

University of Bahrain

College of Engineering

**Department of
Chemical Engineering**



Conversion of Municipal Plastic Waste to Liquid Fuels Using Hierarchical Zeolite Catalysts: Optimization & Kinetic Studies

Thesis submitted in partial fulfillment of the requirements for the
degree of M.Sc
In Chemical Engineering

Prepared by:

Faisal Mumtaz Ahmad

ID number: 20101361

Supervised by:

Dr. Muhammad Faisal Irfan

(Assistant Professor)

University of Bahrain

Kingdom of Bahrain

July 2020

Defense committee's approval page

University of Bahrain

College of Engineering

Department of Chemical Engineering

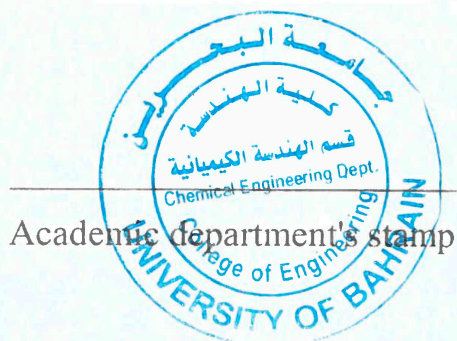
M.Sc. in Chemical Engineering

Student: Faisal Mumtaz Ahmad with ID number: 20101316 defended his thesis by which he fulfilled the requirement for the degree of M.Sc. in Chemical Engineering entitled 'Conversion of Municipal Plastic Waste to Liquid Fuels using Hierarchical Zeolite Catalysts: Optimization and Kinetic Studies' on this day of June 2020.

The committee recommends awarding of M.Sc. Degree with the grade of: **B +**

(Defense Committee)

Name		Signature
Dr. M. Faisal Irfan	Supervisor	
Dr. Shakeel Ahmed	External Examiner	
Dr. Shaker Haji	Internal Examiner	



Abstract

The project aims at hydrocracking of waste plastic mixture to produce useful liquid fuel. The plastic mixture used for this study is 24.76% LDPE, 29.85% HDPE, 10.57% PP and 34.82% PS. This project is novel in its work as; catalyst optimization and process optimization are carried using the optimized hierarchical zeolite catalyst in the reaction to degrade plastic mixture of waste origin to produce useful liquid product yield. Optimization is carried out using response surface methodology (RSM) with Central Composite Design (CCD). For preliminary experiments and catalyst synthesis optimization atmospheric setup is used, as for process parameters optimization a different autoclave setup is used. Preliminary experiments were carried out using mesoporous ZSM-5 and Beta Zeolite (BZ), where desilicated alumina impregnated BZ (DBZA) showed best results in terms of liquid yield. Optimization of alumina loading on desilicated catalyst were carried out, where alumina loading and synthesis temperature were considered as factors in the design of experiment. In catalyst optimization, on using 20g of mixed plastic waste as feed, a liquid yield of 9.9g (per 1g of catalyst) was achieved on using optimized mesoporous BZ catalyst which was desilicated at 0.1M NaOH at 75°C and doped with 3g aluminium nitrate per 5g of zeolite (22wt% Al₂O₃/zeolite) at 90°C, in comparison to parent BZ that gave only 2.1g of liquid yield. These experiments were carried out at catalyst to plastic (C-P) ratio of 1:20 at a temperature of 400°C. The optimized catalyst was then used in process optimization. The parameters selected for process optimization were temperature (360-440 °C), pressure (1-40 bars) and C-P ratio (1:5-1:40). The results indicated that pressure and C-P ratio parameters were not as statistically significant in comparison to temperature. At optimized conditions of 420°C, 20 bar and C-P ratio of 1:30, 11.27g (per 1g of catalyst) of oil yield was achieved. Two quadratic regression models were developed for each optimization i.e. process optimization ($R^2 \sim 91\%$) and catalyst optimization ($R^2 \sim 95\%$). These obtained R^2 values showed good fit with the experimental data. Various differential and integral mathematical methods were used based on the TGA data of ZSM-5, BZ and mesoporous Beta Zeolite (MBZ) catalysts. The range of activation energy values was found to be 91.68-170.80 kJ/mol, 51.10-86.80 kJ/mol and 44.74-67.40kJ/mol for ZSM-5, BZ, and MBZ, respectively. It is evident that on using MBZ, the process requires lowest activation energy in comparison to parent BZ or ZSM-5.

Dedication Page

This work is dedicated to my parents, wife and my daughter born during the journey of this master's degree.

Acknowledgement

To begin with I thank almighty Allah for His countless blessings on me and my family.

I express my sincere gratitude to my project supervisor Dr. Muhammad Faisal Irfan, Assistant Professor, Department of Chemical Engineering, University of Bahrain for his kind support, guidance, constructive criticism and timely advice without which our project would not complete. I would like to thank Dr. Mohammed Bin Shams, Associate Professor, Department of Chemical Engineering, University of Bahrain for inspiring and motivating me to pursue this master's degree back when I was an undergraduate student in 2012. I would also like to thank Dr. Muhammad Rashid Usman for making the collaboration with Sultan Qaboos University possible for this research, Dr. Abdullah Shatter for getting the EDS and SEM analyses done for us, Dr. Zakir Hussain for his support with DOE and Ms. Alya Islam for the XRD analysis. I would also like to thank Dr Yusuf Khan and Dr Ahsan-ul-Haq Quraishi from King Fahd University of Petroleum and Minerals (KFUPM) for their help in doing the TGA for us.

I would also like to thank the lab team which includes Ms. Eman, Ms. Mariam and Mr. Moayyed Hasan. Without their support, lab work would have been difficult.

I thank the company I work for 'p2mberlin middle east' and it's director Mr. Hubertus Schrage for his continuous support. It would be unimaginable to pull off a full-time job with a full time master's degree if it wasn't for the flexible work time culture.

Finally, I must express my very profound gratitude to my parents Mumtaz and Fareeda and my better half Mariam for providing me with unfailing support and continuous encouragement throughout my years of study and through the process of researching and writing this thesis.

Lastly, I would rejoice my daughter Anam born within the duration of this master's course i.e. Feb 2018, who would always be an integral part of this journey in terms of motivation.

This accomplishment would not have been possible without them all. Thank you.

Table of Contents

Subject	Page
Defense committee's approval page	A
Abstract	B
Dedication page	C
Acknowledgement	D
List of Figures	I
List of Tables	M
List of appendices	O
Abbreviations	P
Chapter One Introduction to the study	
1.1 Introduction	2
1.2 Research problem	5
1.3 Research questions	6
1.4 Research objective	7
1.5 Research significance	9
1.6 The study's setting and limitations	13
1.7 Research terminologies	14
Chapter Two Theoretical framework and literature review	
2.1 Plastics	20
2.1.1 Plastic types	21
2.1.2 Most commercial plastics	24
2.2 Plastic waste types	27
2.2.1 Municipal plastic wastes (MPW)	27
2.2.2 Industrial plastic wastes (IPW)	27
2.3 Plastic waste handling methods	29
2.4 Plastic waste disposal via chemical recycling	33
2.4.1 Partial oxidation/gasification	34

2.4.2 Depolymerisation	34
2.4.3 Pyrolysis/cracking	35
2.4.3.1 Thermal cracking	35
2.4.3.2 Catalytic cracking	36
2.4.3.3 Hydrocracking	39
2.5 Zeolites as catalysts	41
2.5.1 Limitations of zeolites	45
2.5.2 Acidity of zeolites	46
2.5.3 Basic difference between ZSM-5 and Beta zeolite	48
2.6 Hierarchical zeolites catalyst	50
2.6.1 Dealumination	52
2.6.2 Desilication	53
2.7 Influence of various process parameters	60
2.7.1 Influence of catalyst employed	62
2.7.2 Influence of using different types plastics	63
2.7.3 Influence of process reaction time	65
2.7.4 Influence of process reaction temperature	66
2.7.5 Influence of process reaction pressure	67
2.8 Concise summary of literature review	69
Chapter Three Methods and Procedures	
3.1 Optimization methodology	74
3.2 Kinetic studies approach	79
3.2.1 Differential isoconversional approach	82
3.2.1.1 Friedman method	82
3.2.1.2 Ozawa method	82
3.2.1.3 Freeman and Carolls method	83
3.2.2 Integral isoconversional approach	83
3.2.2.1 Doyles approximation method	83
3.2.2.2 Coats Redfern method (CR)	84
3.2.2.3 Modified Coats Redfern method (MCR)	84

3.2.2.4 Flynn-Wallace-Ozawa (FWO) method	84
3.2.2.5 Kissinger-Akahira-Sunose (KAS) method	85
3.2.2.6 Distributed Activation Energy Model method (DAEM)	85
3.3 Experimental methodology	87
3.3.1 Materials used	87
3.3.2 Catalyst modification methodology	90
3.3.2.1 Desilication method	91
3.3.2.2 Dealumination method	92
3.3.2.3 Alumina Impregnation method	93
3.3.3 Experimental procedure for atmospheric setup	93
3.3.4 Experimental procedure for pressure setup	97
Chapter 4 Results, Discussion and Recommendation	
4.1 Preliminary results	101
4.1.1 Preliminary experiments and analysis using ZSM-5	102
4.1.2 Preliminary experiments and analysis using BZ	107
4.2 Catalyst optimization results	115
4.3 Process parameters optimization results	132
4.4 Kinetic study	149
4.5 Conclusion	156
4.6 Future recommendations	159
4.7 Economic prospects of plastic recycling	162
References	164
Publication list	202
Appendices	203
Abstract (in arabic)	

List of Figures

No.	Subject	Page
1	Common plastics derived from oil industry.	21
2	Schematic structures of thermoplastic and thermoset polymers	22
3	Repeating units of different polymers	23
4	Types of plastics that are most commercially used	24
5	(a) Applications and (b) type of commonly used plastic	26
6	Range of processing temperature for plastics	26
7	Diagram of a sorting machine for domestic waste	28
8	Routes for plastic waste management	29
9	Defined categories of plastic waste recycling	30
10	Main routes of chemical recycling of waste plastics	33
11	Various schematics of zeolites structures	42
12	Graphic depiction of the effect of pore size on the diffusion of large and small molecules and the effects of pore diameter on molecular diffusivity (D) and of the activation energy (E _a) on diffusion	46
13	Bronsted and Lewis acid sites in zeolite	47
14	Schematic diagram of ZSM-5 structure	48
15	Structural comparison between Beta Zeolite and ZSM-5	49
16	Application of hierarchical zeolites in catalytic reactions	50
17	Routes to transform zeolite to hierarchical zeolites	51
18	Schematic for comparison of ZSM-5 catalysts for catalytic pyrolysis of pinewood	54
19	Pictographic contrast of zeolite desilication by TBAOH and NaOH	57
20	Influence of NaOH on zeolite structure based on its Si/Al ratio	58

