, and a leak test was conducted to ensure the system's integrity [15]. The reaction products were analyzed using a micro gas chromatograph (Micro-GC) equipped with both flame ionization (FID) and thermal conductivity (TCD) detectors. This analytical setup allowed for the quantification and identification of the various hydrocarbon components in the product stream. The conversion and selectivity were calculated based on the following definitions:

- *Conversion*: The extent of change of the LSRN feed into various products.
- *Selectivity*: The relative distribution of the desired products, such as olefins, among the total product slate.

$$\text{Naphtha/ conversion (wt. \%)} = \text{Total gas (wt. \%)} + \text{Coke (wt. \%)} \dots\dots\dots 35$$

$$\text{Yield of product (wt \%)} = \frac{\text{Mass of the species}}{\text{Mass of total product}} \times 100 \% \dots\dots\dots 36$$

Table 3: Obtained Properties and Values from PIONA for LSRN Feed

Property	Value
Research Octane Number	57.80
Motor Octane Number	55.60
Initial boiling point by mass IBP (Deg F)	96.91
Vapor Pressure	2.45
Paraffins Total Mass%	34.13
I-paraffins Total Mass %	22.60
Olefins Mass%	27.90
Naphthene Mass %	12.96
Aromatic Mass %	1.38
Total C14+ Mass %	0
Total Unknowns	0.61
Average Molecular weight of Hexane	85.57
Average Molecular Weight of Pentane	70.85

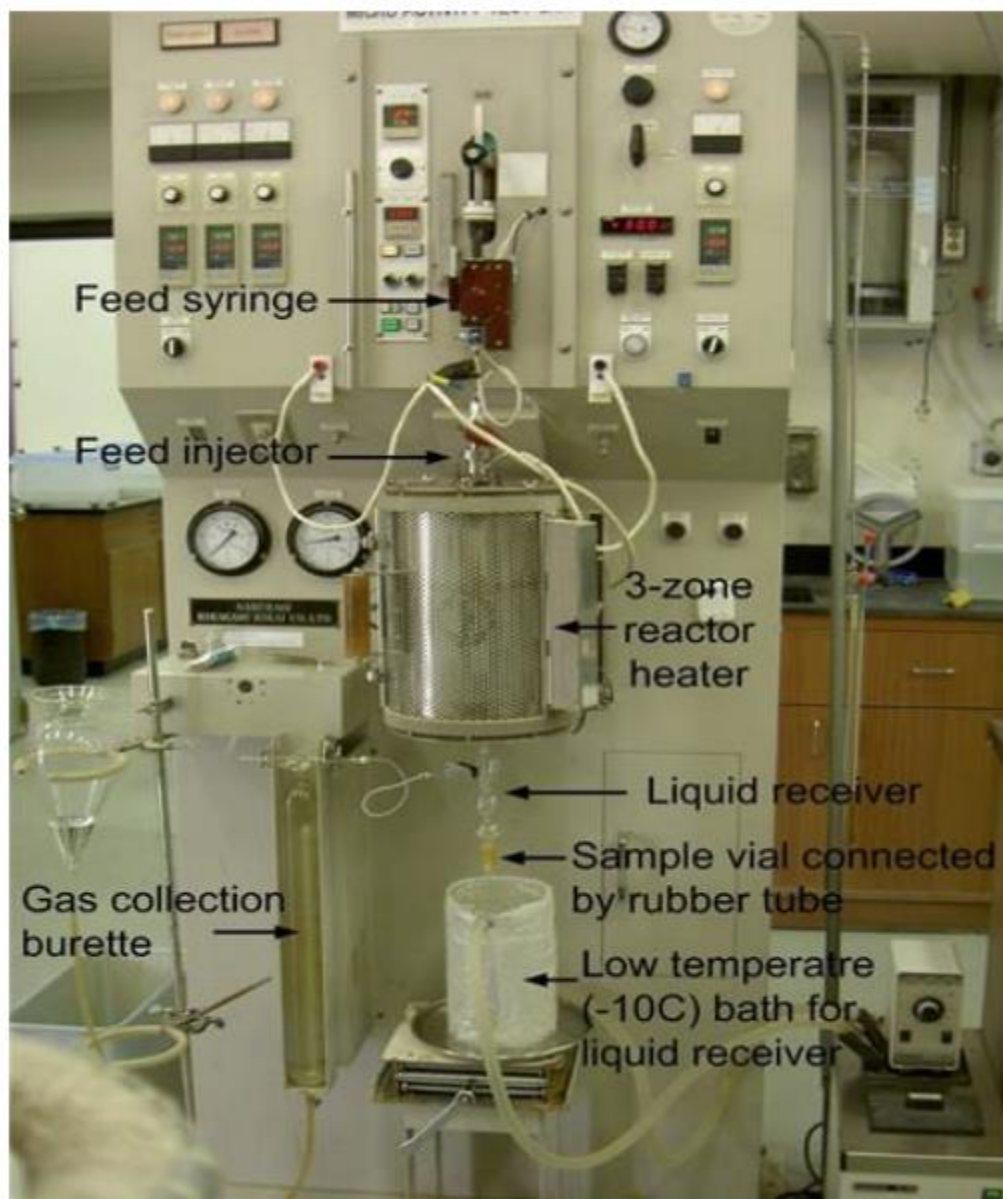


Figure 11: Micro-activity Test Unit (MAT) Real Picture labelled with part

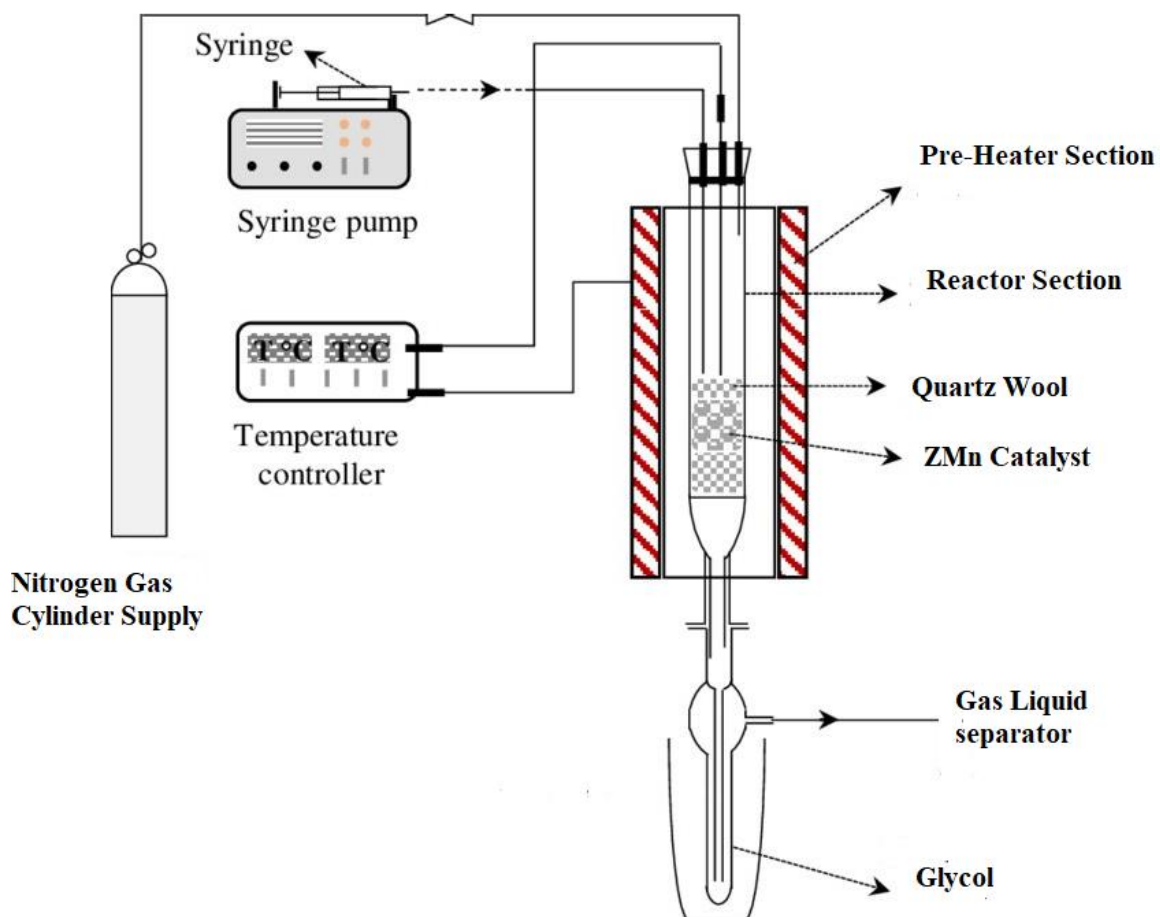


Figure 12: Schematic Diagram of MAT (Fixed Batch Reactor)

Chapter 5: Results and Discussion

5.1. Catalyst Characterization

5.1.1. Scanning Electron Microscopy (SEM)

The scanning electron microscopy (SEM) analysis (Figure 13 a, b, and c) shows the morphological characteristics of the resulting matrix. All matrices ZMn5, ZMn10 and ZMn15 showed similar morphologies of zeolites (that is, ZSM-5 and Y zeolite) as well as montmorillonites structures. The ZSM-5 samples are in the submicron range, while Zeolite Y samples are few microns large.

Complementing the SEM analysis, the energy-dispersive X-ray (EDX) technique was employed to obtain the elemental mapping of the catalyst for ZMn-5 as a case study (figure 13 d & e). The mapping analysis gives us an insight into the dispersion of Mn in the catalyst matrix. We observed from that Mn is well dispersed in the catalyst matrix. Furthermore, the elemental analysis in figure 1 f shows the overall elemental content in ZMn5.

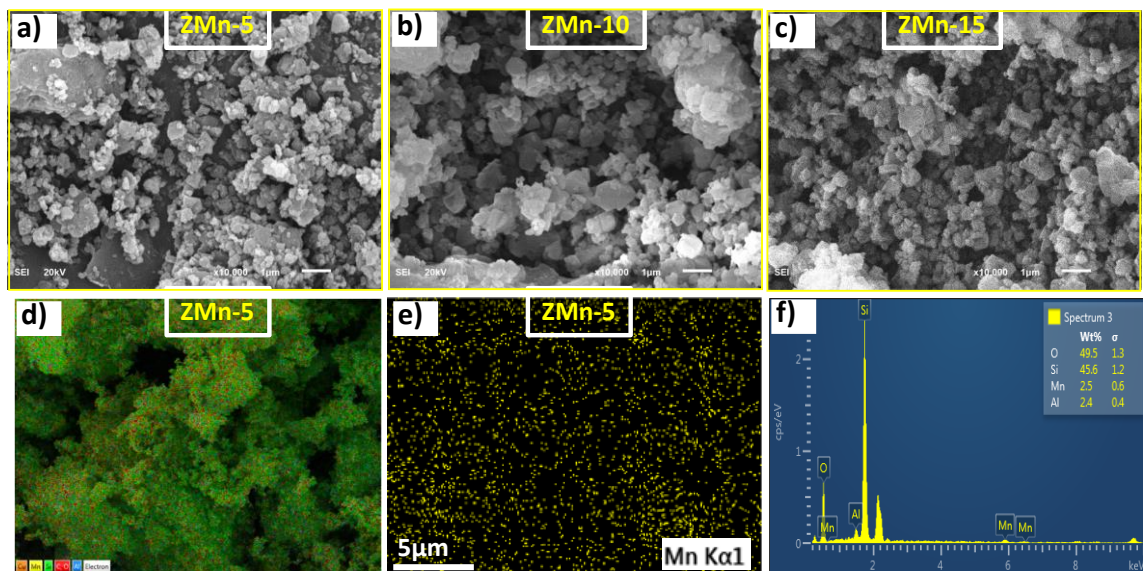


Figure 13: SEM micrograph Screened Catalyst and EDS of ZMn-5

5.1.2. X-ray diffraction (XRD)

Figure 13 shows the X-ray diffraction patterns of prepared zeolite/montmorillonite manganese oxide matrices, as well as the spectra of pure zeolite species. ZMn5, ZMn10, and ZMn15 show characteristic zeolite Y and ZSM-5 peaks. Furthermore, we observed that the introduction of MnOx species did not result in any significant changes to the zeolite's topological structure or crystallinity [50], [51].

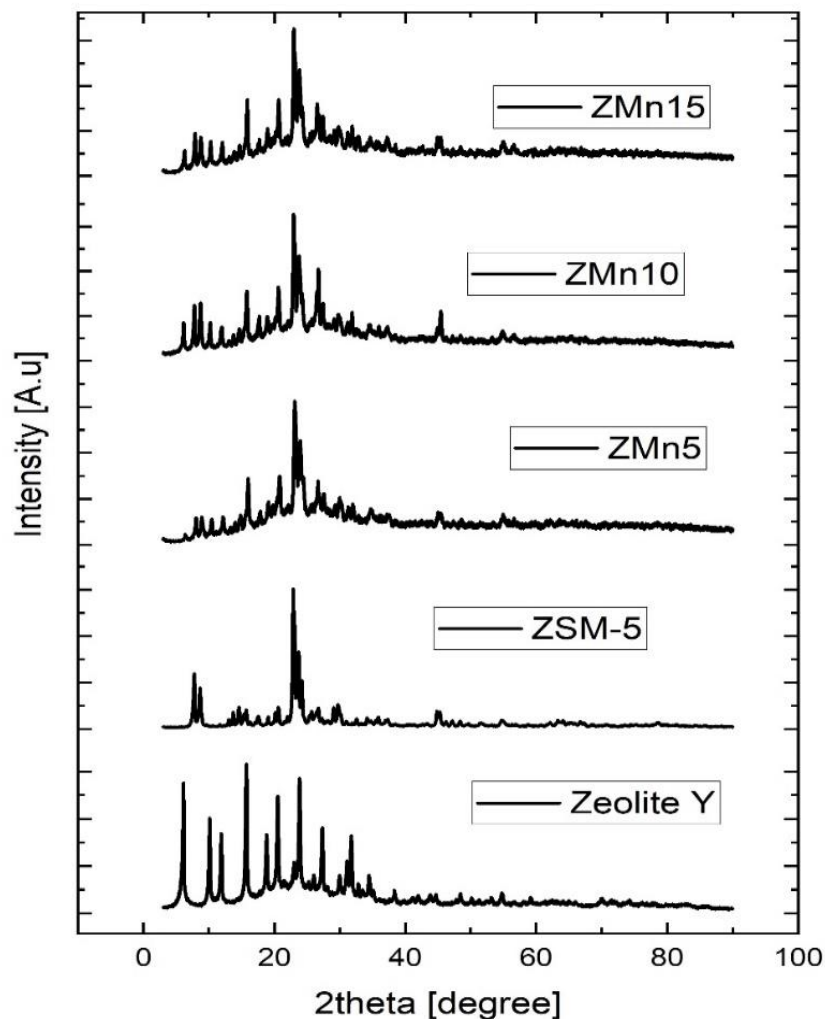


Figure 14: XRD of Zeolite and Catalysts with Manganese Loadings

5.1.3. Fourier Transform Infrared Analysis (FTIR)

Figure 15. shows the FTIR spectra of prepared ZMn matrices. All prepared matrices showed characteristics asymmetric stretching vibrations of the Si-O-Al bonds observed in the range of $950\text{--}1090\text{ cm}^{-1}$. In addition, we observed OH Stretching Symmetric & Asymmetric between $2700\text{ to }3200\text{ cm}^{-1}$ ($\sim 2971\text{ cm}^{-1}$). These stretches are common to zeolites as well as clays such as montmorillonite [16]. It worth mentioning that we observed a shift

to higher wave number in the asymmetric stretching vibrations observed in the range of 950-1090 cm^{-1} as the Mn content increase in our matrices (that is ZMn15 stretching in this region were of higher magnitude that those of ZMn10 and in the same order ZMn10 has higher magnitude than those of ZMn5) [52]. This observation shows the substitution of Mn for Al in the montmorillonite framework, since the Mn species were deposited on the montmorillonite support during catalyst preparation.