21	Results of hydrocracking of model waste plastic carried out at 425 °C, H ₂ pressure of 20 bar, reaction time of 60 min, feed to catalyst ratio equal to 20:1	62
22	Influence of various types of plastics on product yield	64
23	Influence of reaction time on hydrocracking of plastic waste, on liquid yield, gas yield and conversion	65
24	Influence of hydrogen pressure on the reaction	67
25	Comparison of 3-level BBD (red) with CCD (green)	75
26	Sample of waste plastics used	87
27	Zeolyst International's ZSM-5 and BZ stock	88
28	Various material used	89
29	(a) Zeolite samples being heated while magnetically stirred (this apparatus has a maximum attainable temperature of only 80°C), (b) Vacuum filtration setup of the synthesized zeolite, (c) Hierarchical zeolite samples after filtration, (d) Samples after over night oven drying at 100°C.	92
30	Drying oven, used for drying the catalyst samples	93
31	Glass tube furnace with single set point controller.	94
32	Schematic diagram of the setup	95
33	Weight of liquid yield produced	96
34	(a) High pressure parr autoclave vessel setup, (b) close-up of the pressure setup, (c) gas collecting bag of 1000ml volume, (d) 300ml vessel of the pressure setup	97
35	SEM images of (a) Parent ZSM-5 (b) Desilicated ZSM-5 (c) Dealuminated ZSM-5	104
36	XRD comparison of ZSM-5 with hierarchical ZSM-5	105
37	Graphical and tabulated representation of preliminary experiments	106
38	XRD of BZ and DBZA	111

39	SEM images of (a) Parent BZ (b) desilicated BZ (c) desilicated alumina impregnated BZ	111
40	Graphical and tabulated representation of preliminary experiments-2	114
41	Pareto chart of optimization of the catalyst	119
42	Residual plots of optimization of the catalyst	119
43	Main effects plot for the optimization of the catalyst	120
44	2D contour plot for the effect of aluminum loading and synthesis temperature on maximum liquid yield (g)	120
45	3D surface plot for the of effect of aluminum loading and synthesis temperature on maximum liquid yield (g)	121
46	Response optimizer plot for liquid yield for the catalyst optimization	121
47	Model predictions vs. experimental data for liquid yield (g) from waste plastic mixture (for all factors and interactions)	125
48	Graphical and tabulated representation of catalyst optimization experiments with GCMS data	128
49	(a) Exp. 8 liquid product weighted (b) optimum experiment's liquid yield weighted	129
50	Liquid product in gasoline range and conversion of plastic	129
51	SEM images of some DBZA catalyst samples	130
52	Pareto chart for process optimization	137
53	Residual plots of process optimization	137
54	Main effects plots of pressure, temperature and C-P ratio for response oil yield in process optimization	138
55	Interaction plots of all factors for the process parameter optimization	138
56	Temp vs Press Surface and contour plot for oil yield	139
57	Press vs C-P ratio Surface and contour plot for oil yield	139

58	Temp vs C-P ratio Surface and contour plot for oil yield	139
59	Response optimizer plot for oil yield for process optimization	140
60	Fitted line plot	144
61	Experimental vs predicted oil yield from the model	144
62	Summary of product oil yield (g) based on experiments carried out	144
63	Solid, liquid and gas yield distribution of the product yield	145
64	Amt. of oil percentage achieved in liquid yield and conversion of all experiments carried	145
65	TG-Conversion plot for mixed plastics at 10°C/min heating rate for ZSM-5, BZ and Hierarchical BZ (HBZ)	150

List of Tables

No.	Subject	Page
1	Most commercial plastic types and their characteristics, applications and role in pyrolysis	25
2	Calorific values of plastics compared with conventional fuels	32
3	Difference between thermal cracking and catalytic cracking	37
4	Zeolite classification based on pore size	43
5	Zeolite classification based on silica to alumina ratio	44
6	Routes for secondary porosity generation in zeolites	52
7	List of selected literature review on process parameters and catalyst used in degradation of plastic	60
8	CCD coded value for 2 factors	76
9	BBD coded value for 3 factors	77
10	CCD coded value for 3 factors	78
11	Details of zeolites used (Zeolyst, 2018)	88
12	Reaction process conditions	101
13	Parameters involved in catalyst preparation for preliminary experiments	102
14	Ratio of Si/Al and crystallite size of modified ZSM-5	104
15	Parameters involved in catalyst preparation of DBZA	109
16	Ratio of Si/Al and crystallite size of modified BZ	110
17	Coded levels of each factor with actual values using CCD for catalyst optimization	115
18	DOE Table for 2 factor CCD design for catalyst optimization with results	116
19	Analysis of Variance(ANOVA) with remarks	123

20	Experimental vs predicted using model equation of optimziation of catalyst	124
21	Ratio of Si/Al from EDS data for DBZA samples	130
22	Parameters involved in bulk catalyst preparation of optimized DBZA for process parameters optimization	133
23	5-levels of the DOE Table for 3 factor CCD design for process optimization	133
24	Tabulated results of experiments carried as per DOE (with coded values in bracket) along with the optimum	133
25	ANOVA Table for process optimization	142
26	Experimental vs predicted liquid yield from the model	143
27	Comparison of present study with the past five years	148
28	Activation energy calculated from TGA data using various methods	151
29	Pre-exponential factor calculated from TGA data using various methods	151
30	Order of reaction comparison with literature	152
31	Activation Energy comparison with literature	153

List of Appendices

Appendix No.	Subject
I	Tabulated Literature Review
II(A)	MSDS of Catalyst used, ZSM-5 and BZ
II(B)	Characterization (BET) of BZ and ZSM-5
II(C)	List of chemicals used
III	GCMS data for preliminary experiment-1
IV	GCMS data for preliminary experiment-2
V	GCMS data for catalyst synthesis optimization
VI	Observations on desilication of BZ
VII	Kinetic analysis graphs
VIII	Catalyst & liquid products characterization techniques
IX	Various other methods of Hierarchical zeolites preparation

Abbreviations

- 2k – two level, k factors
- Adj MS – Adjusted mean of squares
- Adj SS – Adjusted sum of squares
- BBD – Box Benkh Design
- BZ – Beta Zeolite
- CCD – Central Composite Design
- DBZA – Desilicated Alumina Impregnated Beta Zeolite
- DBZ – Desilicated Beta Zeolite
- DF - Degree of Freedom
- DOE - Design of Experiment
- GC/MS – Gas Chromatography Mass Spectrometer
- HBZ – Hierarchical Beta Zeolite
- HDPE – High Density Polyethylene
- IPW – Industrial Plastic Waste
- LDPE – Low Density Polyethylene
- LLDE – Linear Low Density Polyethylene
- MPW – Municipal Plastic waste
- MS - Mean of squares
- MSW – Municipal solid waste
- MT - metric tons
- Nc – number of center points
- PET – Polyethylene Terephthalate
- PP – Polypropylene
- PS – Polystyrene
- PVC – Polyvinyl Chloride
- R^2 – Coefficient of Determination
- $R^2(\text{adj})$ - Adjusted Coefficient of Determination

- S/N - Signal to Noise Ratio
- SS - Sum of Squares
- SWP – Solid Waste Plastic
- TGA - Thermogravimetric Analyzer
- XRD – X-ray Diffraction

Chapter 1

Introduction to the study

Table of contents

Subject	Page Number
Chapter One Introduction to the Study	1
1.1 Introduction	2
1.2 Research problem	5
1.3 Research questions	6
1.4 Research objective	7
1.5 Research significance	9
1.6 The study's setting and limitations	13
1.7 Research terminologies	14

1.1 Introduction

These days, increase in energy demand and environmental degradation, which are caused by the increase in population and rapid industrialization, are of grave concern (Doğan et al. 2012). Increasing population, changing consumption pattern, economic development, urbanization and industrialization as well as modernization of life style resulted in the increased generation of waste that should be put away, transported, treated and arranged. The overall amounts of municipal solid waste (MSW) are quickly expanding. It is assessed that around 2.5 billion MT of MSW was created worldwide in 2000, which is projected to reach 5.3 billion MT by 2030. Bahrain is said to be amongst the highest waste per capita generator which is estimated to be about 1.7kg per capita per day. It is evaluated that more than 4,000 tons/day of MSW is being created in Bahrain which ends up in the Asker city landfill site, 25km far from the downtown area in quarry regions (Zafar, 2017). Among the 4,000 tons/day of MSW produced in Bahrain, 15-25% could be generally approximated as plastic waste as indicated by Environmental Protection Act, USA.

Bahrain being an island with limited area to spare, it is adamant to come up with alternatives, for instance; segregating plastic waste and treating it to produce fuels of such quality that certain revenue is generated instead of adding to the burden of land filling practice, which is the silent motive of this project. Today, plastics materials are exceptionally important in day to day life and give an essential commitment to our public. The composition of a general waste stream is polyolefin 66.8%, polystyrene 13.4%, polyvinylchloride 10.2%, polyethylene terephthalate 5.6% and others 4.2%. Most parts of waste plastic spends its lifetime as waste on the landfill (Kaminsky and Zorriquetta, 2007). Transfer of waste plastics causes genuine ecological issues. In this way, plastic waste reusing

has been a concentration of numerous analysts in the previous couple of decades. Analyst have come up changes in approaches to utilize plastic waste some of it being plastic reuse, plastic roads, pyrolysis and so on. Thermoplastic waste for the most part comprises of polyethylene terephthalate (PET), high density polyethylene (HDPE), polyvinyl chloride (PVC), low density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS). Most part PE and PP materials are utilized in nourishment bundling. As for PP, it is more impervious to warmer, harder, denser and more straightforward than polyethylene (Ramesh, 2017).

As far as the commitment from chemical engineering researchers is concerned, pyrolysis gives off an impression of being promising method of transformation of solid waste plastic (SWP) to much more Marketable products or materials, for example, gas fuel as well as fuel oil that could be used to high esteem feedstock for the synthetic business. Plastic recycling for reuse or breaking it down to other useful feedstock (i.e: chemical recycling) in highly encouraged around the globe. Methods like catalytic cracking, pyrolysis, gasification and hydrocracking can be employed in plastic recycling to convert it to fuels.

The degradation of plastic waste to fuel and other valuable products through chemical recycling, specifically pyrolysis has got noticeable attention both as waste management approach as well as an alternate energy generation technology.

“The pyrolysis process comprises of the thermal degradation of the wastes in the absence of oxygen or air. In pyrolysis, the polymeric plastic materials are warmed to high temperatures, so their macromolecular structures are disintegrated into small particles and an extensive variety of hydrocarbons are formed. These pyrolytic items can be partitioned into a gas division, a fluid portion comprising of paraffins, olefins, naphthenes

and aromatics, and strong deposits. Pyrolysis has all the earmarks of being a system which can change over MPWs into gasoline extend hydrocarbons” (Demirbas, 2004; Ratnasari, Nahil, and Williams, 2017). Pyrolysis and catalytic reforming of MPW including plastic types PE, PP and PS have been studied by Wang and Wang, (2011) over nickel-loaded silica alumina catalysts. Bhaskar et al. (2003) has compared the thermal degradation products from MPW and modelled mixed plastics, which also gives higher quality liquid products in comparison.

Hydrocracking is a process to convert plastic waste to fuel under the influence of hydrogen and in the presence of catalyst. The product contains less amount of olefins and heteroatoms like sulphur, nitrogen, chlorine, and oxygen etc. It is an exothermic reaction in nature and requires low temperatures and more branched (*iso*) products are the results (Munir et al. 2017). In addition, the presence of hydrogen lowers the rates of deactivation of cracking catalyst. The hydrocracking procedure, which essentially changes high-boiling molecules into more attractive smaller molecules by consecutive hydrogenation and carbon bond breaking. It is not only the important method utilized in current oil refineries, but it is also amongst the most encouraging procedures for the transformation of plastic wastes. There have been various studies regarding the utilization of hydrocracking reaction in the presence of acid catalysts for the conversion of plastic into fuel (Sriningsih et al. 2014, Munir et al. 2018).

1.2 Research problem

Tons of plastics wastes are being generated which mainly ends up in landfill, making the land no more usable and has numerous other environmental issues to it. Hence, there is a need to resort to other plastic waste handling methods. There are many routes to opt from, amongst which tertiary recycling or pyrolysis is a viable option, as it gives useful products like liquid fuel. However, one of the main reasons for pyrolysis process to be held back in treating mixed waste plastic is the conversion and its inability to obtain a decent liquid fuel yield that could serve as a Marketable product to be consumed. Besides, there are numerous researchers who have attributed the low conversion related with porosity in the zeolite catalyst, as long chain or branched hydrocarbon cannot access the active sites due to their larger size compared to zeolites being nano/microporous in nature. This consequently reduces the access as well as transport of reagents from and to the catalyst active sites. The delayed transport of reagents facilitates transformation of these molecules into undesired by-products, which can constitute coke precursors. This causes blocking of the micropores of the zeolite catalyst that consequently leads to deactivation of the catalyst, lowering catalyst life-span as well.

Having said the above, this project deals with two research problems. Firstly, problems with plastic waste management's current practices, solution to which is explored in other viable route of waste plastic disposal which is 'pyrolysis'. Secondly, research problem being limited with zeolite catalyst in this application, solution to which is proposed in this project through synthesis techniques like desilication and dealumination of zeolite catalyst by transforming them to hierarchical zeolites.

1.3 Research questions

Answers to questions that is sought in this thesis would be:

- How would desilication of zeolite catalyst affects the performance of prepared catalyst in the conversion of mixed plastic waste to fuels?
- How would dealumination of zeolite catalyst affects the performance of prepared catalyst in the conversion of mixed plastic waste to fuels?
- How would desilication and alumina impregnation of zeolite affect the performance of zeolite catalyst in the ‘conversion of mixed plastic waste to fuels? (Dealumination and impregnation isn’t carried out as BZ catalyst has barely any alumina in it with Si/Al ratio of 300; hence it is only desilicated and not dealumination. Furthermore, it is impregnated to increase its alumina content)
- Does optimization of catalyst matter and make a difference in the enhancement of the liquid yield?
- What would be the optimum parameters to run the experiments based on DOE for the given apparatus setup? Does process optimization make any significant difference?
- How would the data fit with well-known kinetic models?

These are the core questions to be answered in this research which intern would add novelty to the project as this hasn’t been carried out to date.

1.4 Research objective

The general aim of the project is to study the hydrocracking of plastic waste mixture of 24.76% LDPE, 29.85% HDPE, 10.57% PP and 34.82% PS to produce optimum oil yield. To achieve this goal:

- Different hierarchical zeolite catalysts will be modified using commercial zeolite using post modification approaches like desilication and dealumination processes using HZSM-5 and Beta-zeolite catalyst.
- The prepared catalysts will be analyzed by different analytical techniques such as XRD, SEM and EDS.
- Preliminary experiments will be carried out using ZSM-5 and BZ, where it will be modified and proceeded with by desilication, dealumination and impregnation methods. Best catalyst will be selected based on the modification approach that results in a catalyst that gives better liquid yield on hydrocracking of mixed waste plastic.
- Catalyst optimization will be carried out varying the synthesis parameters of preparing the catalyst using 2 factor CCD to achieve a catalyst that is enhanced to result in maximum possible liquid yield (in useful fuel range).
- On getting the optimum prepared catalyst, it is then employed in experiments that involves process parameters optimization using 3 factor CCD to achieve maximum oil yield, where hydrocracking reaction is performed by using a stainless-steel reactor at different sets of temperature, pressure and plastic to catalyst ratio.

- A kinetic study will be performed using data from Thermogravimetric Analyzer (TGA) for finding the kinetic parameters such as activation energy. Furthermore, for calculation of activation energy numerous developed differential and integral models from literature.

1.5 Research significance

Hierarchical zeolites with secondary levels of pore size are advantageous for many industrially important catalytic reactions. The highly inter-connected porosity of hierarchical zeolite structures is favorable to overcome the mass-transfer issues associated with microporous zeolites. Thus, the diffusion and steric limitations of bulky molecules and the pore-blocking effect of deposited coke species can be reduced, affording high utilization efficiency, prolonged catalytic lifetime, and improved catalytic performance of zeolite catalysts. The addition of secondary pores can be done by various post modification approaches and desilication/dealumination are among them which are more simple and easy to apply (Feliczak-Guzik, 2018). This research related to the conversion of plastic waste mixture to fuel by hydrocracking using micro-meso composite zeolites and optimized under the influence of pressure is important significant research as this and is a novel work to the best of our knowledge. Modification of zeolite catalysts for this process is done by desilicated/dealumination methods which has also not been carried out yet. This research will ponder on how various parameters like temperature, pressure and catalyst to plastic ratio influences the degradation of mixed plastic of waste origin in the presence of a catalyst that is a hierarchical zeolite and what the optimum conditions are for a selected range. Furthermore, products that are achieved from this process can be commercialized that can find its applications in other various industries.

Significant researches have been carried out in the field of catalyst, application of which is intended to be explored in the sector of plastic waste management and processing. To begin with, the catalysts engaged can be homogeneous and heterogeneous in the catalytic degradation of plastic waste. The heterogeneously catalytic degradation is the preferred option

since there are trouble with homogeneously catalytic degradation of plastic waste in terms of recovery, separation of the catalysts from the products. Many materials have been cited in literature for heterogeneously catalytic degradation of plastic waste such as silica-alumina, mesoporous materials and zeolites. “The product fuel produced over silica alumina and mesoporous materials contained high amounts of olefins that were inclined to polymerization and oxidation during preservation whereas the product fuel formed over zeolites are rich in aromatics” (Sonawane et al. 2017; Gao et al. 2014). Moreover, zeolites with extended outside surface region and appropriate acidity for the most part show predominant performance in polyolefin degradation (Gao et al. 2014). Hence the focus of this project is to prepare a mesoporous catalyst for hydrocracking of waste plastic.

Mesoporosity in zeolites can be made by numerous procedures, in any case, among them desilication is in every way one of the slightest costly and generally clear. Desilication is a strategy based on the zeolite treatment in alkaline environment for instance NaOH or Na₂CO₃. Ma et al. (2013) and Vennestrom et al. (2011) examined the synergistic activity of Fe balanced ZSM-5 desilicated with sodium and guanidine hydroxide, separately.

The advantage of desilication is the improvement of mesopores to the disservice of microporosity, which sounds promising in the usage of this endeavor. With a specific end goal to advance the exchange between upgraded mesopore surface territory and micropore volume, Perez-Ramírez et al. (2009) reported a novel desilication strategy with the utilization of pore directing agent. “Pore directing agents act as pore-growth moderators and reduce the effect of zeolite crystals leaching, resulting in better preserved intrinsic zeolite properties” (Ramirez et al. 2009).

Verboekend et al. (2012) studied various quaternary ammonium cations and amines in mesopores formation using USY and BZ catalysts. They found that their influence on desilication depends on PDAs (Pore directing agents) charge and size. Moreover, the results showed that depending on the concentration of PDA the external surface and mesopore size can be tuned. Sadowska et al. (2013) studied desilication of ZSM-5 zeolite with NaOH of different concentrations and with NaOH/TPAOH (tetrapropylammonium hydroxide) combinations of various ratios between bases. It resulted in generation of mesoporosity with instantaneous reduction in micropore volume and crystallinity of the samples and rise in the surface acidity on alteration of ZSM-5 zeolite by desilication with NaOH and NaOH/TPAOH combination. Hierarchical zeolites achieved with the use of NaOH and TPAOH were characterized by mesopores of larger volume and surface area, but with reduced diameter than in case of the use of NaOH (Sadowska et al. 2013a; Sadowska et al. 2013b; Rutkowska et al. 2017)

The combination of desilication and dealumination treatments applied for different zeolite frameworks showed better results, especially in terms of diffusion and mass transfer (Groen et al. 2004; Verboekend et al. 2012; Laak et al. 2010; Qin et al. 2011; Verboekend et al. 2011; Verboekend et al. 2010; Haggam et al. 2017). Another usually employed method for decreasing external acid sites is the indiscriminate elimination of Al in the zeolite framework by acid dealumination. The framework structure of Al is liable for the acidity of the zeolite and the dealumination treatment would preferentially reduce external acid sites. “Acid dealumination is a chemical process using H^+ to remove acid sites. Severe dealumination might cause the structure to collapse at the entrance of pores. However, at extreme dealumination treating conditions, H^+ may diffuse into the inner channels

and pores of catalysts and alter the inner pore structure. The equilibrium between external acid sites coverage or removal and consequent change of pore structure by acid dealumination is considerably important, which governs the performance of ZSM-5 in the catalytic conversion of biomass pyrolysis vapors” (Xue et al. 2017).

1.6 The study's setting and limitations

This research is carried out at the Isa Town campus of the University of Bahrain. Catalyst preparation are carried out at 27-124, the pyrolysis experiments setup exits in 27-118, the bulk mixed waste plastic samples are placed in 27-120 and for oven drying and other various laboratory equipments like centrifuges are used from lab 28-123.

This study focuses on primarily catalyst preparation that brings novelty to the project. The approach of modifying zeolite to prepare hierarchical zeolites and optimizing it in application of converting mixed waste plastic to fuel under influence of hydrogen pressure has not been explored in literature, hence the focus of this thesis. This topic of study touches on many aspects, it can be looked as an alternate energy solution, advancement in waste management approach, fine tuning of catalyst, process parameters optimization etc.

There are no significant limitations to this thesis project, however the pressure range of this process at University of Bahrain cannot be explored over 1 bar due to limitations of the very experimental setup used. Hence to tackle this it is intended to collaborate with 'Sultan Qaboos University, Oman' to explore the possibilities of carrying out the experiments for a wider range of pressure for over 100 bar. Inability to carry out N_2 adsorption analysis and acidity test for catalyst. Furthermore, the in-availability of all analysis required at one spot. For instance, the SEM and XRD analytical lab being in the Sakheer which requires coordination between departments/colleges and non-existent of TGA for which it is intended to explore the options to carry on at 'KFUPM, Saudi Arabia' on whom we are highly dependent. These analyses completely depend on the coordination that takes place.

1.7 Research terminologies

- Degradation: the breakdown of an organic compound
- Pyrolysis: is the thermal decomposition of materials at high temperatures but in an inert atmosphere of lack of oxygen.
- Cracking: is the process in which longer organic molecules are broken down into smaller ones.
- Hydrocracking: is the process of breaking down long chain hydrocarbons into shorter ones assisted by presence of hydrogen gas.
- Catalyst: is a substance to alter the rate of the chemical reaction
- Catalytic cracking: is cracking process in presence of a catalyst like silica-alumina or zeolites.
- Mesoporous material: is a material containing pores of diameter between 2-50nm.
- Nanoporous material: is a material containing pores of diameter less than 100nm.
- Zeolites: are microporous aluminosilicate material very commonly used as commercial adsorbents or catalysts.
- Hierarchical Zeolites: modified zeolite that have additional porosity
- Dealumination: is the chemical removal of alumina from a material.
- Desilication: is the chemical removal of silica from a material.
- Calcination: is heating at high temperatures in air or oxygen.
- Balanced design: “An experimental design where all cells or treatment combinations have the same number of observations” (Montgomery et al. 2009).
- Blocking: “A schedule for conducting treatment combinations in an experimental study such that any effects on the experimental results

due to a known change in raw materials, operators, machines, etc., become concentrated in the levels of the blocking variable. The reason for blocking is to isolate a systematic effect and prevent it from obscuring the main effects. Blocking is achieved by restricting randomization” (Montgomery et al. 2009).