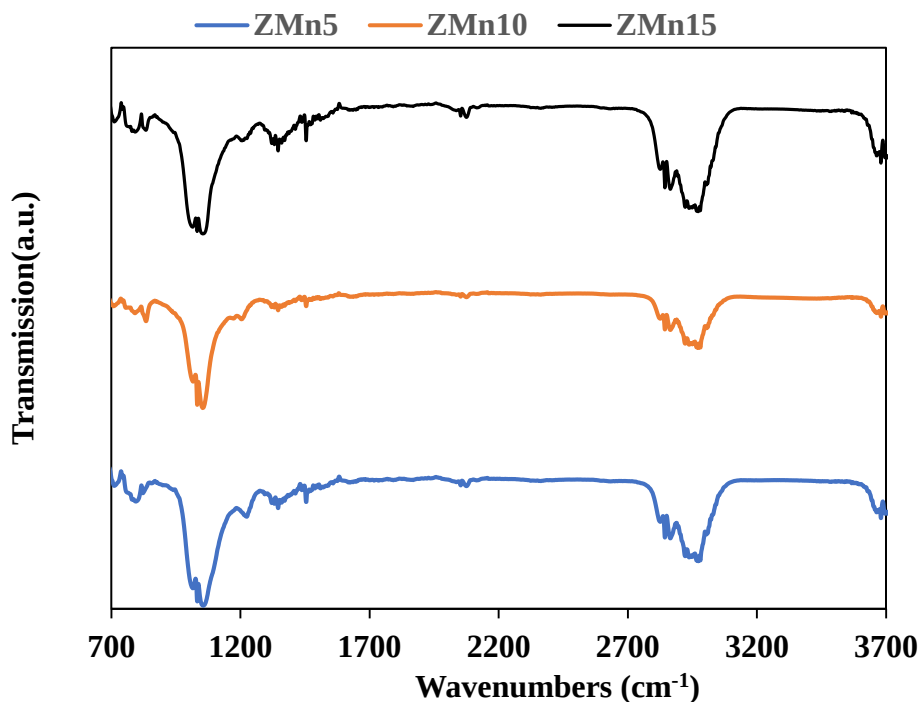


Figure 15: FTIR of ZMn-5, Zmn-10 and Zmn-15 Catalyst

5.1.4. Temperature-Programmed Desorption (NH_3 -TPD)

The catalytic cracking of light straight-run naphtha (LSRN) into olefins and other products is primarily driven by the active acidic sites present on the catalyst surface. These active centers can be classified into two categories: low-strength and high-strength acid sites. The balance between the concentration and strength of these acid sites is crucial for achieving

optimal catalytic performance in the oxidative dehydrogenation of LSRN. During the reaction, the catalyst's acidity should be carefully tuned to avoid excessive cracking of the light feedstock, which can lead to the formation of undesirable products such as coke and methane. The accumulation of these byproducts can result in catalyst deactivation and reduced selectivity towards the desired olefin products. Temperature-programmed desorption of ammonia (NH₃-TPD) is a widely used technique for the characterization of catalyst acidity [53], [54].

Figure 16 presents the NH₃-TPD profiles of the ZMn catalyst matrices, which provides an insight to the acid strength and distribution. The NH₃-TPD analysis allows for the quantification of the total acidity and the identification of low-strength and high-strength acid sites based on the desorption temperature ranges. As observed in Figure 16, all ZMn samples have two main adsorption peaks, one at lower temperatures at ~ 100 °C and a second at higher temperatures at about 400°C. Basically, All ZMn catalyst systems had similar zeolite compositions, thus the change in acidity observed can only be attributed to the MnOx species supported on montmorillonite. Hence, acid distribution in the matrices is a function of MnOx species content. Clearly, we see that as the MnOx species increase, the low temperature peak becomes narrower (low band peak in ZMn15 is more than ZMn10 and ZMn10 narrower than ZMn5). In addition, the desorption temperature is lower as the content of MnOx increases. Hence, we can infer that MnOx species played a crucial role in reducing the acid strength of the whole catalyst matrix.

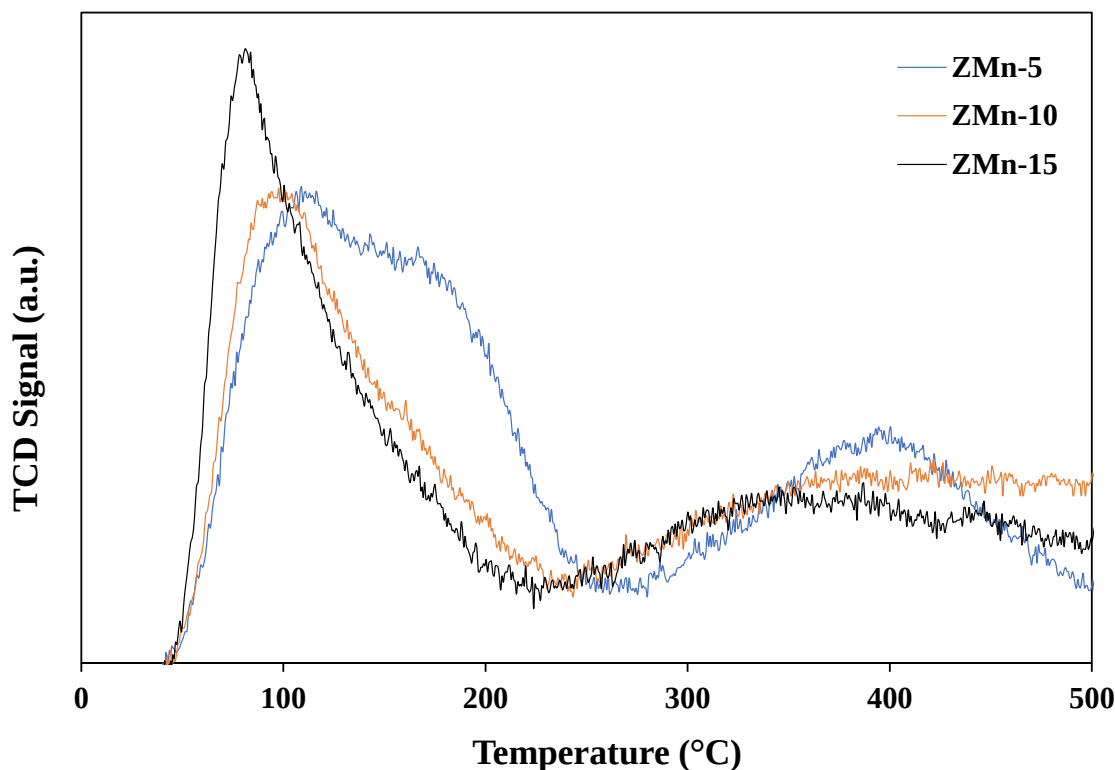


Figure 16: *NH₃ Temperature-programmed desorption (NH₃-TPD) of ZMn catalyst matrices*

5.1.5. Temperature-Programmed Reduction (H₂-TPR)

The reducibility and nature of the oxide phases present on the catalyst surface were investigated through hydrogen temperature-programmed reduction (H₂-TPR) experiments for the three fresh catalysts: ZMn5, ZMn10, and ZMn15. The TPR profiles of the fresh catalysts are shown in Figure 17. The ZMN15 catalyst exhibited the highest reduction peak, followed by ZMn10 and ZMn5, which had the smallest peak among the three. Each catalyst displayed two distinct reduction peaks [55], [56] The first, smaller peak was observed in the temperature range of 300-500 °C, while the second, larger peak occurred in the range of 500-700 °C. These reduction peaks are attributed to the stepwise reduction of the manganese oxide species supported on the zeolite framework. The factors influencing the

reducibility and nature of the oxide phases include the catalyst synthesis method, the type of active metal oxide, the support material, and the calcination temperature during catalyst preparation. The first reduction peak, in the lower temperature range, is likely associated with the reduction of Mn_2O_3 to Mn_3O_4 [57]. The second, larger reduction peak at higher temperatures corresponds to the consumption of hydrogen and is related to the reduction of MnO_2 to Mn_2O_3 [58].

The overlapping of these reduction peaks suggests that the manganese oxide species are well-dispersed and intimately integrated into the zeolite support structure. The differences in the reduction profiles among the three catalysts indicate variations in the manganese oxide species and their interactions with the ZSM-5 zeolite framework. The TPR analysis provides valuable insights into the redox properties of the manganese-based catalysts, which are crucial for understanding their catalytic performance in the oxidative dehydrogenation of light straight-run naphtha. The information obtained from the TPR profiles can be correlated with other characterization techniques, such as XRD and SEM-EDS, to develop a comprehensive understanding of the catalyst's structure-activity relationships. Selectivity: The relative distribution of the desired products, such as olefins, among the total product slate.

The comprehensive experimental setup and analytical techniques employed in this study provided a robust framework for evaluating the catalytic performance of the $\text{MnO}_x/\text{ZSM-5}$ catalyst in the oxidative dehydrogenation of light straight-run naphtha. The systematic variation of operating parameters, such as temperature and catalyst-to-oil ratio, enabled the researchers to gain valuable insights into the catalyst's activity, selectivity, and potential for industrial applications.

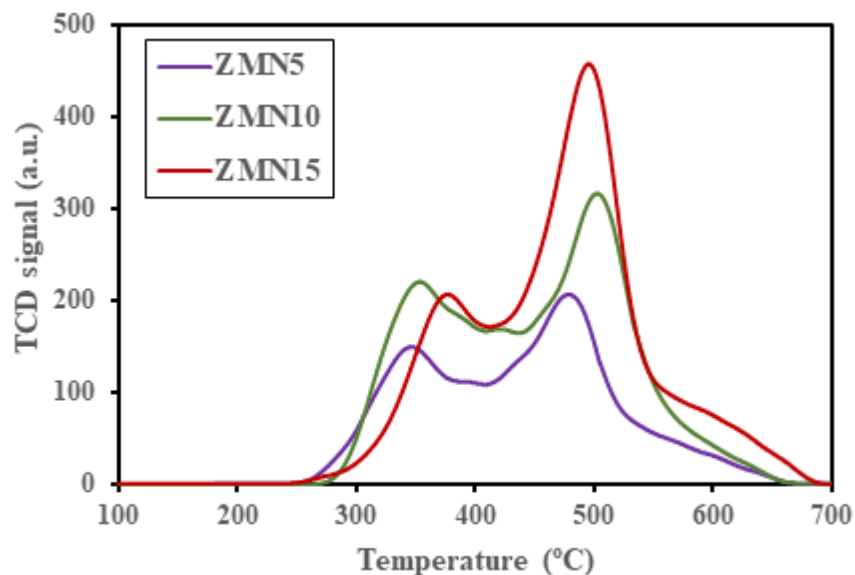


Figure 17: TPR Profile of the $\text{MnO}_x/\text{ZSM-5}$ Catalysts with Loadings of 5%, 10% and 15%.

5.1.6 Nitrogen Adsorption Isotherms Analysis

The nitrogen adsorption isotherm of the $\text{MnO}_x/\text{ZSM-5}$ catalyst, shown in Figure.6, corresponds to type IV adsorption isotherm according to the IUPAC classification. The adsorption behavior of the $\text{MnO}_x/\text{ZSM-5}$ catalyst indicates the existence of mesopores at higher relative pressures (between 0.5 and 1). These pore structures are likely created during the catalyst synthesis process, such as through desilication-recrystallization. The BET surface area of the $\text{MnO}_x/\text{ZSM5}$ catalyst sample is $412.4 \text{ m}^2/\text{g}$, with a total micropore area of $204.9 \text{ m}^2/\text{g}$ and a mesopore area of $211.5 \text{ m}^2/\text{g}$. For $\text{MnO}_x/\text{ZSM-10}$ and $\text{MnO}_x/\text{ZSM-15}$ the same isotherm type IV is seen in the plots. However, the total surface area is smaller being $322.54 \text{ m}^2/\text{g}$ and $328.18 \text{ m}^2/\text{g}$ respectively.

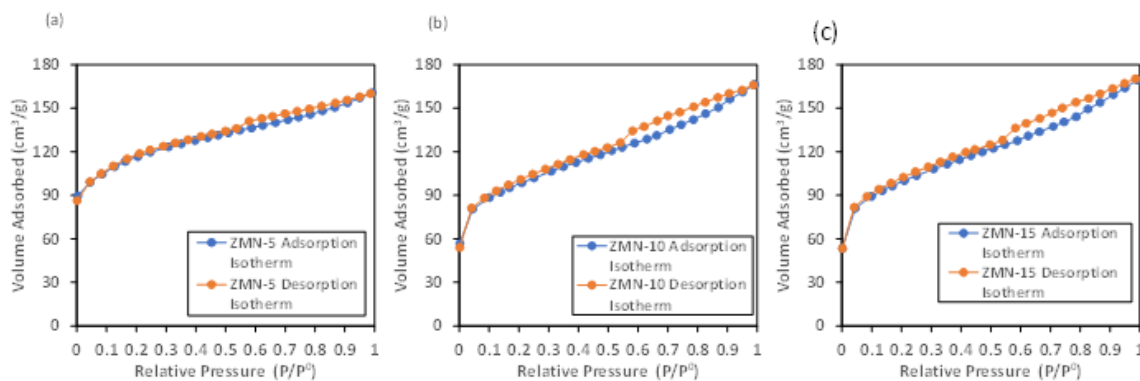


Figure 18:(a). Nitrogen adsorption/desorption isotherm of $\text{MnO}_x/\text{ZSM-5}$ (ZMn5)

This study investigates MnO_x on a montmorillonite mixed with zeolites (Zeolite Y and ZSM-5) catalysts for the oxidative cracking of LSRN to light olefins. It was hypothesized that the zeolites provide the cracking functionality, while MnO_x offers controlled oxidative dehydrogenation functionality – resulting to high olefin yield. We have prepared different matrices varying the MnO_x content. Thereafter we employed different characterization techniques such as X-ray diffraction (XRD), temperature-programmed reduction (TPR), and Brunauer-Emmett-Teller (BET) surface area analysis to explore the correlation between catalyst properties and performance. The study also examines the impact of reaction parameters such as temperature and catalyst to oil ratio on light olefin yield and selectivity. The findings offer valuable insights into developing efficient, sustainable processes for producing light olefins from LSRN using MnO_x supported on zeolites-based catalyst.