- Design: “A set of experimental runs which allows the fit of a model and the estimate of effects” (Montgomery et al. 2009).
- DOE: “Design of experiments. An approach to problem solving involving collection of data that will support valid, defensible, and Supportable conclusions” (Montgomery et al. 2009).
- Effect: “How changing the settings of a factor changes the response. The effect of a single factor is also called a main effect” (Montgomery et al. 2009).
- Error: “Unexplained variation in a collection of observations. DOE's typically require understanding of both random error and lack of fit error” (Montgomery et al. 2009).
- Experimental unit: “The entity to which a specific treatment combination is applied” (Montgomery et al. 2009).
- Factors: “Process inputs an investigator manipulates to cause a change in the output” (Montgomery et al. 2009).
- Lack-of-fit error: “Error that occurs when the analysis omits one or more important terms or factors from the process model. Including replication in a DOE allows separation of experimental error into its components: lack of fit and random (pure) error” ” (Montgomery et al. 2009).
- Model: “Mathematical relationship which relates changes in a given response to changes in one or more factors” (Montgomery et al. 2009).

- Random error: “Error that occurs due to natural variation in the process. Random error is typically assumed to be normally distributed with zero mean and a constant variance. Random error is also called experimental error” (Montgomery et al. 2009).
- Randomization: “A schedule for allocating treatment material and for conducting treatment combinations in a DOE such that the conditions in one run neither depend on the conditions of the previous run nor predict the conditions in the subsequent runs” (Montgomery et al. 2009).
- Replication: “Performing the same treatment combination more than once. Including replication allows an estimate of the random error independent of any lack of fit error” (Montgomery et al. 2009).
- Responses: “The output(s) of a process. Sometimes called dependent variable(s)” (Montgomery et al. 2009).
- Treatment: “A treatment is a specific combination of factor levels whose effect is to be compared with other treatments” (Montgomery et al. 2009).
- Confidence interval: “It is a measure of the reliability of an estimate. More specifically, the meaning of the term "confidence level" is that, if confidence intervals are constructed across many separate data analyses of repeated (and possibly different) experiments, the proportion of such intervals that contain the true value of the parameter will match the confidence level; this is guaranteed by the reasoning underlying the construction of confidence intervals. Whereas two-sided confidence limits form a confidence interval, their one-sided counterparts are referred to as lower or upper confidence bounds” (Montgomery et al. 2009).

- Residual plot: “A residual plot is a graph that shows the residuals on the vertical axis and the independent variable on the horizontal axis. If the points in a residual plot are randomly dispersed around the horizontal axis, a linear regression model is appropriate for the data; otherwise, a non-linear model is more appropriate” (Montgomery et al. 2009).
- Normality plot: “The normal probability plot is a graphical technique for normality testing: assessing whether or not a data set is approximately normally distributed. The data are plotted against a theoretical normal distribution in such a way that the points should form an approximate straight line. Departures from this straight line indicate departures from normality” (Montgomery et al. 2009).

Chapter 2

Theoretical framework and literature review

Table of contents

Subject	Page Number
Chapter Two Theoretical framework and Literature Review	
2.1 Plastics	20
2.1.1 Plastic types	21
2.1.2 Most commercial plastics	24
2.2 Plastic waste types	27
2.2.1 Municipal plastic wastes (MPW)	27
2.2.2 Industrial plastic wastes (IPW)	27
2.3 Plastic waste handling methods	29
2.4 Plastic waste disposal via chemical recycling	33
2.4.1 Partial oxidation/gasification	34
2.4.2 Depolymerisation	34
2.4.3 Pyrolysis/Cracking	35
2.4.3.1 Thermal cracking	35
2.4.3.2 Catalytic cracking	36
2.4.3.3 Hydrocracking	39
2.5 Zeolites as catalysts	41
2.5.1 Limitations of zeolites	45
2.5.2 Acidity of zeolites	46
2.5.3 Basic difference between ZSM-5 and BZ	48
2.6 Hierarchical zeolites catalyst	50

2.6.1 Dealumination	52
2.6.2 Desilication	53
2.7 Influence of process parameters on hydrocracking	60
2.7.1 Influence of catalyst employed	62
2.7.2 Influence of using different types plastics	63
2.7.3 Influence of process reaction time	65
2.7.4 Influence of process reaction temperature	66
2.7.5 Influence of process reaction pressure	67
2.8 Concise summary of literature review	69

2.1 Plastics

Plastic is a material comprising of vast variety of synthetic or semi-synthetic natural aggravates which are malleable and hence, they can be shaped/molded into any strong shape based on the application. Plastics are commonly natural polymers of high atomic mass and frequently contain different substances. They are normally engineered, most usually obtained from petrochemicals, be that as it may, a variety of variations are produced using inexhaustible materials. “Because of their minimal effort, simplicity of fabrication, flexibility, and impenetrability to water, plastics are utilized as a part of a huge number of results of various scale, including paper clasps and rocket. They have beaten customary materials, for example, wood, stone, horn and bone, cowhide, metal, glass, and fired, in a few items beforehand left to regular materials.

There are numerous pathways to derive plastics, a schematic of which is briefly depicted in Fig. (1). Plastic items can be manufactured into a solid or foam state. The essential properties of a plastic item are affected and restricted by the physical and chemical properties of the plastic resin from which it is made. Plastic resins are for the most part characterized by their capacity to stream under heat/pressure. Thermoplastic resins and thermoset resins are the 2 noteworthy classes of resins that can be utilized to fabricate plastic items. Even though most resins can be categorized as one of these two classes a few resins can be named both as both thermoplastic and thermoset (Eastern research group, 1998).

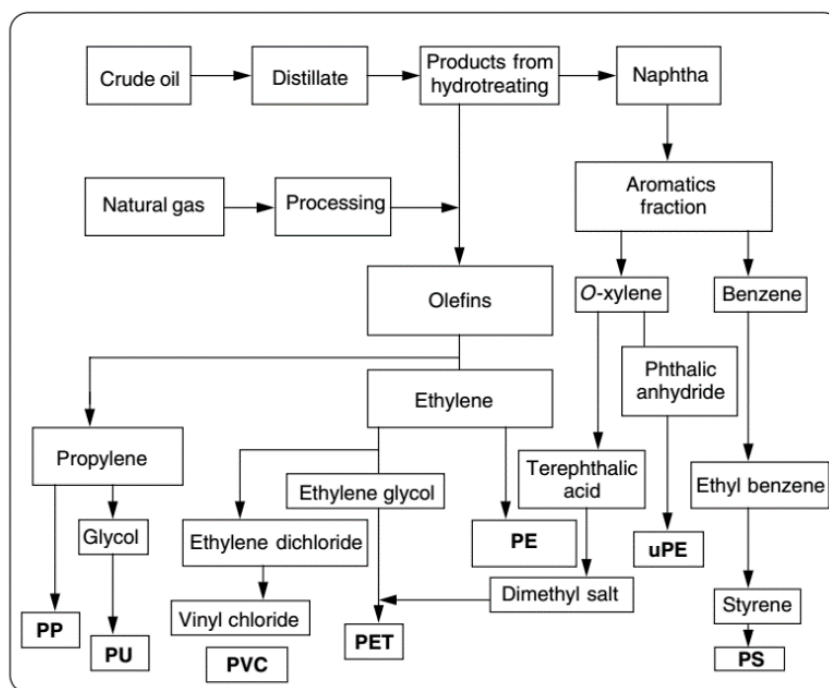


Fig. 1: Common plastics derived from oil industry (Gregory and Andrady, 2003).

2.1.1 Plastic types

Thermoplastics are plastic that will over and over turn out to be delicate and soft when warmed and hard when cooled. Under absolute normal circumstances, thermoplastics don't experience a chemical change while forming. Plastic manufacturing firms usually uses solid plastic pellets for processing. Thermoplastics account for significant part of plastic production. The following six thermoplastics are prepared in the largest quantities (Eastern research group, 1998):

- Low-density polyethylene and Linear low-density polyethylene
- High-density polyethylene
- Polyvinyl chloride
- Polypropylene
- Polystyrene

In contrast to thermoplastics, upon heating, pressurizing or reacting with hardening agent the Thermoset resins have a chemical reaction and become permanently solid. Differing from thermoplastics, thermosets are available in liquid/powder form for processing. Thermosets can't be easily remolded or refabricated. Structures of thermoplastic and thermoset polymers are depicted in Fig. (2). In any case, scraps from thermoset handling operations can be utilized as fillers for different items. Some broadly utilized thermosets incorporate (Eastern research group, 1998).

- Polyurethane (PUR)
- Epoxy
- Phenolic
- Unsaturated polyester and Urea.

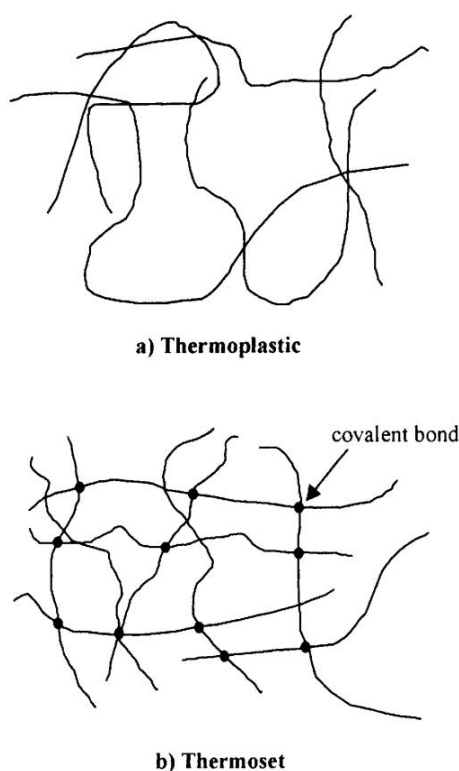
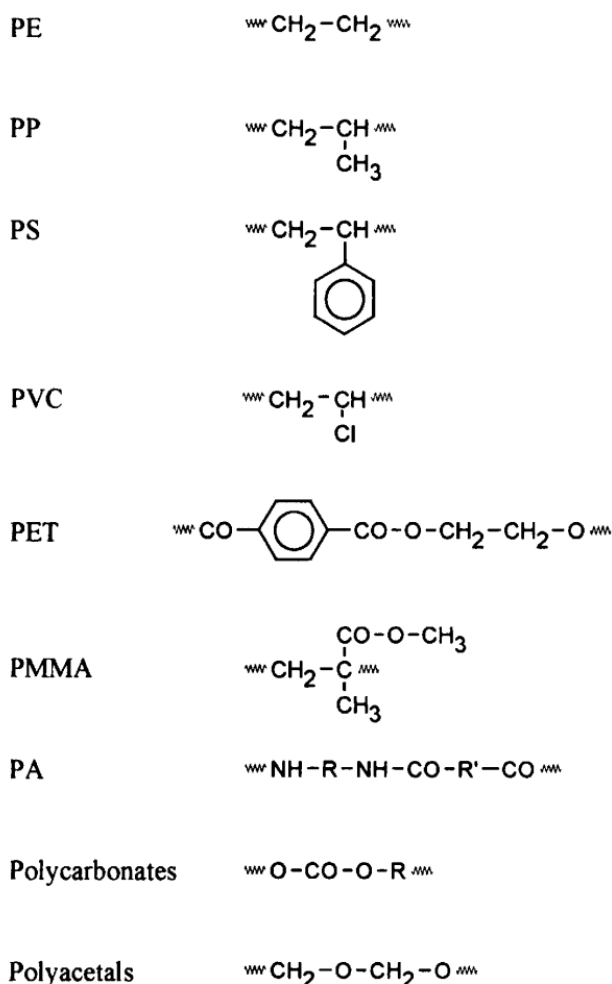


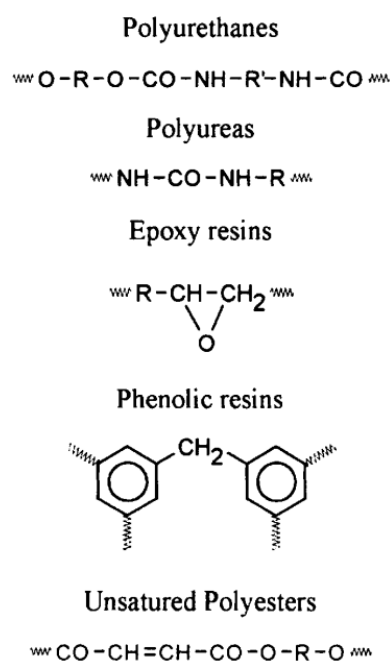
Fig. 2: Schematic structures of thermoplastic and thermoset polymers (Aguado and Serrano, 2007)

Elastomers can be classified as third type of plastic based on its thermal behavior. Just like thermosets, it has a network structure setup by crosslinking between the polymer chains, as seen Fig. (3). It is imperative to note that the amount of links are lesser compared to thermosets due to which elastomer materials has elastic properties. These can be disproportioned on exercising force. The moment the forces are withdrawn it goes back to its original form. Examples of elastomers include natural rubber, polybutadiene etc (Eastern research group, 1998).

Thermoplastics



Thermosets



Elastomers

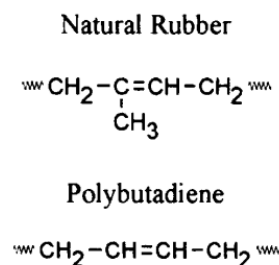


**Fig. 3: Repeating units of different polymers
(Aguado and Serrano, 2007)**

2.1.2 Most commercial plastics

The expansion in the utilization of plastic materials in all divisions of industry and in regular day to day existence have prompted a constant increment in plastic wastes. Because of the broad utilization of plastics in packing, various types of the plastics waste is found in domestic refuse. The most commonly used plastic types that are found in domestic waste are PP, PVC, LDPE, HDPE, PS, PET etc., as seen in Fig. (4) and Fig. (5). Most commercial plastic types and their characteristics, applications and role in pyrolysis are illustrated in Table (1).

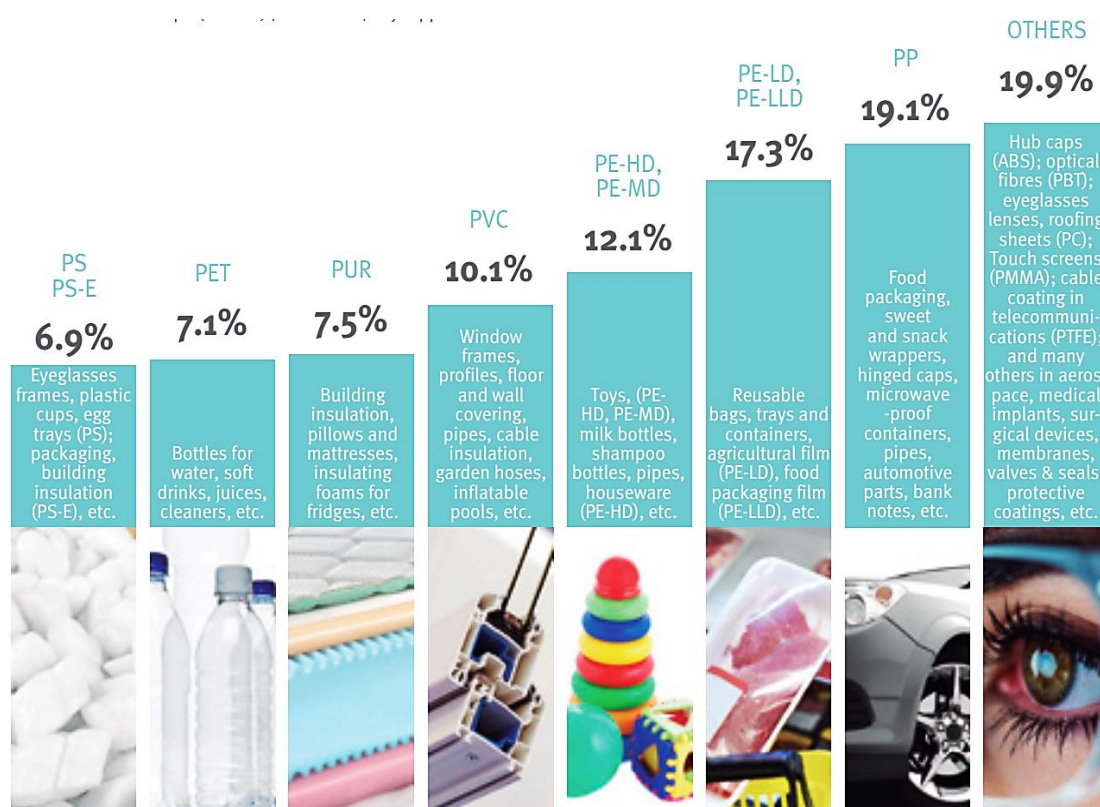
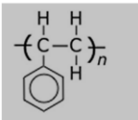
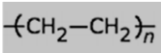
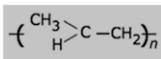
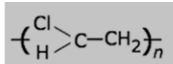
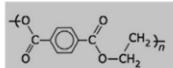


Fig. 4: Types of plastics that are most commercially used (Messe Düsseldorf and Plastics Europe Deutschland, 2016)

Table (1): Most commercial plastic types and their characteristics, applications and role in pyrolysis (Miandad et al. 2017).

Plastic Types	Characteristics	Applications	As Pyrolysis feedstock	Pyrolysis oil composition
Polystyrene (PS) 	~Heat resilience ~Lightness ~High strength ~Reasonable durability	~Toys ~Medical stuff ~Electronics ~Food packaging ~Construction stuff	~Needs low temp. in contrast to PP, it also produces less viscous oil in comparison to PE & PP plastic types.	~Styrene ~Toluene ~Ethylbenzene ~Benzene ~Xylene ~Cumene ~Benzene ~Naphthalene ~Anthracene ~Di/triphenylbenzene
Polyethylene (PE) 	HDPE ~It is a long polymer chain Highly crystalline ~High strength properties polymer	~Toys ~Oil containers ~Detergents ~Bottles ~Milk bottles	~Needs high temp. > 500C because of its long chained structural nature. ~It converts into wax instead of liquid fuel in thermal pyrolysis ~Wax formation is occurred on external site of catalyst while further cracking of wax into gases and liquid occurred in internal site of catalyst	~1- & 3-methylcyclopentene ~1-hexene ~Cyclohexene, ~1-octene ~1-nonene ~1-decene ~Benzene ~Toluene ~Xylene
	LDPE ~Less tensile strength ~Less hardness ~Excellent water resistant ~Desirable polymer for various applications	~Trash bags ~Wrapping foil for packaging ~Plastic bags	~Same as above.	~Benzene ~Toluene ~Xylene ~Di and trimethylbenzene Indane ~Indene ~Aphthalene ~Fluorene ~Acenaphthene
Polypropylene (PP) 	~Good heat and chemical resistance ~Low density ~High rigidity ~High hardness	~Pail ~Carpets ~Furniture ~Storage box ~Office folder ~Flower pot ~Car bumpers	~Requires high temp. ~Difficult to degrade under thermal pyrolysis ~Produces liquid yield with high aromatic compounds under catalytic pyrolysis	~Benzene ~Toluene ~Xylene ~Ethylbenzene ~Indene ~Biphenyl ~1-heptene ~1-octene ~2-methyl-1-pentene
Polyvinyl Chloride (PVC) 	~Resistant to fire ~ersatile plastic	~Automotive interior ~Credit cards ~Medical devices ~Packaging ~Electrical insulation ~Food foil Boots	~Produce hazardous chlorine gas ~Dechlorination via low temp. (250-320 C) or physical or chemical adsorption ~Presence of chlorine and deposition of coke affect the catalytic activity of catalyst	~Azulene ~Biphenyl ~Phenanthrene ~9H-fluorene ~Naphthalene and its monomers
Polyethylene Terephthalate (PET) 	~Lightweight ~Pressure resistance ~Larger capacity ~Versatile polymer	~Food packaging ~Electrical insulation ~Magnetic tapes ~X-ray ~Printing sheet ~Photographic film	~It contains heteroatom's	~1-Propanone ~Benzoic acid ~Biphenyl ~Fluorene ~Diphenylmethane ~Anthracene ~Benzophenone ~1-butanone

Polyethylene (PE) is the most widely used class of plastics in the world as depicted from stats seen in Fig. (4) and Fig. (5). From Table (2) it

is obvious as to how different types of plastics with various different properties find its application in all sorts of industrial, commercial and day-to-day application. At the same time from Table (1) it can be understood that the nature of oils which can be derived when these types of plastics undergo pyrolysis. Fig. (6) shows the melting points of various common plastics.

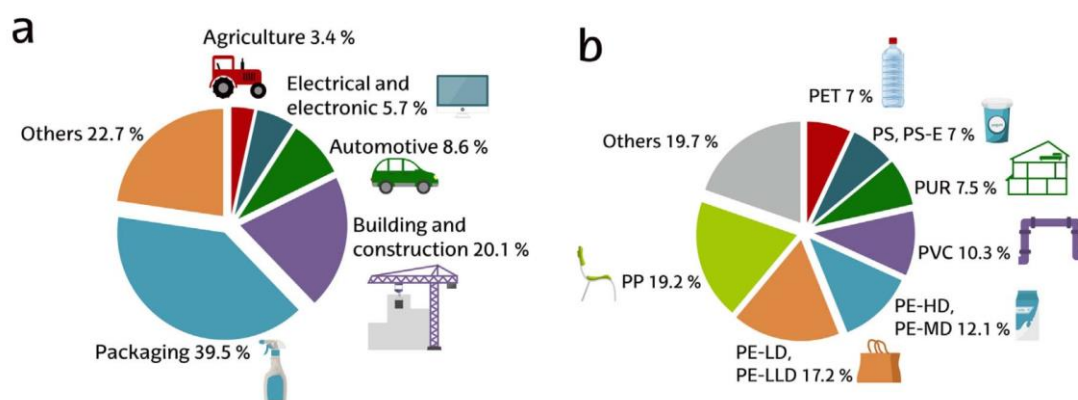


Fig. 5: (a) Applications and (b) types of commonly used plastics (Lopez et al. 2017)