5.2. Oxidative Cracking of Naphtha on $\text{MnO}_x/\text{ZSM-5}$

The catalytic performances of the synthesized ZMn catalysts in oxidative cracking were carried out in a Micro Activity Test Unit (MAT) using LSRN as a feedstock. A systematic reaction study delivers reliable decision driven by data obtained from catalyst composition

for achieving high conversion and desirable product yields under the specified reaction conditions. It also provides with information/data for a possible fine-tuning of the catalyst properties, such as acidity, redox behavior, and active site distribution – which eventually optimize the conversion of the feedstock and the selectivity towards the target olefin products. In this regard, the reaction temperature was selected between 550-660 °C, while the catalyst-to-oil ratio was varied from 2 to 6. The catalyst regeneration ability was also examined by regenerating the catalyst between two catalytic runs by circulating air through the fluidized catalyst bed at 650 °C for 20 mins. Following the catalyst regeneration cycle, the entire system was cleaned by argon to confirm the gas phase oxygen free environments. This cyclic catalytic cracking of LSRN and regeneration of catalyst approach facilitate attaining the twin effects of the reactor of both catalytic cracker and catalyst regenerator. The experiments were repeated several times to confirm that the product distribution is reproducible. The LSRN conversion and product selectivity in the repeated run were found to be within the standard deviation of ± 6.1 %. Table 4 summarizes the LSRN conversion and cracking/dehydrogenated product distribution during cracking of LSRN over $\text{MnO}_x/\text{ZSM-5}$ (ZMn) catalysts at 575 °C and catalyst-to-oil ratio of ~ 4 . One can see from the production distribution table that dry gas ($\text{H}_2\text{-C}_2$), LPG ($\text{C}_3\text{-C}_4$), olefins ($\text{C}_2=$, $\text{C}_3=$, $\text{C}_4=$), gasoline, HCO and LCO are the major products under the studied reaction conditions. For comparison, Figure 19 plots the LSRN conversion and olefin yields of using the ZMn catalysts. One can clearly see that ZMn5 displayed both high LSRN conversion and propene yields. These results are consistent to the highest acidity and comparable reducibility of the ZMn5 catalyst, as found in $\text{NH}_3\text{-TPD}$ and $\text{H}_2\text{-TPR}$ analysis, respectively. This observation agreed with the previous works of the present research group [43], [44].

Consequently, ZMn5 catalyst was selected for further evaluation at various catalyst-to-oil ratios and reaction temperatures.

Table 4. Product distribution of oxidative cracking of LSRN using MnO_x/ZSM-5

Catalysts	ZMn5	ZMn10	ZMn15
LSRN Conversion %	86.1	77.2	87.9
Total Gas	62.51	43.80	66.25
<i>H₂-C₂ (dry gas)</i>	11.35	9.13	11.69
<i>C₃-C₄ (LPG)</i>	51.16	34.67	54.56
<i>C₂= - C₄= (olefins)</i>	23.01	18.78	20.81
<i>C₃ = +C₄=</i>	17.25	14.30	15.35
<i>C₄= (Butenes)</i>	6.77	5.50	6.06
Gasoline	23.63	33.40	21.63
LCO	7.88	12.97	6.90
HCO	5.98	9.83	5.23

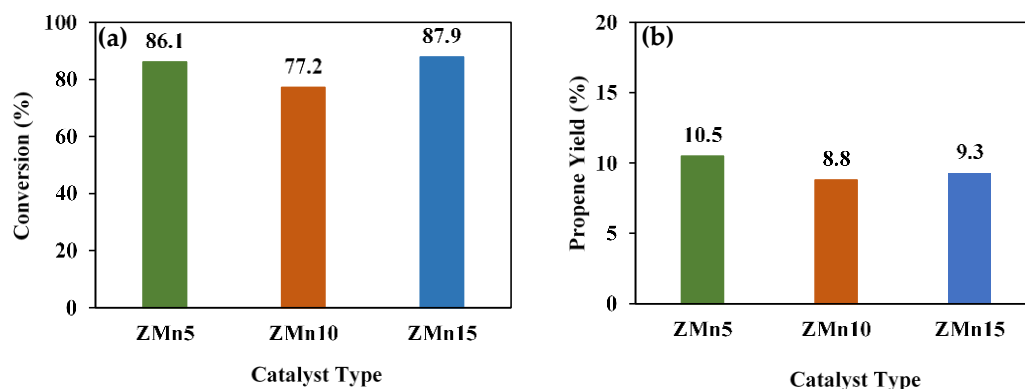


Figure 19: (a) LSRN Conversion and Propene Selectivity of Screened Catalyst

Figure 20 presents a bar chart illustrating the olefin product yields, while the line represents the corresponding conversion of LSRN. One can see from Figure 20 that the catalyst-to-oil ratio contributes both the increase of LSRN conversion and olefins yield. However, increase in olefins selectivity is more significant, which suggest the contribution of the oxidative dehydrogenation to enhance the olefins selectivity. For further analysis, the experiments were conducted at various catalyst-to-oil ratios and temperatures. The results of these experiments are shown in Table 5. This comprehensive set of data provides insights into the relationship between the catalyst acidity and reducibility and operating conditions, conversion, and olefin production using the $\text{MnO}_x/\text{ZSM-5}$ catalyst system [45], [46].

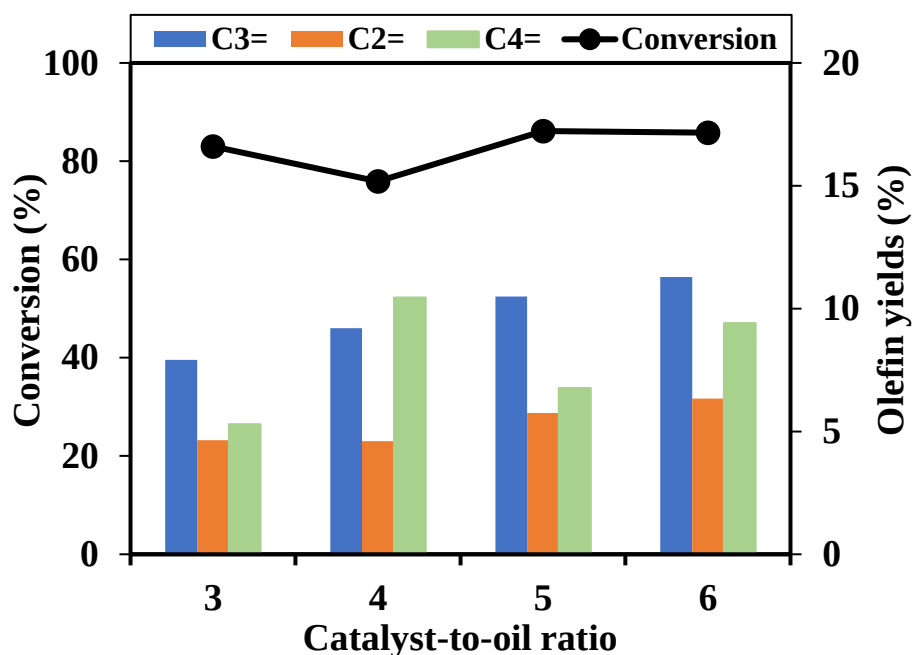


Figure 20: Conversion and Olefins Yield for LSRN over MnO_x/ZSM-5

Table 5: Propene Yield (%) for MnO_x/ZSM-5 at Different Temperatures and C/O

Temperature (°C)	Catalyst to oil ratio			
	3	4	5	6
550	7.48	7.38	8.12	8.67
575	7.91	9.21	10.49	11.29
600	11.97	10.29	13.28	13.80
625	12.21	9.71	11.58	14.69

Figure 9 shows the selectivity toward olefins and hydrogen produced from the experimental work conducted using MAT unit. The highest propene yield recorded for this

catalyst type is at 625 °C and a catalyst-to-oil ratio of 6. This is expected due to the higher catalyst concentration (active sites) to process the feed. Additionally, the amount of propene is also high at a temperature of 550 °C, compared to the screened catalyst (i.e. ZMn10) tested at a catalyst-to-oil ratio of 6. The trend observed in Figure 21(a) can be attributed to the use of zeolite as the catalyst support, which favors the production of propene. The analysis also includes the yields of other olefins, such as ethene Figure 21 (b) and 1,3-butadiene, as shown in Figures 22 (a) and hydrogen in Figure 22 (b).

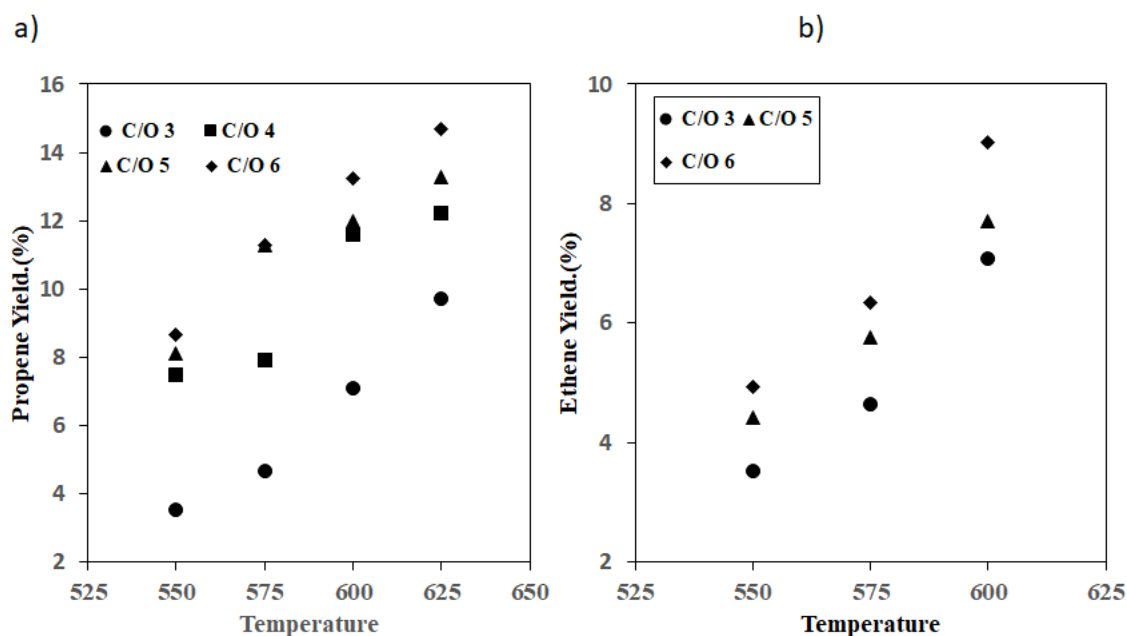


Figure 21: Yields of (a) Propene, (b) Ethene

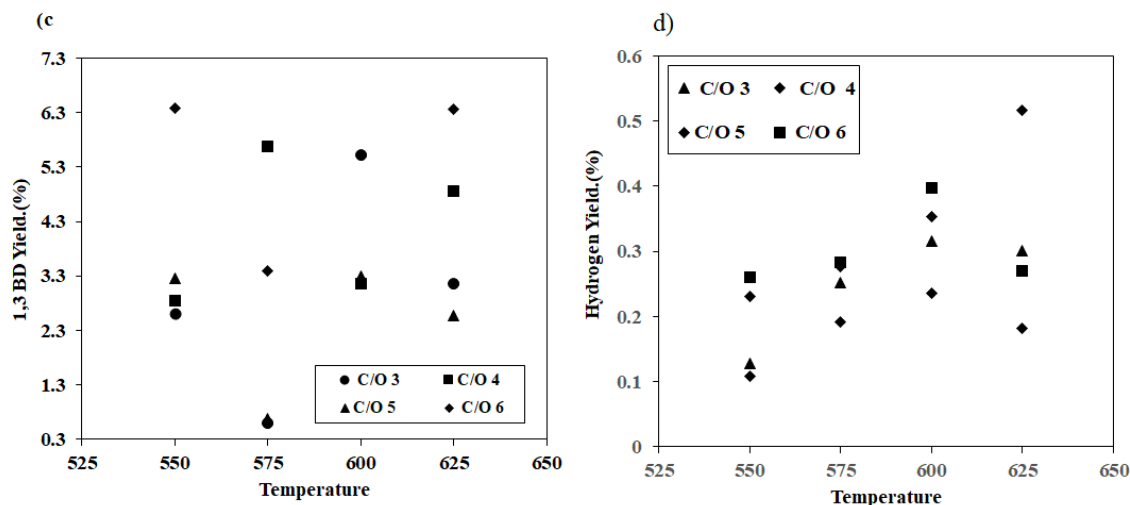


Figure 22: Yields of (a) 1,3 Butadiene, (b) Hydrogen

The production of 1,3-butadiene (1,3 BD) using the MnOx/ZSM5 catalyst at four different temperatures and catalyst-to-oil ratios. The results indicate that the selectivity towards 1,3-butadiene is highest at the high temperature of 625 °C and a high catalyst-to-oil ratio of 6. However, the trend in 1,3-butadiene production is not entirely straightforward. It is observed that increasing the temperature does not always result in higher 1,3-butadiene selectivity. For example, at a catalyst-to-oil ratio of 5, the yield of 1,3-butadiene is lower at 575 °C compared to 550 °C. The coke deposition on the catalyst surface increases with higher catalyst-to-oil ratios, as shown in Figure 24 (c) for a temperature of 550 °C. The final products analyzed from the MAT unit are Light Cycle Oil (LCO) and Heavy Cycle Oil (HCO) in Figure 24 (d). These products show a decreasing trend when the catalyst-to-oil ratio is increased, which is a result of using the ZSM-5 catalyst. Both the LCO and HCO yields exhibit a decreasing trend, which is favorable for this catalyst. The purpose of the catalyst is to increase olefin production rather than target light and heavy cycle oils. [47],[48],[49]

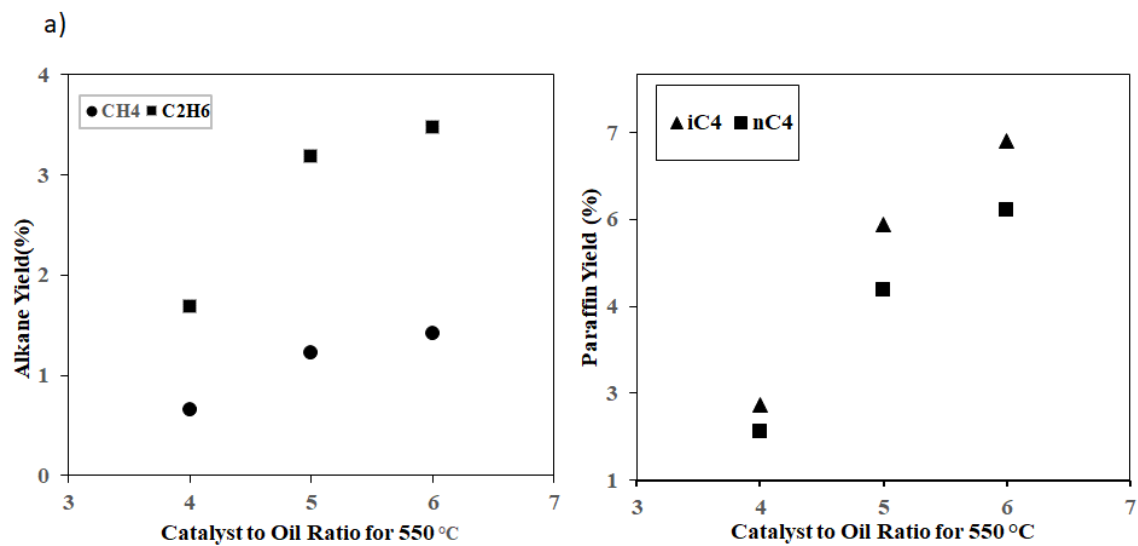


Figure 23: Yields of (a) C1-C2 alkane, (b) Paraffins

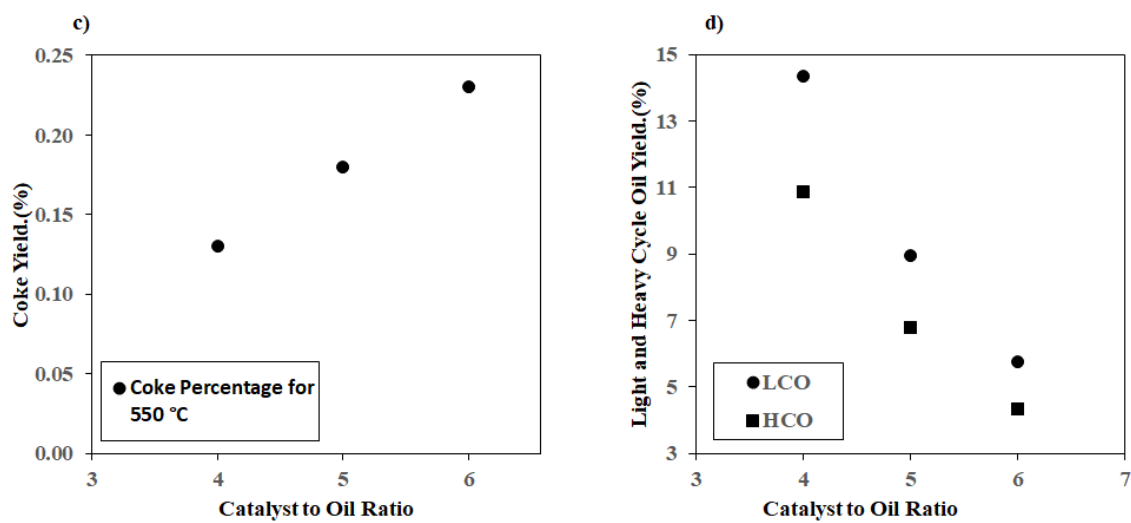


Figure 24: Yields of (c) coke, (d) LCO and HCO

Chapter 6: Kinetic Modelling

6.1. Introduction to Kinetic Modelling of Light Straight Run Naphtha

The kinetic model was developed and evaluated based on two reference models from the literature. The first model, developed by Longstaff, was based on a 4-lump approach[59]. The second model was developed for a reaction network for oxidative cracking of n-hexane by Amusa[60], [61]. The reaction networks for both these models are shown in Figure 252 and Figure 26, respectively, to facilitate the evaluation of the two models.