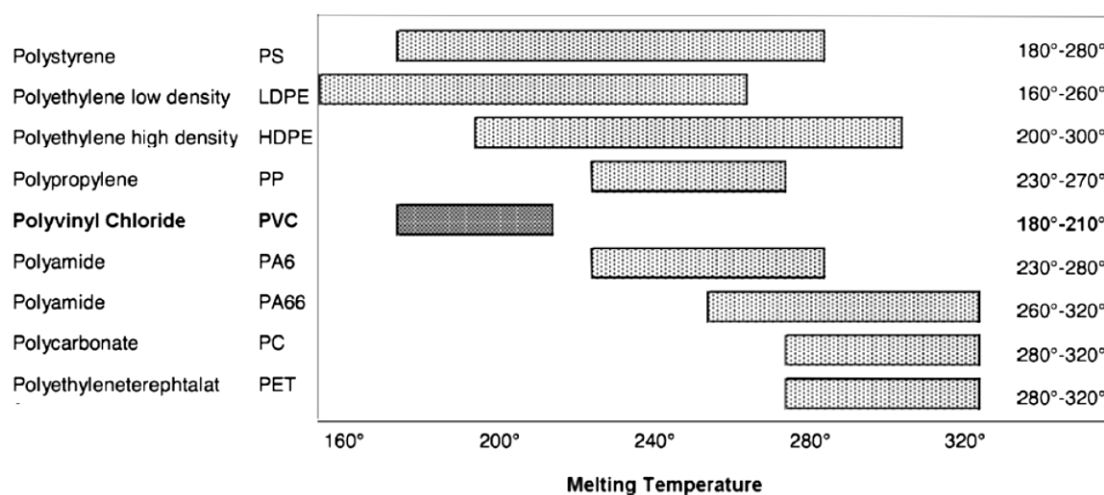


Fig. 6: Range of processing temperature for plastics (Ragaert et al. 2017)

2.2 Plastic waste types

Based on the origin of the plastic wastes, they can be categorized as industrial plastic waste and municipal plastic waste. Both of these plastic wastes have different traits and properties and hence they are dealt differently (Panda et al. 2010).

2.2.1 Municipal plastic wastes (MPW)

Municipal plastic wastes are a part of the municipal wastes normally collected by the municipality. As indicated in the background section, about 15-25% of the municipal wastes can be identified as municipal plastic wastes. The sources of municipal plastic wastes can include domestic items like disposable cutleries, plates, glasses etc, pipes of all kinds, food containers, various drinks bottles, all kinds of electronic items, all kinds of films and packaging etc. Thus the very nature of waste plastics derived from the municipal wastes are of mixed nature which in major has components of PE, PP, PS, PVC, PET etc. Plastic segregation can be achieved by processes like wet separation in which the mixed plastics can be categorized and divided into two on the basis of density compared to water. PET and PVC have densities greater than water whereas PE, PP and PS have densities lower than water which are present in majority in municipal waste. In the past decade, waste segregation has been a highlight in this regard so it could be processed accordingly (Panda et al. 2010).

2.2.2 Industrial plastic wastes (IPW)

On the other hand, industrial plastic wastes are those that arise in bulk from various industrial sources as discards while packaging, manufacturing, constructions, spare-parts, automobile industrial wastes etc. Industrial plastic waste generally possesses great attributes compared

to plastics in municipal wastes i.e. “they are adequately spotless and free of defilement and are accessible in genuinely substantial amounts. MPW’s are heterogeneous, whereas IPW’s are homogeneous in nature. Methods like repelletization and remolding appear to be a basic and powerful methods for reusing. In any case, when plastic wastes are heterogeneous or comprise of blended gums, they are inadmissible for recovery” (Panda et al. 2010).

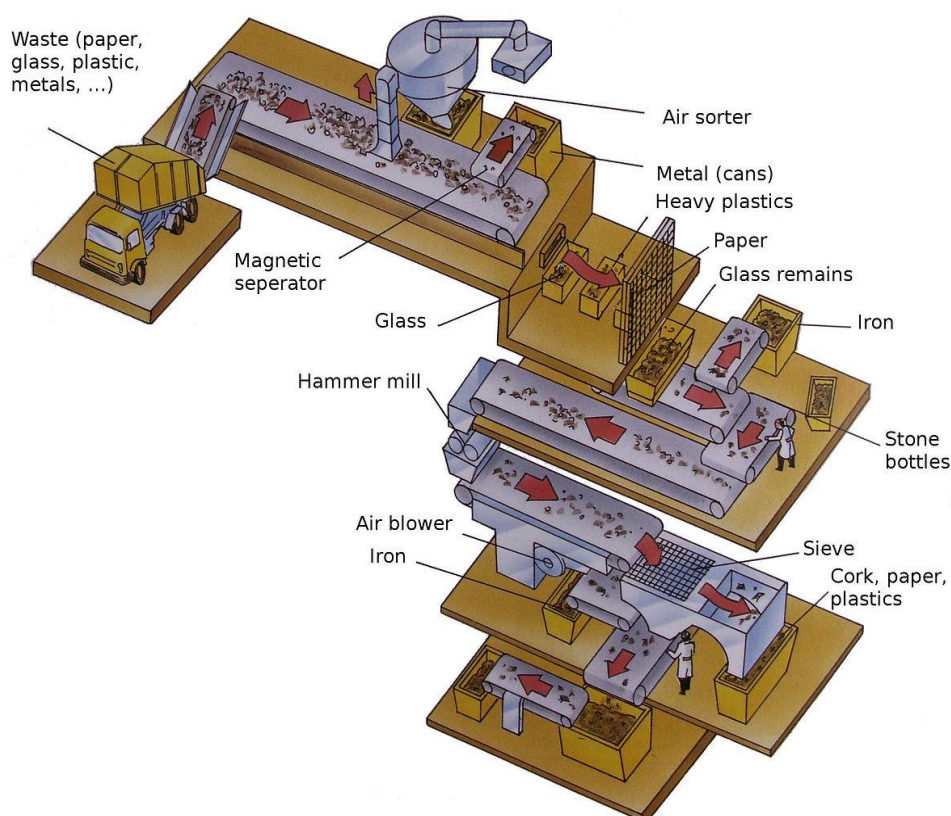


Fig. 7: Diagram of a sorting machine for domestic waste (Kerrod, 1994)

Fig. (7) portrays a general schematic of physical/mechanical steps involved in sorting of domestic municipal waste. The municipal domestic waste which includes various kinds of materials including paper, glass, metals gets separated ending with types of materials segregated.

2.3 Plastic waste handling methods

There are many ways to dispose industrial plastic wastes (IPW) and Municipal plastic wastes (MPW) as indicated in Fig. (8). It depends mostly on the country's economy as to the type of method adopted for plastic waste handling. For instance, countries with high economy are more environmentally aware and concerned and accordingly place sufficient national budget for the same compared to low economy countries. For instance, Bahrain in the past never had any sort of solid waste management besides landfill, but in the past decade the ministry of sanitary engineering has tendered for waste-to-energy projects (thanks to recent economic diversity and development), although it is being on hold as of now. Early this decade, landfill remained the preferred method in the world to dispose plastic wastes, by about 65% practicing it and following is incineration at 20%, whereas recycling amount to mere 15%.

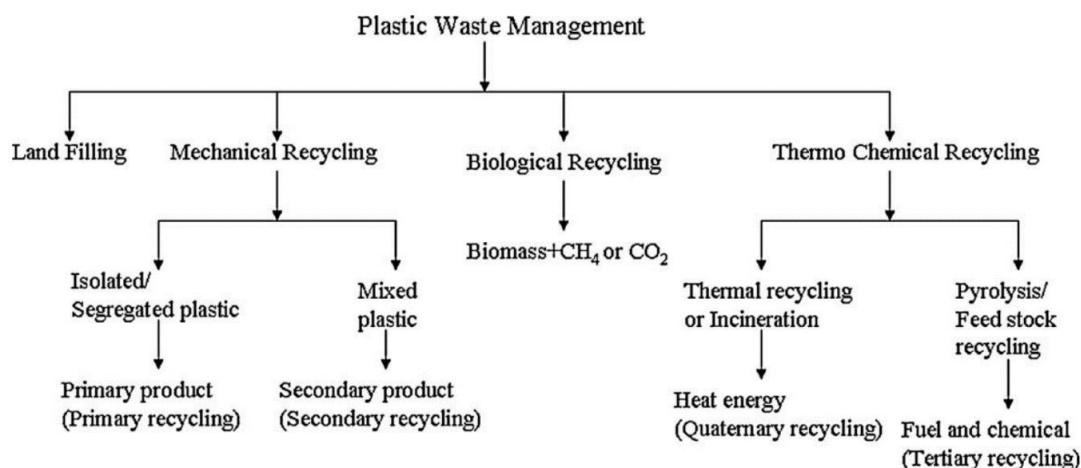


**Fig. 8: Routes for plastic waste management
(Buekens and Huang, 1998)**

Plastic wastes management can be broadly categorized as landfilling, mechanical recycling, biological recycling or chemical recycling as indicated in Fig.(8). Explicitly they can be categorized as primary, secondary, tertiary or quaternary recycling, being 4 approaches for

recycling (Buekens and Huang, 1998; Panda et al. 2010). Fig. (9) is self-explanatory and further clarifies Fig. (8), in terms of defining categorization of plastic waste recycling.

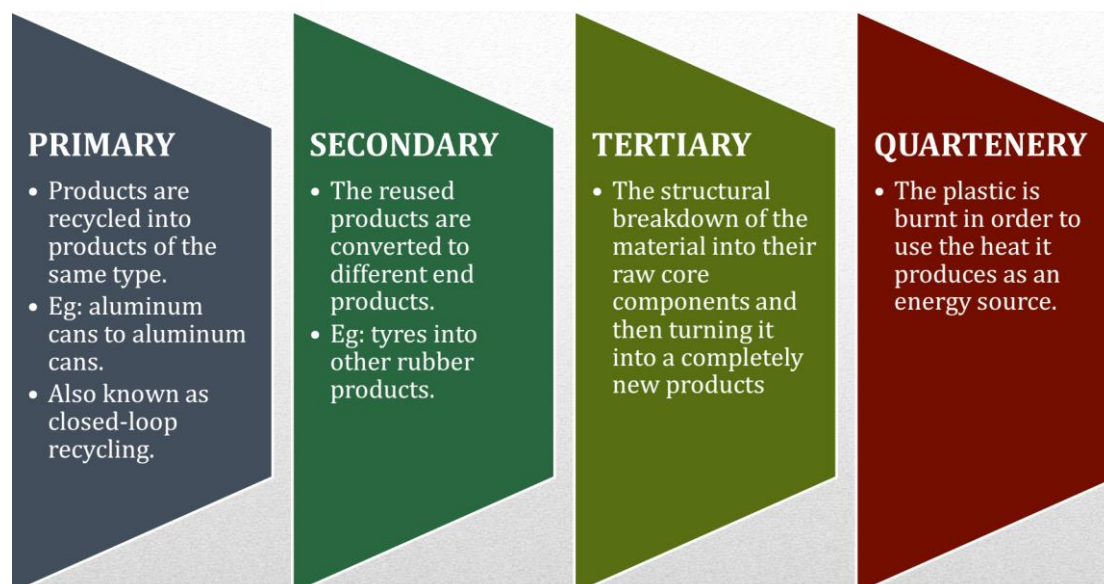


Fig. 9: Defined categories of plastic waste recycling

As mentioned earlier, the most preferred way to dispose solid waste including plastics is landfill. It is the most preferred method of plastic waste disposal in low income countries. Be that as it may, discarding the wastes to landfill is getting to be noticeably unwanted because of authoritative displeasure over landfill, increasing costs, the release of greenhouse gases like methane and very poor biodegradation of generally used plastics (Panda et al. 2010)

Mechanical recycling is further processing or reprocessing of waste or used plastic to form nearly same compatible products. Conversion of plastic waste to products have quality level which is compared to that of original products made of unrecycled feed. In primary recycling waste, plastic is either recycled as is or mixed up with raw fresh material to ensure the quality of the final product and keep up with the standards. Mostly no precaution is required besides proper waste collection in plant. Where as

in secondary recycling conversion of waste plastic to products don't require that standard of quality level as compared to primary recycling (Kumar et al. 2011)

There is so much going on lately on biological recycling in terms of biodegradable plastics. Generally speaking, of environmental friendly plastics, it could either be eco-recycled plastics which are just plastics recycled instead of prepared from fresh feed, or they could be bioplastics made from materials like corn starch, or they can also be biodegradable plastics made from traditional petrochemical routes itself but engineered to break down way quicker (Bioplastics, 2018). The utilization of these materials may prompt an expansion in plastics waste and litter if individuals trust that disposed of plastics will basically vanish" (Plastics, 2018). Because of these issues biodegraded plastics can't replace all the application territories of synthetic plastics.