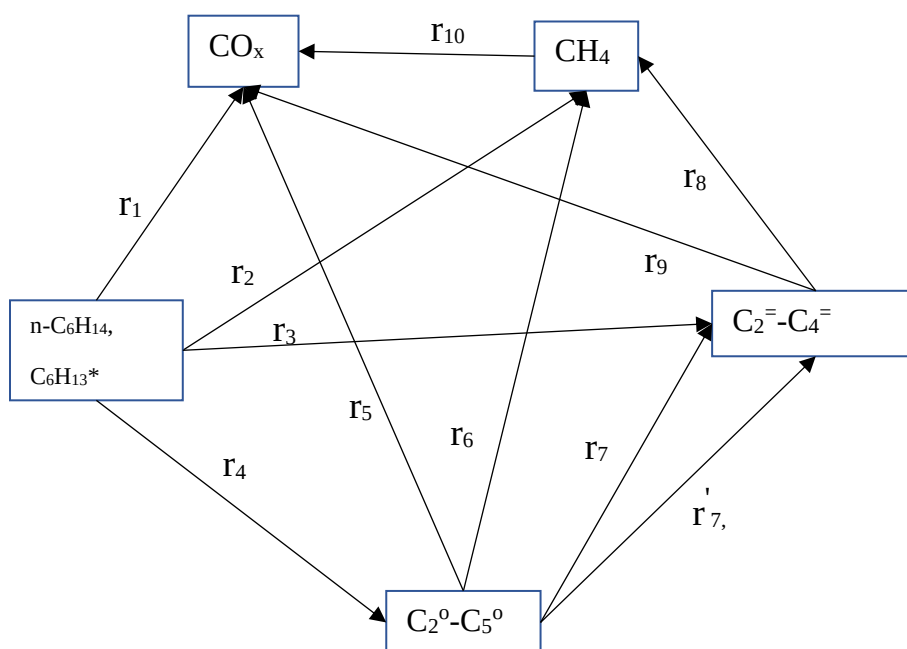


Figure 25: Reaction Network Developed for Oxidative Cracking of n-Hexane[62].

The reaction network developed for the oxidative cracking of n-hexane estimates 21 parameters, including activation energies, reaction rate constants, and deactivation functions. This model assumes that the reactions occur in both series and parallel, including

cracking steps explained by the carbenium ion mechanism and oxidative dehydrogenation steps explained through the Langmuir-Hinshelwood mechanism. The detailed equations for this reaction network are provided by Hussian A. Musa[63] .

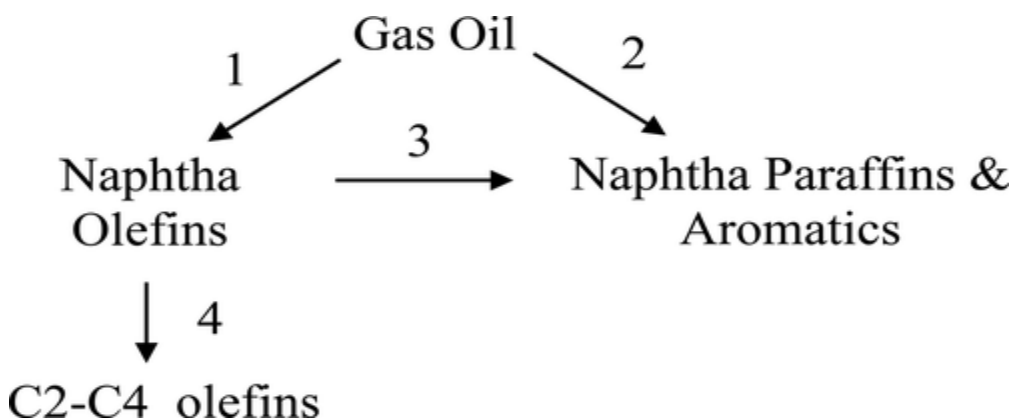


Figure 26: Reaction Network Developed for Catalytic Cracking of Naphtha[64]

The reaction network shown in Figure 26 assumes a four-lump kinetic model. The order of the reaction derived from this network for naphtha conversion is a first-order reaction, which is also assumed for developing the model[65]. The validity of the first-order assumption was verified by plotting $\ln(K)$ vs. $1/T$, as detailed in the rate equations of this model provided by Longstaff[77]. This kinetic model developed assumed two series-parallel mechanisms following a first-order reaction, considering a third mechanism, which is thermal cracking. The cracking mechanisms are the classical carbenium ion mechanism and the non-classical carbonium ion mechanism. The mixture of Y-zeolite/ZSM-5 zeolite blend contains high hydrogen transfer reactivity because of the Y-zeolite function. The propene selectivity from the cracking reaction by β -scission is attributed to the Y-zeolite, in which naphtha olefins are produced following diffusion into ZSM-5. The other mechanisms for kinetic modeling of the oxidation reaction are explained through the Langmuir-Hinshelwood and Eley-Rideal mechanisms, as well as the alkane oxidation via

the Mars and Van Krevelen mechanism. The cracking step involves the production of alkanes, which are further converted to olefins through oxidative dehydrogenation by the free lattice oxygen, following the Langmuir-Hinshelwood mechanism to olefins. However, the contribution of this mechanism is not as significant for propene production as the cracking by ZSM-5, as can be noticed in the propene results shown previously. Since the reaction is occurring on the surface of the catalyst, and a metal oxide catalyst is used, the Langmuir-Hinshelwood mechanism could provide some explanation for the kinetics of two adsorbed species, assuming a constant energy between the adsorbent and the adsorbate when coverage is increased. The formation of light olefins is also attributed to the lattice oxygen in the catalyst, which works on the oxidative dehydrogenation of alkanes to olefins from the subsurface oxygen produced by MnOx. This comprehensive kinetic analysis, incorporating various reaction mechanisms, provides a deeper understanding of the complex processes involved in the oxidative cracking of hydrocarbons to produce valuable olefin products[66].

6.2. Modelling Approach and Assumptions:

Kinetics of oxidative cracking of light straight naphtha (LSRN) to olefins is currently under development, and hence, this research is exploring the fitting of a kinetic model to the experimental data. This will be investigated to design a reaction network in order to select the desired reaction path, which could enhance olefins yield for the selected catalyst, MnOx/ZSM-5, and conditions for optimum yield and conversion at 600°C and a catalyst-to-oil ratio of 6. The following assumptions are used to develop the kinetic model:

1. Limitations due to mass transfer are negligible.
2. Catalyst deactivation is negligible.
3. The cracking reaction due to Y-zeolite and ZSM-5 is more dominant than the oxidative reaction due to free lattice oxygen.
4. The conversion of LSRN is modeled through a first-order reaction using the Power-Law model.

By incorporating these assumptions and developing a suitable kinetic model, researchers can better understand the complex reaction pathways involved in the oxidative cracking of light straight naphtha to olefins[80]. This knowledge can be used to optimize the reaction conditions and catalyst performance, ultimately leading to higher yields of valuable olefin products.

6.3. Lumped Kinetic Data for Model Development

To formulate the kinetic model for the MnOx/ZSM-5 catalyst system based on the experimental data, various plots have been created below. These plots display the different products and conversion at selected temperatures and catalyst-to-oil ratios. The purpose of creating these plots is to estimate the kinetic parameters based on the trends observed in the data produced during the experimental work. The key aspects of the kinetic modeling approach are:

- Plotting the experimental data: The yields of various products, such as olefins, paraffins, and other byproducts, are plotted against the reaction conditions, including temperature and catalyst-to-oil ratio.

- Identifying trends and patterns: By analyzing the plots, researchers can identify the trends in product yields and conversion as a function of the reaction parameters. These trends provide valuable insights into the underlying reaction kinetics.
- Estimating kinetic parameters: Based on the observed trends, the researchers can estimate the kinetic parameters, such as rate constants, activation energies, and reaction orders, which can be used to develop a comprehensive kinetic model for the oxidative cracking of light straight naphtha over the MnOx/ZSM-5 catalyst.
- Model validation and optimization: The developed kinetic model can be validated against additional experimental data and used to optimize the reaction conditions for maximizing the yield of desired olefin products.

This systematic approach to kinetic modeling, based on the analysis of experimental data, is crucial for understanding the complex reaction mechanisms and improving the performance of the MnOx/ZSM-5 catalyst system for the oxidative cracking of light straight naphtha.

Table 6: Lumped Data of Temperature 550 °C to Construct Kinetic Model

C/O	Conversion (%)	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)
	C6	C1	C2-C5	C2= - C4=	CO _x	Coke
4	74.78	0.66	12.56	17.51	0.15	0.13
5	84.25	1.23	29.01	20.44	0.22	0.18
6	92.21	1.42	34.73	25.12	0.24	0.23

In Table.6 the first lumped data are collected for a temperature of 550 °C which separates the experimental data has been lumped into six categories for the kinetic modeling: olefins (first lump), paraffins (second lump), CO_x (third lump), coke (fourth lump), methane (fifth lump), and LSRN (sixth lump). These kinetic data collected will be useful in determining the number of parameters to be estimated and the model accuracy, which can be assessed using a parity plot. An increasing trend is observed in these data, as shown in Figure X. This trend is favorable for model fitting and development, as it provides a clear relationship between the reaction conditions and the product yields. The advantages of this lumping approach are:

1. Simplification of the reaction network: By grouping the products into broader categories, the complexity of the kinetic model is reduced, making it easier to develop and solve.
2. Identification of key products: The lumping allows for the identification of the most important products, such as olefins, which are the primary target of the oxidative cracking process.

3. Sensitivity analysis: By analysing the trends in each lump, researchers can identify the most sensitive parameters and reaction pathways, which can guide further optimization efforts.
4. Model validation: The lumped kinetic data can be used to validate the developed model by comparing the predicted yields with the experimental data for each lump.

This lumping approach, combined with the observed increasing trend in the data, provides a solid foundation for the development of an accurate and reliable kinetic model for the oxidative cracking of light straight naphtha over the MnOx/ZSM-5 catalyst system.

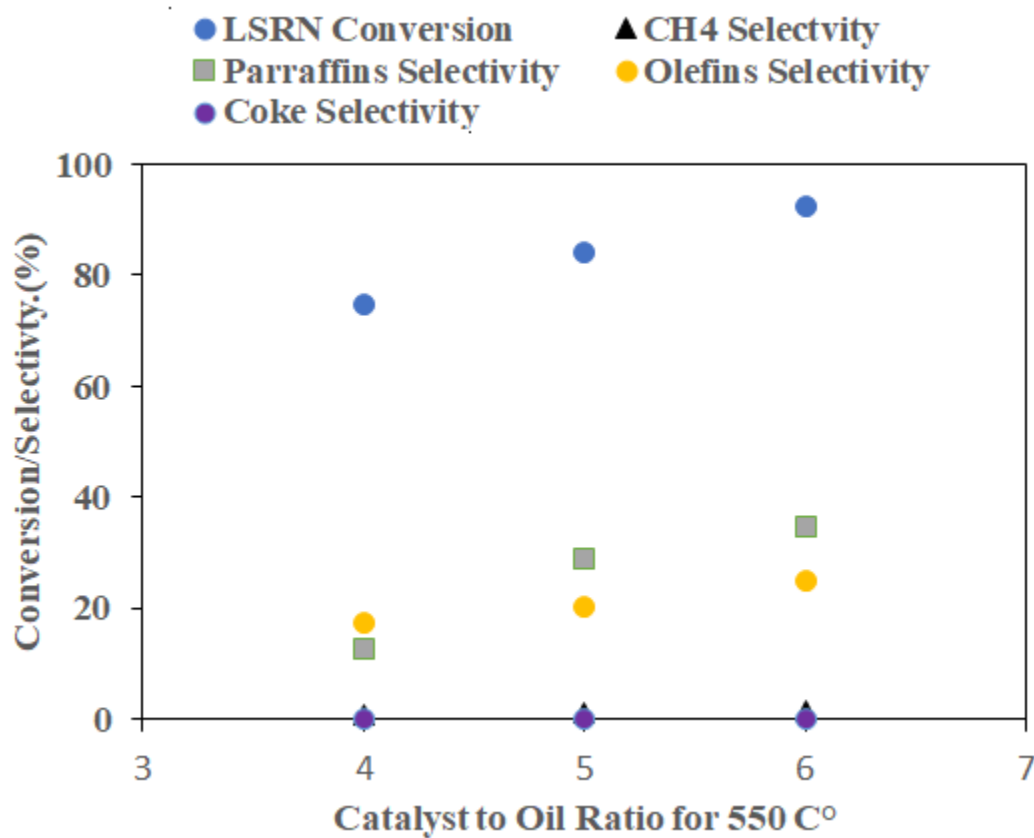


Figure 27: Lumped Kinetic Data and LSRN Conversion for 550 ° C and Various C/O

The kinetic model has been developed for three different catalyst-to-oil ratios and temperatures, corresponding to varying time-on-stream conditions. The increasing trend in olefins production is shown in Table 7 for a reaction temperature of 600°

Table 7: Lumped Data of Temperature 600 °C to Construct Kinetic Mode

C/O	Conversion	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)
	C6	C1	C2-C5	C2= - C4=	CO _x	Coke
4	81.92	1.8	17.16	24.08	0.19	0.18
5	87.75	2.34	22.21	30.73	0.23	0.21
6	91.39	2.65	27.6	33.86	0.25	0.23

The lumped kinetic data for a temperature of 600°C is plotted in Figure 28, showing the experimental data obtained under optimum conditions for olefins production and conversion of light straight naphtha (LSRN)[67]. As evident from the trend, the yellow circles indicating olefins are in higher amounts than the green squares representing paraffins.

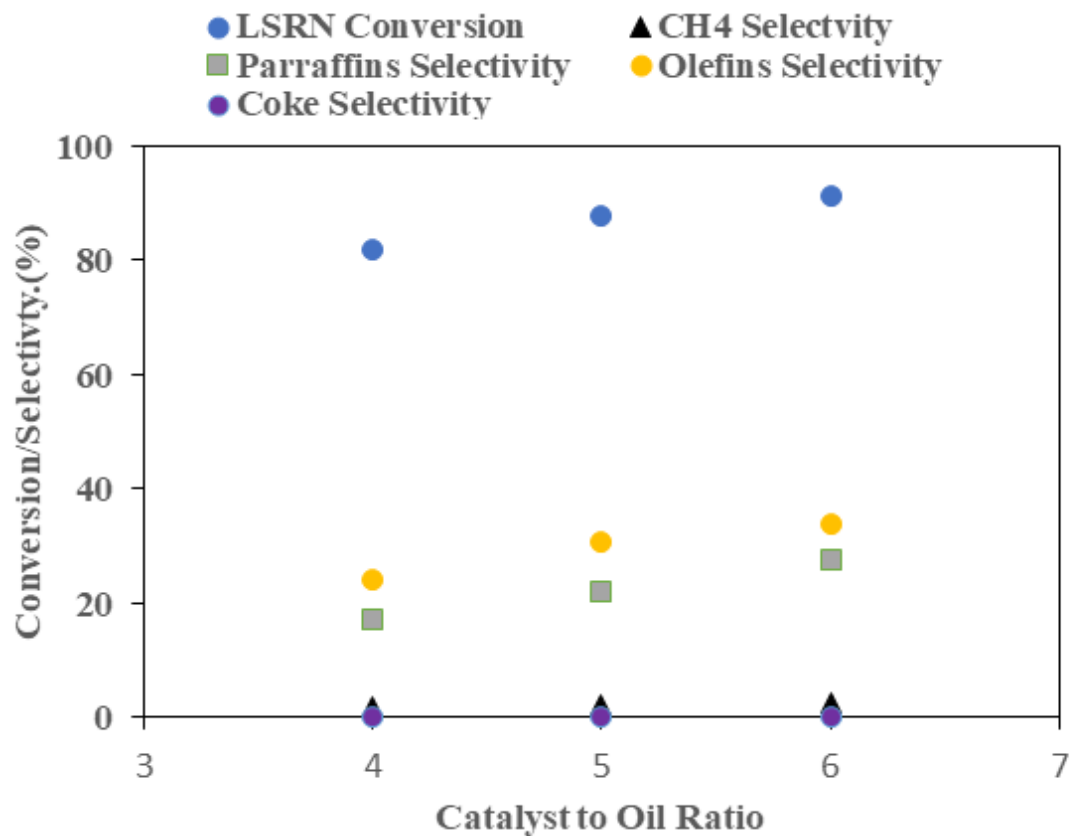


Figure 28: Lumped Kinetic Data and LSRN Conversion for 600 °C and Various C/O

Table 8: Lumped Data of Temperature 625 °C to Construct Kinetic Model

C/O	Conversion	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)	Mass fraction (%)
	C6	C1	C2-C5	C2= - C4=	COx	Coke
4	76.28	1.34	5.38	22.2	0.21	0.18
5	84.27	3.22	22.04	29.62	0.27	0.28
6	84.96	1.8	8.29	30.51	0.31	0.32

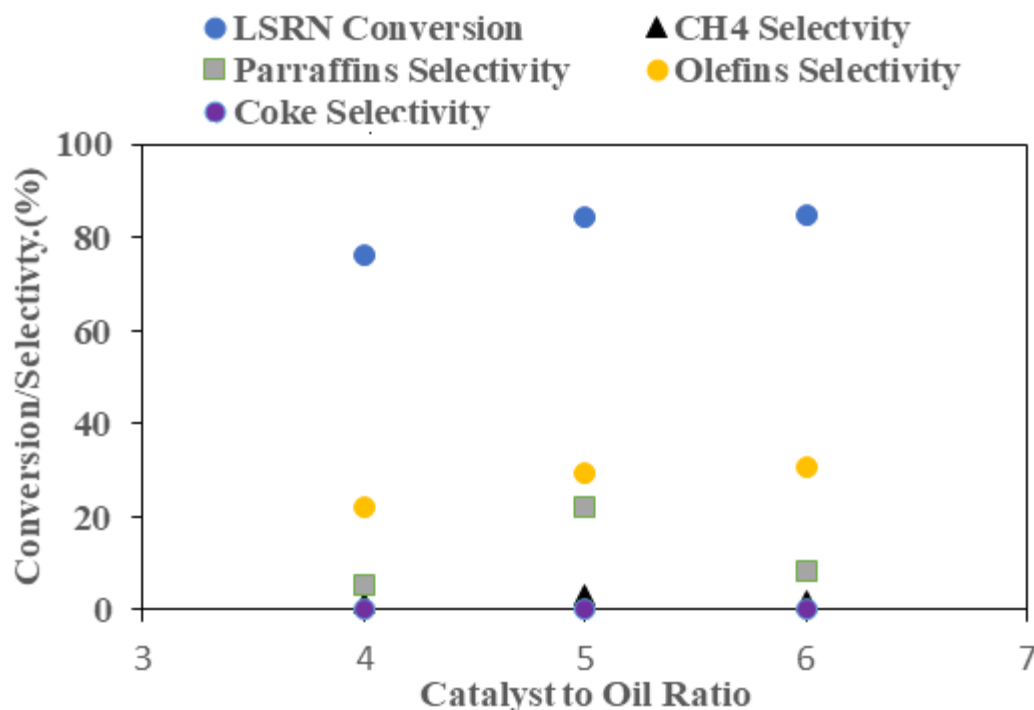


Figure 29: Lumped Kinetic Data and LSRN Conversion for 625 ° C and Various C/O

Lastly, the experimental data obtained for a temperature of 625°C has been lumped to model the reaction network and study the olefins production pathways. This analysis is crucial for estimating the kinetic parameters of the overall process.

6.4. Reaction Networks Development and Order Rate of Reaction

Determination

The reaction networks have been drawn to attempt modeling the oxidative cracking of light straight naphtha (LSRN) over the MnOx/ZSM-5 catalyst, considering six lumps. However, the pathways for each reaction are different for each network. This approach will result in reducing the number of parameters to be tested, simplifying the model and facilitating the determination of the R-squared (R^2) value. Moreover, the rate equations were developed

for naphtha, assuming both second-order and first-order reactions. The following diagrams show the possible reaction networks suggested for this kinetic mode:

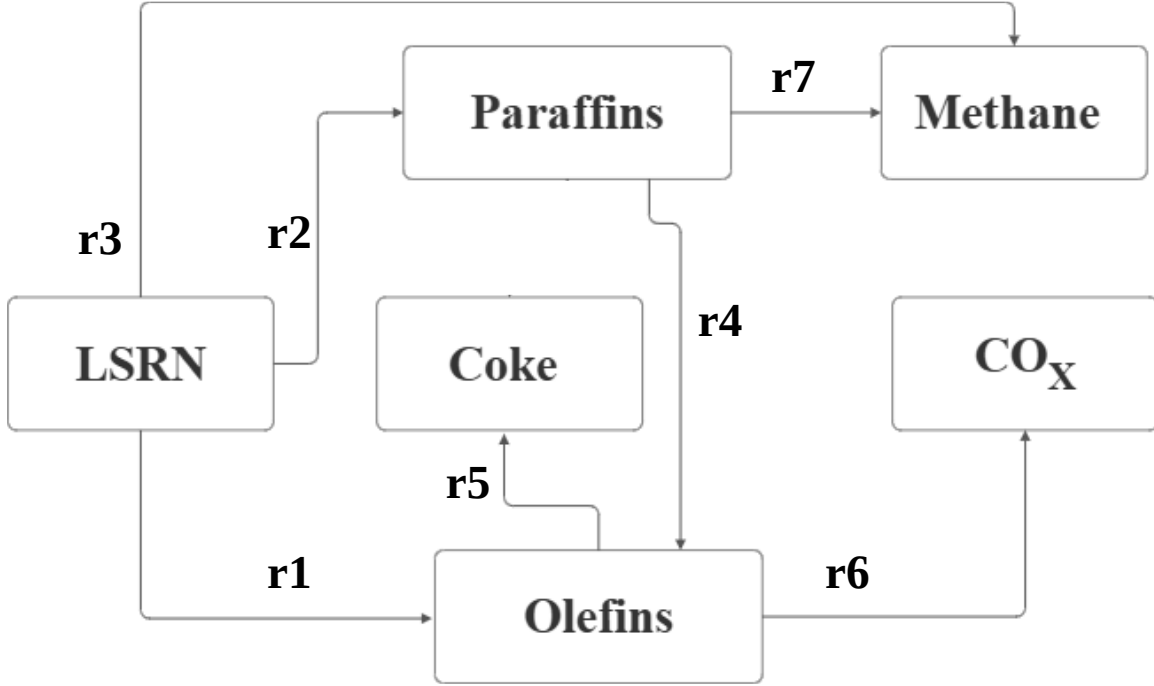


Figure 30: Reaction Network Diagram for Oxidative Cracking of LSRN

The below equations are obtained for this model to estimate 14 parameters for second order of LSRN conversion

$$r_{LSRN} = -(k_1 + k_2 + k_3) \times C_{LSRN}^2 \dots\dots\dots 37$$

$$r_{Olefins} = k_1 C_{LSRN}^2 + k_4 C_{Parrafin} - (k_5 + k_6) C_{oleifns} \dots\dots\dots 38$$

$$r_{parrafins} = k_2 C_{LSARN}^2 - (k_4 + k_7) C_{parrafins} \dots\dots\dots 39$$

$$r_{coke} = k_5 C_{olefins} \dots\dots\dots 40$$

$$r_{CO_x} = k_6 C_{parrafins} \dots\dots\dots 41$$

$$r_{Methane} = k_3 C_{LSARN}^2 + k_7 C_{parrafins} \dots\dots\dots 42$$

The second reaction network developed for this model is based on 24 parameters estimated for first order of LSRN conversion.

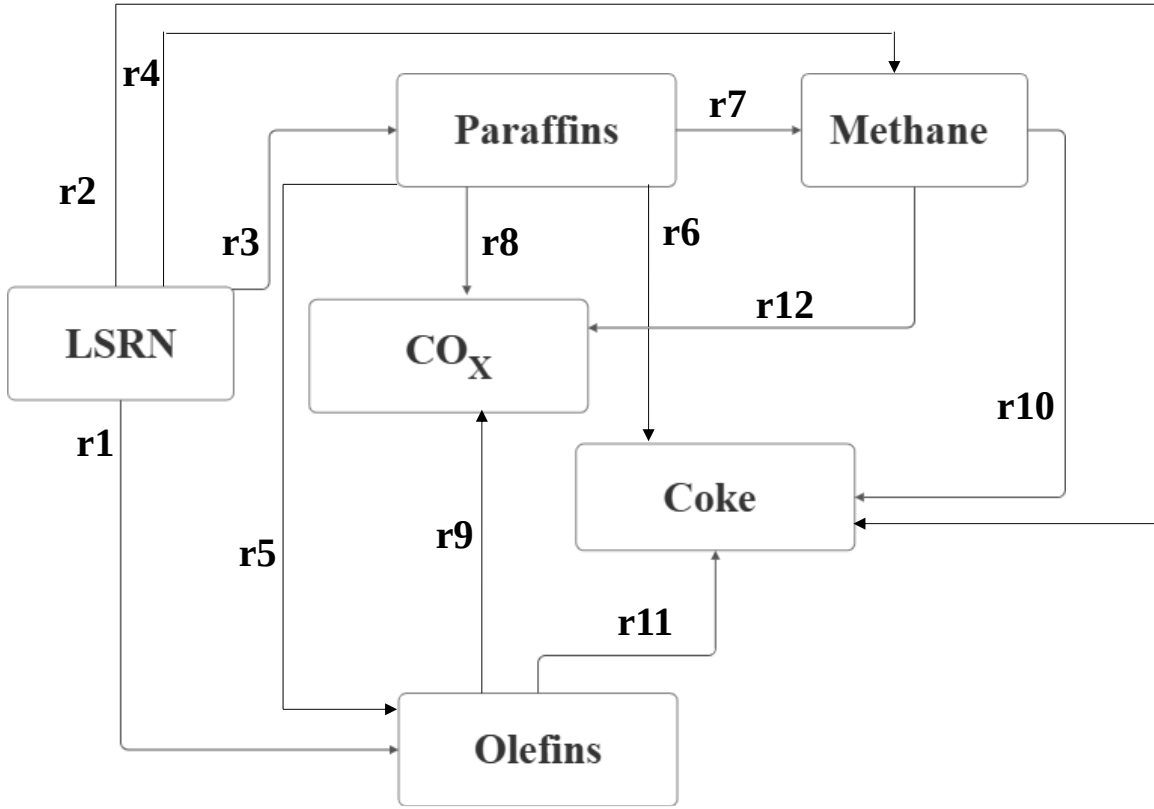


Figure 31: Reaction Network Diagram for Oxidative Cracking of LSRN

Increasing the number of parameters and using the correct order of reaction is found to increase the accuracy of the model and equations of rate for this network are below:

$$r_{LSRN} = -(k_1 + k_2 + k_3 + k_4) \times C_{LSRN} \dots\dots\dots 43$$

$$r_{Olefins} = k_1 C_{LSRN} + k_5 C_{Parrafin} - (k_9 + k_{11}) C_{oleifns} \dots\dots\dots 44$$

$$r_{parrafin} = k_3 C_{LSRN} - (k_5 + k_6 + k_7 + k_8) C_{parrafin} \dots\dots\dots 45$$

$$r_{coke} = k_2 C_{LSRN} + k_6 C_{Parrafin} + k_{10} C_{Methane} + k_{11} C_{oleifns} \dots\dots\dots 46$$

$$r_{CO_x} = k_8 C_{parrafin} + k_9 C_{Olefins} + k_{12} C_{methane} \dots\dots\dots 47$$

$$r_{Methane} = k_4 C_{LSRN} + k_7 C_{paraffins} - (k_{10} + k_{12}) C_{Methane} \dots\dots\dots 48$$

For considering the Oxidative dehydrogenation via L-H mechanism extra rate of equation or step is included shown in Eq.49 below.

6.5. Kinetic Models Explanation

The kinetic model contains 14 kinetic parameters for reaction network developed in Figure 33. The rate constants for the kinetic model estimation were determined via the least-squares regression analysis of the experimental data obtained from the MAT unit at temperatures of 550°C, 600°C, and 625°C. The Arrhenius equation was then used to calculate the pre-exponential factors and apparent activation energies. The composition of light straight run naphtha includes aromatic and non-aromatic carbons, such as naphthenic and paraffinic carbons. During oxidative cracking processes, aromatic compounds are not easily cracked into gaseous products due to the difficulty of conducting reactions involving ring-opening of aromatic carbons. On the other hand, non-aromatic carbons are easily cracked into paraffinic carbons. The feedstock of light straight run naphtha was considered as one lump because, during oxidative cracking, some product gases will be converted into olefins by undergoing secondary cracking reactions or oxidative dehydrogenation, assuming the L-H model. Moreover, the conversion of olefins into liquid by polymerization and aromatization reactions is also possible at higher reaction temperatures[68], [69]. The main olefins targeted for this reaction are light olefins such as propene, ethene, and 1,3-butadiene, and hence, they were considered as one lump. From this reaction, there are also gaseous products such as methane and C₂-C₅ (paraffins), which are considered as two separate lumps. Finally, coke depositing on the catalyst surface and CO_x are produced during the reaction, which are also considered as two separate lumps, although they are in

low yield but are very significant to the cracking reaction. For the oxidative cracking of light straight naphtha to olefins, the reaction network in Figure.27 indicates irreversible second-order reactions for the consumption of LSRN, while in the second network diagram, the conversion of LSRN is a first-order irreversible reaction. On the other hand, the production or consumption of any other products means irreversible first-order reactions, for example, the formation of olefins from paraffins or the production of coke from olefins.