Recovery of the energy contents from plastic wastes via incineration/combustion is often categorized as quaternary recycling (Kumar et al. 2011). Generation of energy by thermal recycling or incineration of waste polymers is in norms very practical since this practice tends to replace natural fossil fuel and hence it does reduce some amount of carbon dioxide emission that burdens on environment. Table (2) indicates the calorific value of fuel and mixed plastic or polyethylene (which is the most commonly used plastic in the world) is nearly same to that of fuels generated on incineration. Incineration is often favored energy recovery choice of establishments as there is financial returns on it by selling off the fuel rather than it going elsewhere like landfill where there are no returns (Panda et al. 2010; Scott, 2000; Scott, 1999). It is important to state that in majority of developed countries incineration isn't least preferred due to public distrust, increased production of greenhouse gases

and various other toxic pollutants which are known to be carcinogenic as well (Environment Australia, 1999). Plastics tend to have high calorific value ranging between 25-50MJ/kg, which makes it very attractive to harness this and convert it to useful fuels.

Table (2): Calorific values of plastics compared with conventional fuels (Panda et al. 2010; Silvarrey and Phan, 2016)

Sr. No.	Fuel	Calorific Value (MJ/Kg)
1	Methane	53
2	Gasoline	46
3	Fuel Oil	43
4	Coal	30
5	Polyethylene	43
6	Polypropylene	50
7	Polystyrene	39
8	Polyethylene terephthalate	25
9	Mixed Plastics	30-40
10	Municipal Solid waste	10

2.4 Plastic waste disposal via chemical recycling

Chemical recycling falls in the category of tertiary recycling. The word ‘chemical recycling’ is also sometimes called feedstock recycling or advanced recycling technologies which intends to convert waste plastics (long chain polymers) into smaller monomers as chemical intermediates via heat with or without catalysts. Different types of chemical recycling processes yield different nature of products as depicted briefly in Fig. (10).

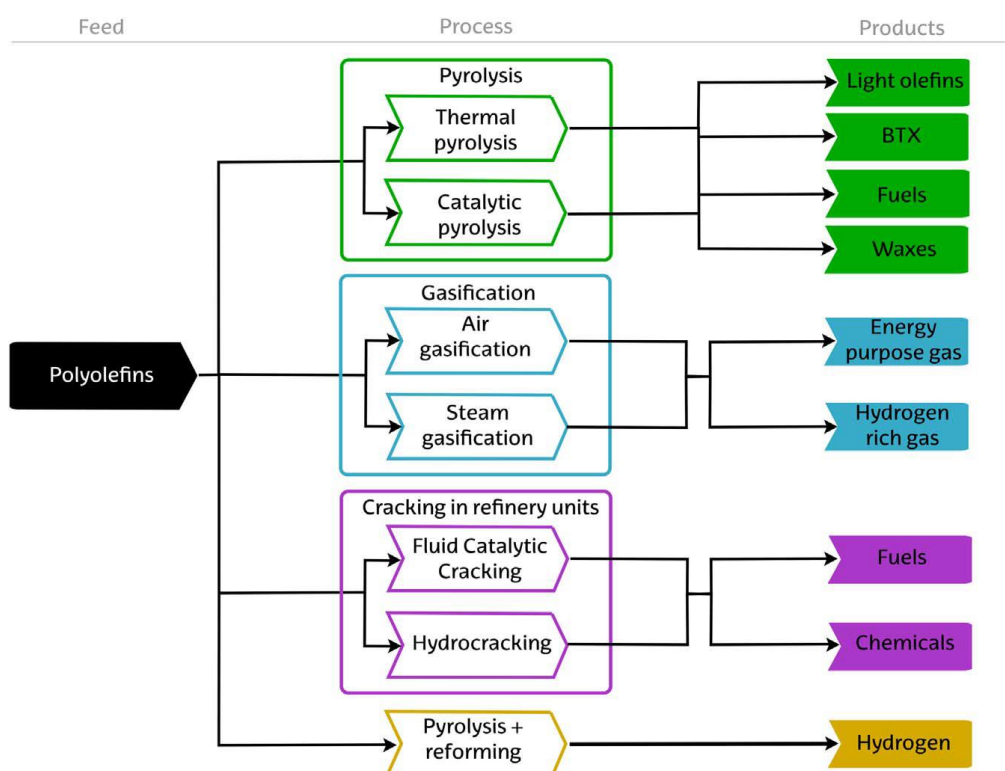


Fig. 10: Main routes of chemical recycling of waste plastics (Lopez et al. 2017)

These products are feed for numerous downstream industrial processes, applications or transport fuels. “The chemical intermediates which are normally liquids or gases but occasionally solids or waxes are appropriate for further usage as is, such as polyamides, polyesters, polycarbonates, polyureas and polyurethanes are resilient to hydrolysis under general conditions of usage. There are three main approaches to

chemical recycling namely depolymerisation, partial oxidation or gasification and cracking” (Kumar et al. 2011; Panda et al. 2010).

2.4.1 Partial oxidation/gasification

Partial oxidation using steam, air, oxygen or mixture of them is a very effective degradation of plastic waste which yields syngas and solid residue as main product. This process can be viewed as feed preparing process which results in syngas that can be used in production of compounds like ammonia, hydrocarbons, methanol etc rather than use of fuel gas. The most significant advantage of this process is that it requires minimum pretreatment and sorting of materials (Aguado and Serrano, 2007)

Recent advances of this process along with pyrolysis (2-stage process) in achieving about 70% of hydrogen production efficiency from plastic waste has been reported by Garforth et al. (2004). Co-gasification of plastic waste with biomass has been reported to reduce the carbon monoxide content while increasing the hydrogen. The production of chemical that are produced in bulk like acetic acid through oxidation using nitrogen oxide and/or oxygen can also be done (Panda et al. 2010).

2.4.2 Depolymerisation

Another method for plastic recycling is the breakdown of the polymers by chemical agents reacting on them driving back to the monomers. These monomers are indistinguishable to the ones used to prepare raw polymers, subsequently the plastics prepped from depolymerisation and monomers are relied upon to have comparative properties furthermore, quality. Based on the chemical agent used to breakdown the plastic, depolymerization can be employed through routes namely hydrolysis, glycolysis, methanolysis, ammonolysis etc. Plastic

recycling through depolymerisation in chemical recycling is the most well-established method of recycling (Aguado and Serrano, 2007).

2.4.3 Pyrolysis/Cracking

The breakdown of heavy molecular weight polymers chains into lighter molecular weight compounds is known as cracking or pyrolysis. The product that is achieved from cracking of plastic can be used as chemicals or fuels. Cracking can be categorized broadly into thermal cracking, catalytic cracking and hydrocracking.

2.4.3.1 Thermal cracking

The approach of chemical recycling which involves the degradation of plastic by heating at high temperatures of 350-900°C in the absence of oxygen is known as thermal pyrolysis or cracking. “On cracking, the subsequent product formed are carbonized char and volatile fraction which can be separated into condensable hydrocarbons like paraffins, isoparaffins, olefins, naphthenes and aromatics and non-condensable high calorific value gas. The quantity, quality, fraction and composition depends on the type of plastic waste and the condition at which reaction is carried out. In cracking process, a fraction of the compounds made directly from the initial degradation reaction are converted into secondary products due to the manifestation of inter/intramolecular reactions. The extent and nature of these reactions depends on the reactor type, placement of products in reaction zone (largely influenced by reactor design), temperature at which reaction is carried out” (Panda et al. 2010).

Furthermore, “reactor design plays a crucial role as it has to tackle issues related to low thermal conductivity as well as high viscosity of melted plastics. Numerous types of reactors have been cited in literature most commonly used being batch reactor and fluidized bed reactor (Kumar

et al. 2010). Characteristics of thermal cracking of heavy hydrocarbons can be outlined with high production of C1s and C2s in the gas product, alkenes (or olefins) tend to be less branched, Diolefins (or diene) are formed at high temperatures, oil products are widely distributed over a variety of molecular weight (i.e: gasoline selectivity poor), gas and coke product formation are high and in comparison with catalytic cracking thermal cracking reactions are slower. Nevertheless, the thermal degradation of waste plastic to lower molecular weight hydrocarbons requires reactions to be carried out at high temperatures which also ends up producing wide variety of product range. Catalytic cracking is another means to tackle these issues” (Panda et al. 2010).

2.4.3.2 Catalytic cracking

In this method of cracking, reaction is carried out in the presence of appropriate catalyst. The presence of catalyst lowers the reaction time as well as the temperature range at which it is carried out. Furthermore, on catalytic cracking of plastic yield majorly lighter hydrocarbon or branched alkanes which burns more easily than straight chain alkanes, which also ends up producing narrower variety of product range at lower temperatures and pressure meaning operation is cheaper as well as effective.

Numerous researches have been carried out for approaches to improve the liquid hydrocarbon yield from plastic waste and subsequent addition of catalyst in pyrolysis process as it has plenty of advantages. The most common plastics like polyethylene and polypropylene has been tested and studied extensively. The lab-scale setup usually employs mostly batch reactor or flow reactor. It is important to differentiate between the 2 ways in which catalyst maybe employed in catalytic cracking. The modes are Liquid-Phase-Contact (LPC) and Vapor-Phase-Contact (VPC). In LPC, the

catalyst along with plastic are placed in the reactor and acts majorly on the partly degraded complex of monomers of the polymer chain. Whereas in the VPC mode, the waste plastic is thermally degraded into vapor which then made to contact the catalyst in vapor phase (Panda et al. 2010; Kumar et al. 2011). Reducing the cost of this process will make this process preferable from commercial standpoint, which can be optimized as well by reusing the catalyst. This approach of plastic waste recycling seems to be very promising which is to be further advanced into a lucrative viable process to solve the environmental concern of waste plastic disposal. The difference between thermal cracking and catalytic cracking can be seen in Table (3).