6.6. Kinetic Model Results and Recommendation:

After running the MATLAB code using the ODE-45 function to solve the equations and estimate the kinetic parameters, the best results were obtained for the power law model with a first-order reaction, as shown in the reaction network (Figure 31). The R-squared (R^2) value obtained is 0.90, in comparison to R^2 values of 0.8771 for the second-order reaction and 0.8 for the Langmuir-Hinshelwood (L-H) model. To validate the first-order reaction assumption, a plot of temperature and reaction constant was created for three catalyst-to-oil ratios under three different temperatures[70], [71]. Tables 12, 13, and 14 include the data for each reaction, considering only the LSRN conversion to validate the correct order of reaction. The advantages of this validation approach are:

- Confirming the reaction order: By comparing the R^2 values for different reaction orders and plotting the temperature dependence, the first-order reaction assumption can be validated.
- Improving model accuracy: Selecting the correct reaction order ensures that the kinetic model accurately represents the underlying reaction mechanisms.

- Consistent parameter estimation: With the validated reaction order, the kinetic parameters can be estimated with higher confidence and consistency across the different catalyst-to-oil ratios and temperatures.
- Optimizing the model: The validated first-order reaction model can be further optimized by fine-tuning the kinetic parameters and exploring additional reaction pathways or lumps, if necessary.

By rigorously validating the reaction order and consistently estimating the kinetic parameters, the researchers can develop a robust and reliable kinetic model for the oxidative cracking of light straight naphtha over the MnOx/ZSM-5 catalyst system. This model can then be used to optimize the process conditions and improve the overall performance of the catalytic system.

Through running the model for a first-order reaction and the selected power law model, the parity plot obtained in Figure 34 shows an R-squared (R^2) value of 0.90, indicating a good fit. The plot exhibits a uniform distribution of the experimental data points along the 45-degree line, demonstrating a strong correlation between the experimental data and the predicted data for the oxidative cracking of light straight naphtha (LSRN) over the MnOx/ZSM-5 catalyst.

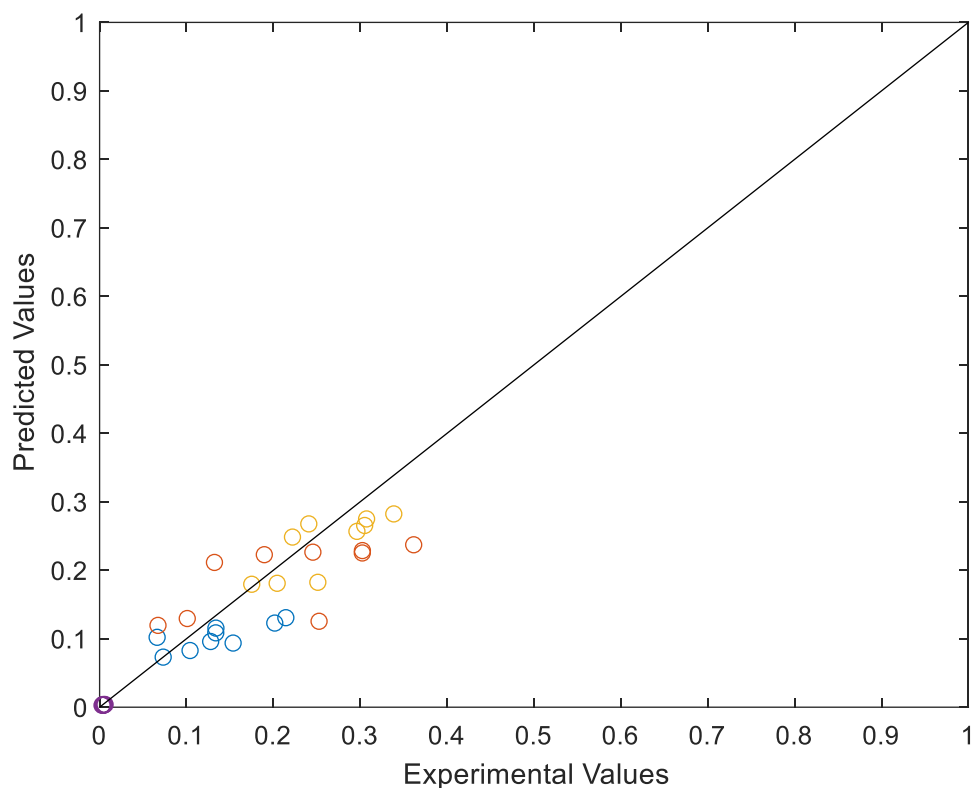


Figure 32: Parity Plot of Experimental Vs Predicted for LSRN Oxidative Cracking

The number of experimental data points is sufficient to demonstrate the fitting of the experimental data with the predicted values, as shown in the parity plot Figure.30. However, including more data points can further increase the accuracy and extend the distribution along the 45-degree line, providing greater clarity and uniformity in the correlation between the experimental and predicted results.

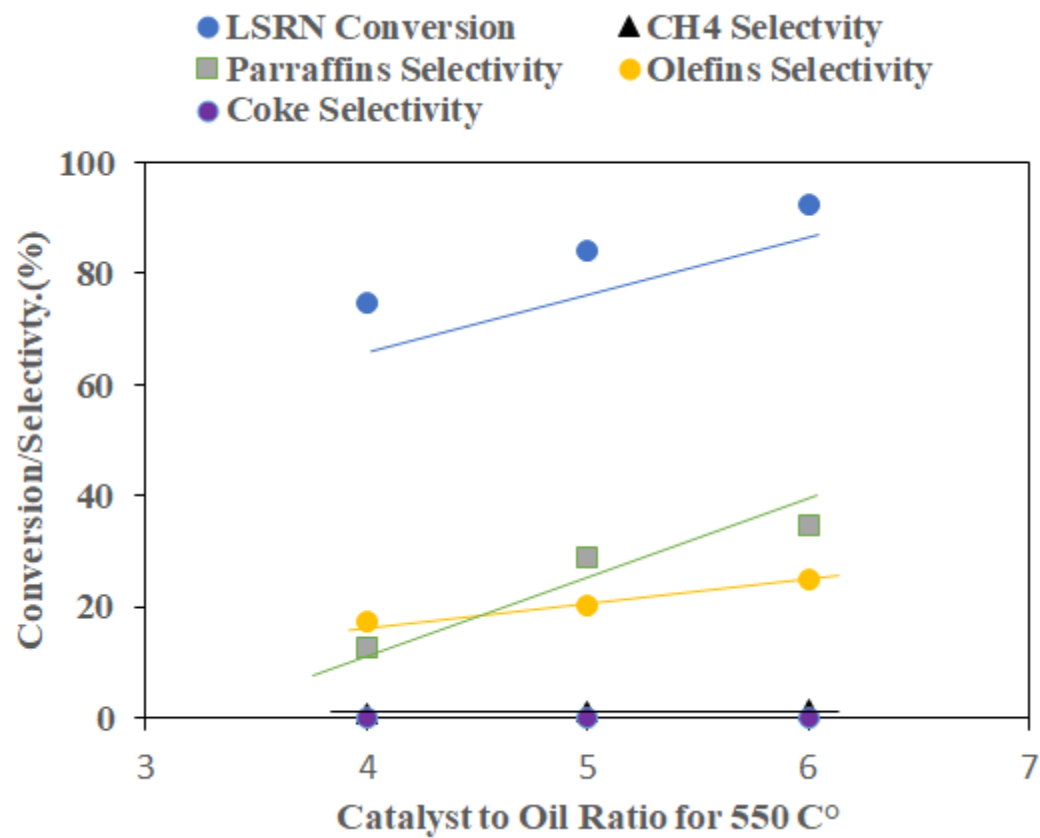


Figure 33: Experimental Data for LSRN Conversion Vs Predicated by Model

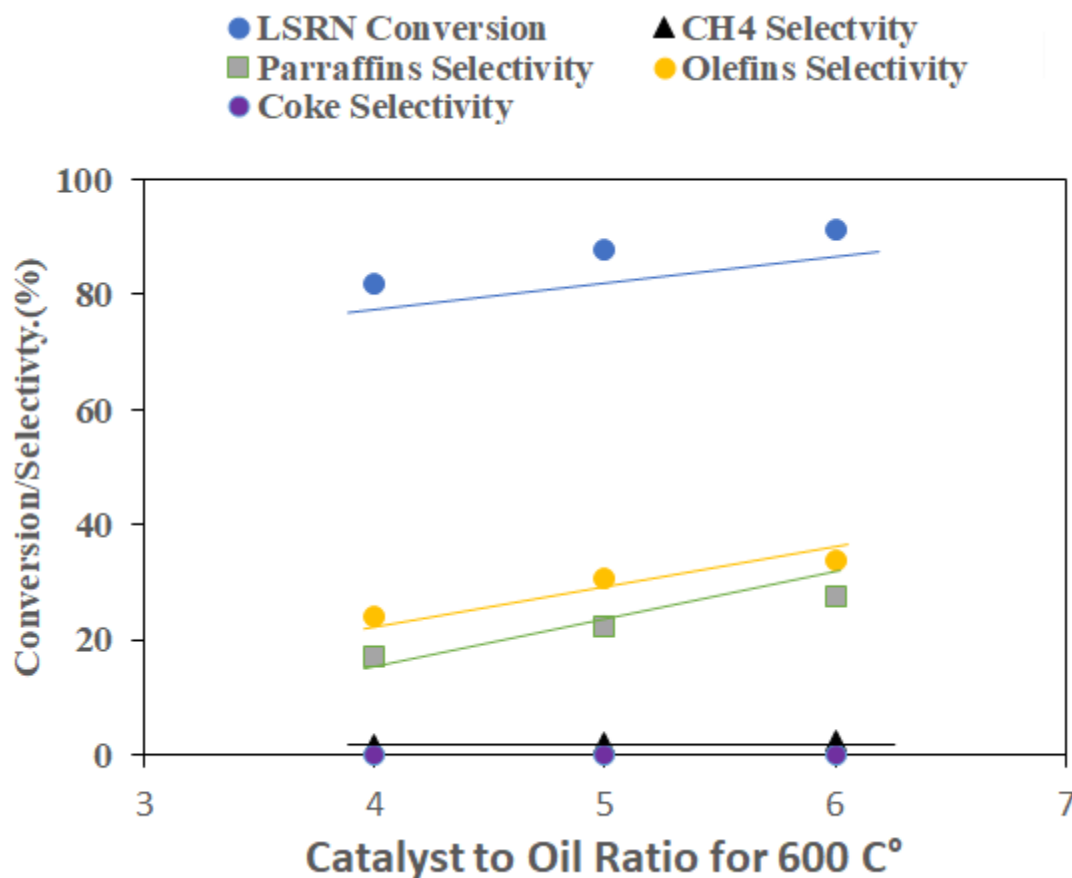


Figure 34: Experimental Data for LSRN Conversion Vs Predicated by Model

The experimental data for the conversion of light straight run naphtha (LSRN) and the predicted data exhibit a good fitting, but the simulated data are slightly underpredicting the experimental values. This discrepancy could be a result of the arrangement of the rate equations or the limitations of the reactor used in the experiments. Despite this minor deviation, the general trend of the model is following the overall trend observed in the experimental data.

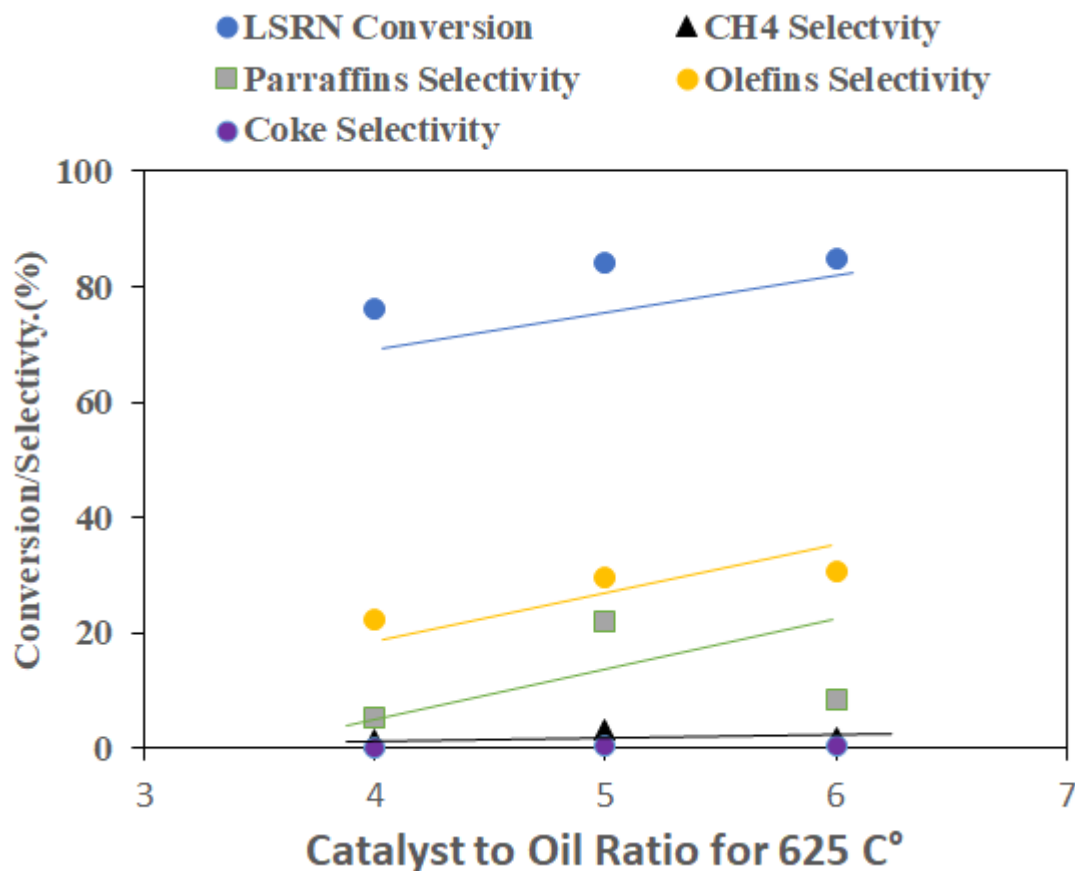


Figure 35: Experimental Data for LSRN Conversion Vs Predicated by Model

The equation expression for the Langmuir-Hinshelwood (L-H) mechanism, when paraffins are converted to olefins by oxidative dehydrogenation, for the developed model follows:

$$r_{Olefins} = \frac{k_6 * C_{paraffins}}{(1 + k_7 * C_{paraffins} + k_8 * C_{olefins})} \dots\dots\dots 49$$

The fit obtained for olefins is in close proximity to the experimental data, but the model still slightly underpredicts the olefin yields. This can be explained by the inclusion of multiple olefins, such as 1,3-butadiene, in a single lump. To improve the fit for specific olefins, separate equations and modeling may be required for each individual component. Despite these potential improvements, the model with 24 parameters has shown higher

accuracy, although some rate constants (k) are equal to zero. This indicates that the steps considered in these cases are not highly significant to the overall reaction. A more sophisticated combination of equations may be needed for a better fit and higher R-squared (R²) values. The estimation of the activation energy for each rate equation is evaluated through the Arrhenius equation[86]. This analysis provides insights into the temperature dependence of the reaction kinetics and can help in optimizing the process conditions to achieve the desired product yields.

$$k_i = k_{i-o} * \exp\left(\frac{-E_i}{R} * \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \dots\dots\dots 50$$

Where i = 1 ... 12 and $T_0 = \frac{550+600+625}{3} + 273.15$. k meaning is kinetic rate constant (S⁻¹ mol⁻¹), A (S⁻¹ mol⁻¹) the Arrhenius constant, Ea (J / mol) the activation energy, R (J/mol.K) the gas constant and T is the temperature in kelvin.

Table 9: Kinetic Parameters Estimation for Proposed Model 1st order of LSRN Conversion

K	Value	Activation Energy	Value
K ₁	0.005	E ₁	15.42
K ₂	0.0002	E ₂	14.68
K ₃	13.06	E ₃	0.91
K ₄	0	E ₄	18.77
K ₅	0.016	E ₅	187.52
K ₆	0	E ₆	21.47
K ₇	0	E ₇	21.46
K ₈	0.019	E ₈	88.19
K ₉	0	E ₉	25.44
K ₁₀	0	E ₁₀	51.09
K ₁₁	0	E ₁₁	12.55
K ₁₂	0.0017	E ₁₂	120.52

The present study is based on kinetics data obtained using a micro-activity test unit (MAT) in order to find conversion and selectivity at various temperatures and catalyst to oil ratio for the determination of reaction mechanism and most optimum conditions resulting in light olefins production.

Chapter 7: Conclusion

7.1. Conclusions

In conclusion, various catalysts and feedstocks have been used for oxidative cracking to produce olefins, such as n-hexane, propane, and natural gas liquids. The conditions and the kinetic model developed for these studied systems were also listed to provide a general idea of the approach that will be followed in designing a kinetic model for the experimental data obtained from the MAT unit. Based on the testing of three catalysts, the best catalyst will be selected by injecting light straight run naphtha at a rate of 0.85 for 30 seconds at four different temperatures and four different catalyst-to-oil ratios. The selected catalyst was also characterized using analytical equipment such as SEM, TPR, TPD, FT-IR, and XRD. It was found that the best catalyst candidate for selectivity and yield is MnOx/ZSM-5 for converting LSRN to olefins, and the optimum conditions for olefins selectivity are 600°C and a catalyst-to-oil ratio of 6. The focus of this work is to conduct the experimental work using this catalyst, so a comprehensive evaluation is carried out, and a kinetic model is developed to describe the reaction mechanism and predict the yield of olefins under different catalyst-to-oil ratios and temperatures. The kinetic model developed in this study provides a good fit to the experimental data, as shown through the parity plot, and also reveals key insights into the reaction pathways due to the use of zeolites as a support and metal oxides for oxidation. The reaction order of LSRN conversion was also found to be thermodynamically consistent with a first-order reaction, which was validated through an R-squared (R^2) value of 0.91. Future research should focus on refining the kinetic model to account for mass transfer and varying operational parameters to scale up the process for industrial applications. Additionally, investigating the catalyst using an advanced catalytic

evaluation unit to see the effect of longer injection time or using other metals as an addition could provide insights into enhancing the oxidation reaction.

7.2. Recommendations

The development of the kinetic model could be further enhanced by suggesting a reaction mechanism that clearly shows the behavior of the oxidative cracking of LSRN. This can be achieved by including a deactivation function and incorporating more parameters for estimation. The current catalyst system suggests that the metal was deposited on the surface of the zeolite catalyst, and hence, the cracking reaction is most dominant, while the oxidative dehydrogenation is secondary. This aspect can also be investigated by improving the catalyst system through the addition of different metals, such as lithium, to promote the oxidation reaction. The following recommendations are suggested for further research work on the oxidative cracking of LSRN to olefins:

1. Addition of metals to promote the oxidation reaction further.
2. Conducting the kinetic model using more data points for temperatures and catalyst-to-oil ratios.
3. Employing other characterization techniques, such as Raman spectroscopy, to determine the activity and deactivation of the catalyst.
4. Improving the model assumptions by considering a deactivation function and incorporating other mechanisms, such as the Mars-Van Krevelen mechanism.
5. Studying the effect of catalyst regeneration on the oxidation reaction

By addressing these recommendations, the kinetic model can be further refined and enhanced to provide a more accurate representation of the oxidative cracking process. The

addition of metals to promote the oxidation reaction, along with the incorporation of a deactivation function and alternative mechanisms, can lead to a more comprehensive understanding of the reaction pathways and the factors influencing the catalyst's performance. Furthermore, conducting the kinetic model with a larger dataset, including more temperature and catalyst-to-oil ratio points, can improve the model's predictive capabilities and robustness. The use of advanced characterization techniques, such as Raman spectroscopy, can provide valuable insights into the catalyst's activity and deactivation mechanisms, guiding the development of more effective catalyst systems. Ultimately, these research recommendations aim to optimize the oxidative cracking process for the production of light olefins from light straight run naphtha, contributing to the advancement of the petrochemical industry.

Reference

- [1] R. E. Emberru, R. Patel, I. M. Mujtaba, and Y. M. John, "A Review of Catalyst Modification and Process Factors in the Production of Light Olefins from Direct Crude Oil Catalytic Cracking," Mar. 01, 2024, *Multidisciplinary Digital Publishing Institute (MDPI)*. doi: 10.3390/sci6010011.
- [2] D. Liu *et al.*, "Thermodynamic appraisal of naphtha to light olefins based on different reaction pathways and independent chemical reactions," *Fuel*, vol. 346, Aug. 2023, doi: 10.1016/j.fuel.2023.128281.
- [3] C. Boyadjian and L. Lefferts, "Catalytic Oxidative Cracking of Light Alkanes to Alkenes," May 24, 2018, *Wiley-VCH Verlag*. doi: 10.1002/ejic.201701280.
- [4] D. Sanfilippo and I. Miracca, "Dehydrogenation of paraffins: Synergies between catalyst design and reactor engineering," in *Catalysis Today*, Jan. 2006, pp. 133–139. doi: 10.1016/j.cattod.2005.10.012.
- [5] J. J. H. B. Sattler, J. Ruiz-Martinez, E. Santillan-Jimenez, and B. M. Weckhuysen, "Catalytic dehydrogenation of light alkanes on metals and metal oxides," Oct. 22, 2014, *American Chemical Society*. doi: 10.1021/cr5002436.
- [6] F. Mirshafiee, S. Movahedirad, M. A. Sobati, R. Alaee, S. Zarei, and H. Sargazi, "Current status and future prospects of oxidative desulfurization of naphtha: a review," Feb. 01, 2023, *Institution of Chemical Engineers*. doi: 10.1016/j.psep.2022.11.080.
- [7] D. Liu *et al.*, "Thermodynamic appraisal of naphtha to light olefins based on different reaction pathways and independent chemical reactions," *Fuel*, vol. 346, Aug. 2023, doi: 10.1016/j.fuel.2023.128281.
- [8] D. J. Ward, D. J. Saccomando, G. Walker, and S. M. Mansell, "Sustainable routes to alkenes: applications of homogeneous catalysis to the dehydration of alcohols to alkenes," Mar. 23, 2023, *Royal Society of Chemistry*. doi: 10.1039/d2cy01690g.
- [9] V. Vislovskiy, T. Suleimanov, My. Sinev, Y. Tulenin, Ly. Margolis, and V. Cortés Corberán, "On the role of heterogeneous and homogeneous processes in oxidative dehydrogenation of C 3-C 4 alkanes," 2000.
- [10] J. S. Valente, R. Quintana-Solórzano, H. Armendáriz-Herrera, and J. M. M. Millet, "Decarbonizing Petrochemical Processes: Contribution and Perspectives of the Selective Oxidation of C1-C3 Paraffins," *ACS Catal*, vol. 13, no. 3, pp. 1693–1716, Feb. 2023, doi: 10.1021/acscatal.2c05161.
- [11] M. Fakhroleslam and S. M. Sadrameli, "Thermal Cracking of Hydrocarbons for the Production of Light Olefins; A Review on Optimal Process Design, Operation, and Control," *Ind Eng Chem Res*, vol. 59, no. 27, pp. 12288–12303, Jul. 2020, doi: 10.1021/acs.iecr.0c00923.

- [12] W. Wang, S. Qu, X. Li, J. Chen, Z. Guo, and W. H. Sun, "Transition metal complex catalysts promoting copolymers of cycloolefin with propylene/higher olefins," Nov. 01, 2023, *Elsevier B.V.* doi: 10.1016/j.ccr.2023.215351.
- [13] M. T. Hossain *et al.*, "Research and application of polypropylene: a review," Dec. 01, 2024, *Springer*. doi: 10.1186/s11671-023-03952-z.
- [14] D. Liu *et al.*, "Inter-conversion of light olefins on ZSM-5 in catalytic naphtha cracking condition," in *Catalysis Today*, Elsevier B.V., May 2014, pp. 52–66. doi: 10.1016/j.cattod.2013.09.060.
- [15] M. W. Da Silva and S. José dos Campos, "How to gain an advantage from the propylene production gap-Part 2." [Online]. Available: https://read.nxtbook.com/gulf_energy_information/hydrocarbon_processing/december_2023/process_optimization_da_silva.html
- [16] M. L. Sun, Z. P. Hu, H. Y. Wang, Y. J. Suo, and Z. Y. Yuan, "Design Strategies of Stable Catalysts for Propane Dehydrogenation to Propylene," Apr. 07, 2023, *American Chemical Society*. doi: 10.1021/acscatal.3c00103.
- [17] A. A. Al-Shammari *et al.*, "Catalytic cracking of heavy naphtha-range hydrocarbons over different zeolites structures," *Fuel Processing Technology*, vol. 122, pp. 12–22, Jun. 2014, doi: 10.1016/j.fuproc.2014.01.021.
- [18] S. Hodoshima, A. Motomiya, S. Wakamatsu, R. Kanai, and F. Yagi, "Catalytic conversion of light hydrocarbons to propylene over MFI-zeolite/metal-oxide composites," *Microporous and Mesoporous Materials*, vol. 233, pp. 125–132, Oct. 2016, doi: 10.1016/j.micromeso.2015.12.044.
- [19] Y. Xu, Y. Zuo, W. Yang, X. Shu, W. Chen, and A. Zheng, "Targeted Catalytic Cracking to Olefins (TCO): Reaction Mechanism, Production Scheme, and Process Perspectives," Nov. 01, 2023, *Elsevier Ltd.* doi: 10.1016/j.eng.2023.02.018.
- [20] L. dos S. Vargette *et al.*, "Comprehensive Fouling Assessment in Steam Crackers: Fossil versus Renewable NEXBTL Naphtha," *Ind Eng Chem Res*, vol. 63, no. 1, pp. 111–120, Jan. 2024, doi: 10.1021/acs.iecr.3c02969.
- [21] Y. Tian *et al.*, "Transition metal modified hierarchical ZSM-5 nanosheet for catalytic cracking of n-pentane to light olefins," *Fuel*, vol. 363, May 2024, doi: 10.1016/j.fuel.2024.130902.
- [22] M. N. Akhtar, A. M. Aitani, A. C. Ummer, and H. S. Alasiri, "Review on the Catalytic Conversion of Naphtha to Aromatics: Advances and Outlook," Feb. 16, 2023, *American Chemical Society*. doi: 10.1021/acs.energyfuels.2c03716.
- [23] L. Chen *et al.*, "Modulated oxygen mobility of perovskite oxides for efficient redox oxidative cracking of cycloalkane to light olefins," *Chemical Engineering Journal*, vol. 477, Dec. 2023, doi: 10.1016/j.cej.2023.146894.

- [24] T. Bathena, T. Phung, V. Murugesan, K. A. Goulas, A. S. Karakoti, and K. Ramasamy, "Transition metal oxides in CO₂ driven oxidative dehydrogenation: Uncovering their redox properties," *Journal of CO₂ Utilization*, vol. 84, Jun. 2024, doi: 10.1016/j.jcou.2024.102848.
- [25] A. McNeeley, C. C. Tsai, S. T. Lin, and Y. A. Liu, "Development of energy-optimum aromatic extraction processes using ionic liquid [EMIM][NTf₂]," *AIChE Journal*, vol. 69, no. 2, Feb. 2023, doi: 10.1002/aic.17888.
- [26] A. Zanina, "Fundamentals determining activity and product selectivity in the oxidative coupling of methane over MnO_x-M₂WO₄/SiO₂ (M=Na, K, Rb, or Cs)," doi: 10.18453/rosdok_id00004386.
- [27] A. A. Al-Absi and S. S. Al-Khattaf, "Conversion of Arabian Light Crude Oil to Light Olefins via Catalytic and Thermal Cracking," *Energy and Fuels*, vol. 32, no. 8, pp. 8705–8714, Aug. 2018, doi: 10.1021/acs.energyfuels.8b01932.
- [28] T. Chiranjeevi, N. Ravichander, D. T. Gokak, V. Ravikumar, and N. V. Choudary, "The selection of fluid catalytic cracking catalysts and additives: The significance of attrition studies," *Pet Sci Technol*, vol. 32, no. 4, pp. 470–478, Feb. 2014, doi: 10.1080/10916466.2011.592894.
- [29] C. Boyadjian and L. Lefferts, "Promoting li/mgo catalyst with molybdenum oxide for oxidative conversion of n-hexane," *Catalysts*, vol. 10, no. 3, Mar. 2020, doi: 10.3390/catal10030354.
- [30] S. Rostom and H. De Lasa, "Propane oxidative dehydrogenation on vanadium-based catalysts under oxygen-free atmospheres," Apr. 01, 2020, *MDPI*. doi: 10.3390/catal10040418.
- [31] X. Tian, R. B. Dudek, Y. Gao, H. Zhao, and F. Li, "Redox oxidative cracking of n-hexane with Fe-substituted barium hexaaluminates as redox catalysts," *Catal Sci Technol*, vol. 9, no. 9, pp. 2211–2220, 2019, doi: 10.1039/c8cy02530d.
- [32] F. Hao *et al.*, "Zeolite-assisted core-shell redox catalysts for efficient light olefin production via cyclohexane redox oxidative cracking," *Chemical Engineering Journal*, vol. 409, Apr. 2021, doi: 10.1016/j.cej.2020.128192.
- [33] M. Bender, "An Overview of Industrial Processes for the Production of Olefins – C₄ Hydrocarbons," Aug. 01, 2014, *Wiley-Blackwell*. doi: 10.1002/cben.201400016.
- [34] A. De Klerk, "Zeolites as catalysts for fuels refining after indirect liquefaction processes," 2018, *MDPI AG*. doi: 10.3390/molecules23010115.
- [35] "Naphtha Market Size, Share & Global Industry 2030".
- [36] F. Hao *et al.*, "Zeolite-assisted core-shell redox catalysts for efficient light olefin production via cyclohexane redox oxidative cracking," *Chemical Engineering Journal*, vol. 409, Apr. 2021, doi: 10.1016/j.cej.2020.128192.

- [37] M. Gao, G. Zhang, L. Zhao, J. Gao, and C. Xu, "Research Progress of Basic Catalyst Used in Catalytic Cracking for Olefin Production and Heavy Oil Utilization," *Ind Eng Chem Res*, vol. 62, no. 3, pp. 1215–1226, Jan. 2023, doi: 10.1021/acs.iecr.2c03939.
- [38] L. Shi, Y. Wang, B. Yan, W. Song, D. Shao, and A. H. Lu, "Progress in selective oxidative dehydrogenation of light alkanes to olefins promoted by boron nitride catalysts," *Chemical Communications*, vol. 54, no. 78, pp. 10936–10946, 2018, doi: 10.1039/c8cc04604b.
- [39] M. N. Chong, Z. Y. Tneu, P. E. Poh, B. Jin, and R. Aryal, "Synthesis, characterisation and application of TiO₂-zeolite nanocomposites for the advanced treatment of industrial dye wastewater," *J Taiwan Inst Chem Eng*, vol. 50, pp. 288–296, May 2015, doi: 10.1016/j.jtice.2014.12.013.
- [40] A. A. Stepanov, L. L. Korobitsyna, and A. V. Vosmerikov, "Investigation of the Properties of Mo/ZSM-5 Catalysts Based on Zeolites with Microporous and Micro-Mesoporous Structures," *Chemistry (Switzerland)*, vol. 5, no. 2, pp. 1256–1270, Jun. 2023, doi: 10.3390/chemistry5020085.
- [41] H. A. Abbas *et al.*, "Enhanced Catalytic Hydrogenation of Olefins in Sulfur-Rich Naphtha Using Molybdenum Carbide Supported on γ -Al₂O₃ Spheres under Steam Conditions: Simulating the Hot Separator Stream Process," *Materials*, vol. 17, no. 10, May 2024, doi: 10.3390/ma17102278.
- [42] M. H. Castaño, R. Molina, and S. Moreno, "Effect of Mg and Al on manganese oxides as catalysts for VOC oxidation," *Molecular Catalysis*, vol. 443, pp. 117–124, Dec. 2017, doi: 10.1016/j.mcat.2017.09.015.
- [43] S. Min and Y. Kim, "Physicochemical characteristics of the birnessite and todorokite synthesized using various methods," *Minerals*, vol. 10, no. 10, pp. 1–17, Oct. 2020, doi: 10.3390/min10100884.
- [44] A. C. Aydoğdu, B. Erkmén, A. Süerkan, A. Ezdesir, B. Guliyev, and G. Celik, "Chemical Upcycling of Polyolefins into Liquid Refinery Feedstock from the Circularity and Chemical Engineering Aspects," *J Environ Chem Eng*, p. 113430, Jun. 2024, doi: 10.1016/j.jece.2024.113430.
- [45] M. C. Shin *et al.*, "An experimental study of the endothermic catalytic cracking of hydrocarbon aviation fuels under extreme conditions," *J Anal Appl Pyrolysis*, vol. 181, Aug. 2024, doi: 10.1016/j.jaap.2024.106613.
- [46] S. Nadeem *et al.*, "Cation Incorporation and Synergistic Effects on the Characteristics of Sulfur-Doped Manganese Ferrites S@Mn(Fe₂O₄) Nanoparticles for Boosted Sunlight-Driven Photocatalysis," *Molecules*, vol. 27, no. 22, Nov. 2022, doi: 10.3390/molecules27227677.
- [47] J. Yang *et al.*, "Insight into N₂O Formation Over Different Crystal Phases of MnO₂ During Low-Temperature NH₃-SCR of NO," *Catal Letters*, vol. 151, no. 10, pp. 2964–2971, Oct. 2021, doi: 10.1007/s10562-021-03541-8.

- [48] S. Nadeem *et al.*, "Cation Incorporation and Synergistic Effects on the Characteristics of Sulfur-Doped Manganese Ferrites S@Mn(Fe₂O₄) Nanoparticles for Boosted Sunlight-Driven Photocatalysis," *Molecules*, vol. 27, no. 22, Nov. 2022, doi: 10.3390/molecules27227677.
- [49] Q. Zhao, F. Li, Y. Wang, Y. Liu, and M. He, "Acid strength-controlled reaction pathways of propylene conversion under olefin cracking conditions over ZSM-5," *Fuel*, vol. 371, Sep. 2024, doi: 10.1016/j.fuel.2024.132077.
- [50] H. B. Asfha *et al.*, "Reaction mechanism study of catalytic conversion of light straight-run naphtha to light olefins over micro-spherical HZSM-5 zeolite catalyst," *Catal Today*, vol. 426, Jan. 2024, doi: 10.1016/j.cattod.2023.114376.
- [51] B. C. Vance *et al.*, "Unlocking naphtha from polyolefins using Ni-based hydrocracking catalysts," *Chemical Engineering Journal*, vol. 487, May 2024, doi: 10.1016/j.cej.2024.150468.
- [52] S. Min and Y. Kim, "Physicochemical characteristics of the birnessite and todorokite synthesized using various methods," *Minerals*, vol. 10, no. 10, pp. 1–17, Oct. 2020, doi: 10.3390/min10100884.
- [53] A. A. Alswata, M. Bin Ahmad, N. M. Al-Hada, H. M. Kamari, M. Z. Bin Hussein, and N. A. Ibrahim, "Preparation of Zeolite/Zinc Oxide Nanocomposites for toxic metals removal from water," *Results Phys*, vol. 7, pp. 723–731, 2017, doi: 10.1016/j.rinp.2017.01.036.
- [54] M. M. Khakzad Siuki, M. Bakavoli, and H. Eshghi, "Cu nanoparticles immobilized on modified magnetic zeolite for the synthesis of 1,2,3-triazoles under ultrasonic conditions," *Appl Organomet Chem*, vol. 33, no. 4, Apr. 2019, doi: 10.1002/aoc.4774.
- [55] A. C. Aydogdu, B. Erkmén, A. Suerkan, A. Ezdesir, B. Guliyev, and G. Celik, "Chemical upcycling of polyolefins into liquid refinery feedstock from the circularity and chemical engineering aspects," *J Environ Chem Eng*, vol. 12, no. 5, Oct. 2024, doi: 10.1016/j.jece.2024.113430.
- [56] J. Yang *et al.*, "Insight into N₂O Formation Over Different Crystal Phases of MnO₂ During Low-Temperature NH₃-SCR of NO," *Catal Letters*, vol. 151, no. 10, pp. 2964–2971, Oct. 2021, doi: 10.1007/s10562-021-03541-8.
- [57] P. Ma *et al.*, "Selectivity descriptors of the catalytic n-hexane cracking process over 10-membered ring zeolites," *Chem Sci*, 2024, doi: 10.1039/d4sc00603h.
- [58] L. Toloza-Blanco *et al.*, "Catalytic oxidation of volatile organic compounds with Mn-zeolites," *Catal Today*, vol. 432, Apr. 2024, doi: 10.1016/j.cattod.2024.114570.
- [59] S. Sanzana *et al.*, "Enhancing manganese sorption: Batch and fixed-bed column studies on activated zeolite," *Environ Technol Innov*, vol. 33, Feb. 2024, doi: 10.1016/j.eti.2023.103495.

- [60] S. Li *et al.*, "Insights into the Acidic Site in Manganese Oxide in Terms of the Sulfur and Water Tolerance of Low-Temperature NH₃ Selective Catalytic Reduction," *Langmuir*, 2024, doi: 10.1021/acs.langmuir.4c01289.
- [61] M. F. Ali *et al.*, "Enhancing the selectivity for light olefins through catalytic cracking of n-hexane by phosphorus doping on lanthanum-modified ZSM-5," *Front Chem*, vol. 12, 2024, doi: 10.3389/fchem.2024.1368595.
- [62] G. He and D. Mei, "Deciphering reaction mechanism network of n-heptane dehydrocyclization over H-ZSM-5 zeolite," *J Catal*, vol. 436, Aug. 2024, doi: 10.1016/j.jcat.2024.115623.
- [63] J. He *et al.*, "Strong metal oxide-zeolite interactions during selective catalytic reduction of nitrogen oxides," *J Hazard Mater*, vol. 465, Mar. 2024, doi: 10.1016/j.jhazmat.2023.133164.
- [64] J. Fals, J. F. Garcia-Valencia, E. Puello-Polo, F. Tuler, and E. Márquez, "Hierarchical Y Zeolite-Based Catalysts for VGO Cracking: Impact of Carbonaceous Species on Catalyst Acidity and Specific Surface Area," *Molecules*, vol. 29, no. 13, p. 3085, Jun. 2024, doi: 10.3390/molecules29133085.
- [65] H. Fujitsuka, M. Yamaji, R. Nakatani, M. Endoh, and T. Tago, "Metal-assisted low-temperature cracking of n-hexane over Rh-encapsulated ZSM-5 catalysts," *Microporous and Mesoporous Materials*, vol. 376, Aug. 2024, doi: 10.1016/j.micromeso.2024.113199.
- [66] S. Soltani, A. Zamaniyan, J. Towfighi Darian, and S. Soltanali, "Improvement of catalyst activity in cracking of n-hexane via metal (Fe/Ga) impregnation over ZSM-12 catalyst," *Journal of Saudi Chemical Society*, vol. 28, no. 3, May 2024, doi: 10.1016/j.jscs.2024.101833.
- [67] O. Aljohani, O. W. Aljohani, and A. M. Aitani, "CONVERSION OF CRUDE OIL TO CHEMICALS The Effects of Temperature and Catalyst on Fluid Catalytic Cracking (FCC) of Crude Feed: A Study Using a Micro Activity Test Unit," 2024. [Online]. Available: <https://www.researchgate.net/publication/381459931>
- [68] M. F. Ali *et al.*, "Enhancing the selectivity for light olefins through catalytic cracking of n-hexane by phosphorus doping on lanthanum-modified ZSM-5," *Front Chem*, vol. 12, 2024, doi: 10.3389/fchem.2024.1368595.
- [69] T. Wang *et al.*, "Regulating framework aluminum location towards boosted light olefins generation in ex-situ catalytic pyrolysis of low-density polyethylene," *Chemical Engineering Journal*, vol. 485, Apr. 2024, doi: 10.1016/j.cej.2024.149737.
- [70] X. T. Tran *et al.*, "Maximizing light olefin production via one-pot catalytic cracking of crude waste plastic pyrolysis oil," *Fuel*, vol. 361, Apr. 2024, doi: 10.1016/j.fuel.2023.130703.
- [71] G. Li *et al.*, "Synergistic catalysis effect of micro-mesoscopic channel for enhanced methyl oleate catalytic cracking to BTX: A molecular simulation study," *Chem Eng Sci*, vol. 295, Aug. 2024, doi: 10.1016/j.ces.2024.120183.

- [72] G. He and D. Mei, "Deciphering reaction mechanism network of n-heptane dehydrocyclization over H-ZSM-5 zeolite," *J Catal*, vol. 436, Aug. 2024, doi: 10.1016/j.jcat.2024.115623.
- [73] D. Zhang, Y. Zhang, X. Tian, and M. Ding, "Chemical looping oxidative dehydrogenation of ethane over Fe-Co/HZSM-5 redox catalyst," *Fuel*, vol. 363, May 2024, doi: 10.1016/j.fuel.2023.130842.
- [74] D. C. Longstaff, "Naphtha Cracking Kinetics and Process Chemistry on γ and ZSM5 Type Catalysts," *Energy and Fuels*, vol. 33, no. 3, pp. 2445–2452, Mar. 2019, doi: 10.1021/acs.energyfuels.8b04128.
- [75] H. K. Amusa *et al.*, "Kinetics of Oxidative Cracking of n-Hexane to Light Olefins using Lattice Oxygen of a VOx/SrO- γ Al₂O₃ Catalyst," *Chem Asian J*, vol. 16, no. 13, pp. 1792–1806, Jul. 2021, doi: 10.1002/asia.202100209.
- [76] H. K. Amusa *et al.*, "Kinetics of Oxidative Cracking of n-Hexane to Light Olefins using Lattice Oxygen of a VOx/SrO- γ Al₂O₃ Catalyst," *Chem Asian J*, vol. 16, no. 13, pp. 1792–1806, Jul. 2021, doi: 10.1002/asia.202100209.
- [77] D. C. Longstaff, "Naphtha Cracking Kinetics and Process Chemistry on γ and ZSM5 Type Catalysts," *Energy and Fuels*, vol. 33, no. 3, pp. 2445–2452, Mar. 2019, doi: 10.1021/acs.energyfuels.8b04128.
- [78] D. C. Longstaff, "Development of a comprehensive naphtha catalytic cracking kinetic model," *Energy and Fuels*, vol. 26, no. 2, pp. 801–809, Feb. 2012, doi: 10.1021/ef201535h.
- [79] J. H. Lee, S. Kang, Y. Kim, and S. Park, "New approach for kinetic modeling of catalytic cracking of paraffinic naphtha," *Ind Eng Chem Res*, vol. 50, no. 8, pp. 4264–4279, Apr. 2011, doi: 10.1021/ie1014074.
- [80] N. T. Luon, L. N. Quang Tu, and N. Q. Long, "Catalytic oxidation of formaldehyde over silver supported on ZSM-5: The role of Ag and mesopores," in *IOP Conference Series: Earth and Environmental Science*, IOP Publishing Ltd, Jan. 2022. doi: 10.1088/1755-1315/964/1/012026.
- [81] J. Shao, S. Cheng, Z. Li, and B. Huang, "Enhanced catalytic performance of hierarchical MnOx/ZSM-5 catalyst for the low-temperature NH₃-SCR," *Catalysts*, vol. 10, no. 3, Mar. 2020, doi: 10.3390/catal10030311.
- [82] S. A. Ali, A. H. Alshareef, R. Theravalappil, H. S. Alasiri, and M. M. Hossain, "Molecular Kinetic Modeling of Catalytic Naphtha Reforming: A Review of Complexities and Solutions," *Catal Rev Sci Eng*, vol. 65, no. 4, pp. 1358–1411, 2023, doi: 10.1080/01614940.2021.2008622.
- [83] Y. Bai *et al.*, "The advance in catalytic pyrolysis of naphtha technology using ZSM-5 as catalyst," Nov. 25, 2021, *Elsevier B.V.* doi: 10.1016/j.apcata.2021.118399.
- [84] S. Al-Khattaf, M. R. Saeed, A. Aitani, and M. T. Klein, "Catalytic Cracking of Light Crude Oil to Light Olefins and Naphtha over E-Cat and MFI: Microactivity Test versus Advanced

Cracking Evaluation and the Effect of High Reaction Temperature,” *Energy and Fuels*, vol. 32, no. 5, pp. 6189–6199, May 2018, doi: 10.1021/acs.energyfuels.8b00691.

- [85] A. Tanimu, M. AlGhrami, M. A. B. Siddiqui, M. F. Aljishi, A. Aitani, and M. Bahhar, “Steam catalytic cracking of vacuum gas oil: Effect of co-feeding naphtha or gas condensate on light olefins yield,” *Chemical Engineering Research and Design*, vol. 207, pp. 392–403, Jul. 2024, doi: 10.1016/j.cherd.2024.06.014.
- [86] D. C. Longstaff, “Development of a comprehensive naphtha catalytic cracking kinetic model,” *Energy and Fuels*, vol. 26, no. 2, pp. 801–809, Feb. 2012, doi: 10.1021/ef201535h.

VITAE

BIO-DATA

Name	Ahmed Alolaywi
Nationality	Saudi
Email	ahmedsami_22@hotmail.com
Number	+9660533122300
Address:	AL Mubarraz Al-Nuzha Prince Masha'el P.O Box 80189

RESEARCH INTERESTS

- Evaluation Techniques of Heterogeneous Catalyst in Fluid Catalytic Cracking
- Interaction between computational methods and Chemical Reaction Engineering

Education

- M.Sc. Chemical Engineering, KFUPM, Saudi Arabia, January 2024
- B. Eng. Chemical Engineering, University of Birmingham, May 2014

Work Experience

- Laboratory Engineer at the Research Institute Center of Refining and Advanced Chemicals 2020-Present
- Laboratory Assistant at the Chemical Engineering Department KFUPM 2016-2020

LIST OF PUBLICATIONS

1. **Ahmed S. AlOlaywi**, Akolade I. Bakare, Ramzi H. Alshugaih, Yahya Gambo, Sagir Adamu, Shaikh A. Razzak, Mohammad M. Hossain, Oxidative cracking of LSRN to olefins over MnOx/ZSM-5, Submitted to Catalysts **(Revised version will be submitted)**
2. **Ahmed S. AlOlaywi**, Akolade I. Bakare, Ramzi H. Alshugaih, Yahya Gambo, Sagir Adamu, Shaikh A. Razzak, Mohammad M. Hossain, Kinetics of oxidative cracking of light naphtha to olefins over MnOx/ZSM-5 under gas phase oxygen free conditions, **(Manuscript developed - to be submitted to a suitable journal)**