Table (3): Difference between thermal cracking and catalytic cracking (Madhusa, 2017)

Particulars	Thermal Cracking	Catalytic Cracking
Definition	Thermal cracking is the process of breaking down large compounds into small compounds at high temperatures and high pressures.	Catalytic cracking is the breakdown of large compounds into small hydrocarbons using an acid catalyst.
Condition	High Temperatures: 400-1000 °C, Pressure: about 70atm, short residence time	Lower Temperature: 450-550°C, Pressure: about 20atm
Mechanism	Homolytic fission forming free radicals	Heterolytic fission forming carbocations
Application	Thermal cracking is used for vis-breaking, thermal gasoline production, and delayed coking.	Catalytic cracking is used to obtain fuel with octane number 65-70.
Main Products	(Ring structures and unsaturated), Low Alkenes, Shorter alkanes, Some hydrogen	(Focused on producing gasoline of high octane), Branched chain alkanes Cycloalkanes, Aromatics

Product Uses	Chemical industry (including polymer)	Fuel, blending etc.
Other products	Branched chain alkanes, cycloalkanes Aromatics	Low Alkenes, shorter alkanes, some hydrogen
Waste generation	Large amount of coke generation	Low coke generation
Gas yields	High	Low

2.4.3.3 Hydrocracking

“Hydrocracking is a process by which long chain hydrocarbon molecules are broken down into simpler molecules that are mostly in the useful liquid range like that of gasoline/kerosene by addition of hydrogen under the influence of high pressure and/or in presence of catalyst” (Miandad et al. 2017). This reaction in case of plastic waste are generally carried in a batch reactor at pressure of 3-10 MPa hydrogen and temperature range of 423-673K. In comparison to cracking carried out without the presence of hydrogen, hydrocracking avoids formation of olefins in liquid fractions leading to formation of highly saturated products which also works financially as further treatment is not required and can be used as fuels. Furthermore, hydrogen promotes removal of atoms like chlorine, nitrogen and sulphur (heteroatoms) that could be present in plastic wastes. “Hydrocracking is exothermic in nature which are carried out at lower temperatures and gives higher quality liquid products compared to catalytic cracking and thermal cracking processes. Hydrocracking has few drawbacks such as the employment of high pressure and cost of hydrogen itself” (Aguado and Serrano, 2007).

In general, researcher’s aim is to hydrocrack plastic waste into high quality liquid yield particularly in gasoline range using variety of feeds. Feeds pointed in research include PE, PP, PET, PS, PVC, mixed plastics,

plastics from municipal solid wastes, co-processing of plastics and coal, co-processing of plastics with refinery oils like VGO (vacuum gas oil), discarded scrap tires, co-mixing with tires with coals etc. Addition of solvents (like 1-methyl naphthalene, tetralin and decalin) to support reaction and mixing has been reported with success too. Catalysts that are typically used in refinery hydrocracking reactions has been assessed which include transition metals like platinum, nickel, iron etc (hydrogenation function) supported on acidic solids like zeolites, alumina, etc (cracking function), they integrate both hydrogenation as well as cracking activities. Although gasoline range products has been produced, nothing major has been reported on effect of catalyst and metal, surface area, Si-Al ratio etc. (Kumar et al. 2011; Panda et al. 2010).

Catalyst has a very important role in hydrocracking process; it decreases the reaction temperature range while increasing the yield, selectivity as well as the quality of the product. In literature, numerous types of acid catalysts have been studied that are usually used in hydrocracking, hydrotreating and cracking processes. Among them, some catalysts are found suitable for processing of plastics to fuel such as microporous acidic zeolites like HZSM-5 (Ali et al. 2004; Ding and Anderson, 1997; Feng et al. 1996; Huffman et al. 1997; Karagoz et al. 2002; Liu and Meuzelaar, 1996; Luo and Curtis, 1996; Shah et al. 1999) HY (Hesse and White, 2004; Ochoa et al. 1996; Walendziewski and Steininger, 2004) and hydrogen ion exchanged ultra stable (HUSY) (Akah et al. 2013; Akah et al. 2015). Catalytic cracking of plastic degradation has restrictions in terms of mass and heat transfer as the polymer molecules size tends to be large, the high viscosity when in a fluid phase poses another limit.

It is noteworthy that majority of converted products consists of gases which are rather in small quantities of liquid, as microporous zeolites restricts the diffusion of larger molecules. Mesoporous materials tackles this very issue as it allows the diffusion of heavy molecules which produces lesser gaseous products than liquid product. However, mesoporous materials exhibit weak acidic character and have lower cracking ability. This is because they are mostly siliceous materials and lack crystalline structure. Hence mesoporous catalyst with induced acidity and micro-mesoporous zeolites should be worth further research for hydrocracking reaction (Munir et al. 2017).

Sriningsih et al. (2014) carried out the hydrocracking process to convert LDPE plastic waste at a temperature of 350°C and hydrogen gas at a flow rate of 20ml/min for 1 hour of reaction time over Co-Mo/Zeolite catalyst (feed-catalyst ratio 5) which produced liquid yield (with higher selectivity in the gasoline range) of 71.49%. Based on GCMS analysis, the liquid fuel is comprised of paraffins, olefins and naphthenes (C₆-C₁₉).

Munir et al. (2017) carried out hydrocracking of plastic waste mixture to obtain high quality liquid fuels over several acidic catalysts like Al-SBA-15 and Al-SBA-16. Experiments were carried out at temperature range of 375-425°C and high pressure of 20 bar in a batch reactor (autoclave) for the residence time of 60 min at a feed to catalyst ratio of 20:1 by weight. It was concluded by Munir et al. (2017) that at elevated temperature, pressure and type of catalyst are not significant.

2.5 Zeolites as catalysts

“Zeolites, carbons, and oxides are individuals from a substantial gathering of permeable/porous materials known as molecular sieves. Amongst them, zeolites are the most appealing contender for modern applications on account of their properties. Numerous parts of our day to day lives are influenced straight way by zeolites” (Koosharyan and Anbia, 2016).

“Natural or synthetic zeolites are microporous materials widely and commonly used as adsorbents and catalyst which are crystalline aluminosilicate of basic origin with well-defined porous structures and pore sizes of molecular dimensions ranging between 0.3-2nm” (Auerbach et al. 2003; Koosharyan and Anbia, 2016; Weitkamp, 2000). They are mainly composed of tetrahedral XO_4 (X being mostly Al or Si) as base building units that are interlinked through corner sharing of oxygen atoms to form a three-dimensional microporous structural framework as seen in Fig. (11). “The General formula of zeolite is, $Q_{2/x}O \cdot Al_2O_3 \cdot ySiO_2 \cdot zH_2O$ where ‘Q’ is any alkali/alkaline earth atom, ‘x’ is the charge on that atom, ‘y’ is the no. of Si tetrahedron varying between 2-10 and ‘z’ is the no. of water molecules varying between 2-7” (Feliczak-Guzik, 2018). They feature numerous properties due to which they are employed in catalysis and many other sector. They have been used as ion-exchangers, catalysts, and adsorbents in a number of fields such as oil refining, petrochemistry, agriculture, and water and wastewater treatment. The properties of zeolite materials can be listed as (Feliczak-Guzik, 2018; Jha and Singh, 2016; Koosharyan and Anbia, 2016; Li et al. 2014):

- Presence of strong acidic centers
- Non-toxicity

- Non-corrosive
- Large specific surface area
- High ability ionic exchange
- Ability to accommodate metal species
- High thermal stability
- Environmentally harmless
- Good cost benefit ratios
- Framework and compositional flexibilities
- Presence of well-defined patterns of micro pores and flexible acidity
- Ease of separation from reaction mixture (as compared to homogeneous catalysts)

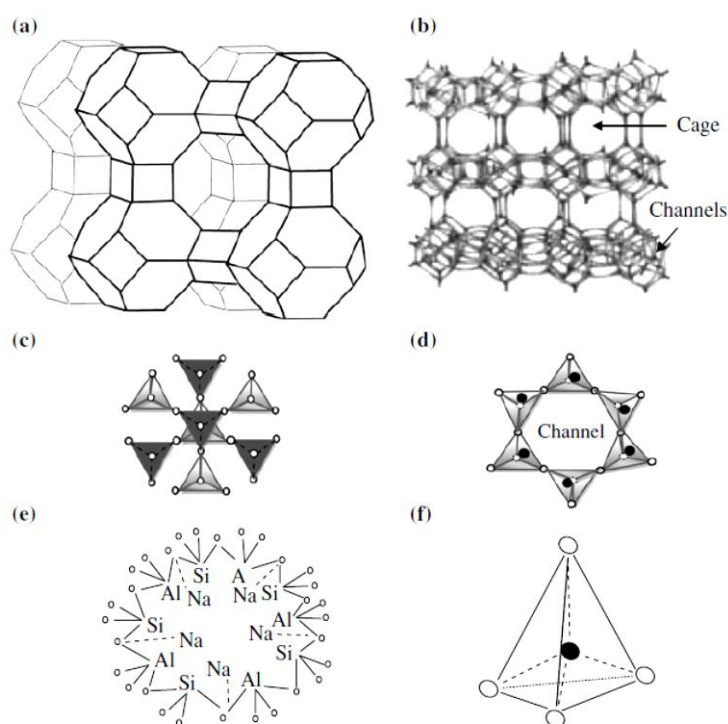


Fig. 11: Various schematics of zeolites structures (Koosharyan and Anbia, 2016)

In Fig. 11, “(a) is the schematic of crystal structure of zeolite 4A, (b) typical zeolite structure showing 3D cages and channels, (c) Simple tectosilicate structure of zeolite where dark and light shades to add 3D

effect and upside down orientation of the tetrahedra for vertex sharing between 2 rings of the zeolite structure in its 2-D view on a picture plane, (d) Single ring tetrahedron structure and framework of a zeolitic mineral, (e) $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ in a ring of sodium zeolite and (f) Graphic illustration of a 3D view of a tetrahedral with centrally located Si or Al atoms, exhibited by dotted lines drawn to represent the portion within the body of the mineral” (Koosharyan and Anbia, 2016). Zeolites can be classified based on pore size as indicated in the Table (4) below.

Table (4): Zeolite classification based on pore size (Kpere-Daibo, 2009)

Pore variety	No. of tetrahedra	Pore (θ) Diameter (nm)	Zeolite Examples
Small pore	8	$0.3 < \theta < 0.5$	Erionite, A, PST-1
Medium pore	10	$0.5 < \theta < 0.6$	ZSM-5, ZSM-11
Large pore	12	$0.6 < \theta < 0.9$	Y, β , Ω , ZSM-12
Extra-large pore	18	$0.9 < \theta$	MCM-9, VPI-5, CTI-5

They can also be classified based on silica to alumina ratio as indicated in the Table (5) below:

Table (5): Zeolite classification based on silica to alumina ratio (Kpere-Daibo, 2009)

Si-Al ratio		Zeolite examples	Properties
Low	1 to 1.5	A, X	Relatively low stability of framework, low stability in acids, High stability in bases, High concentration of acid groups with moderate acid strength Hydrophilic
Intermediate	2 to 5	Natural Zeolites like Mordenite, Clinoptilolite, Erionite etc and synthetic zeolites like L, Y, Omega etc.	-
High	10 to infinity	ZSM-5, ZSM11, EU1, EU2, BZ, MCM-41, MCM-22, MCM36 etc.	Relatively high stability of frame work, high stability in acids and low stability in bases.

Due to zeolites strong bronsted acidity, catalytic cracking reactions make up one of the most significant use of zeolites. Due to various properties of mesopores zeolites mentioned above, they have been

extensively studied in cracking of hydrocarbons of sizes ranging from C6 to hydrocarbon substrates like polyethylene which can have thousands of carbon atoms. Lately, new zeolites have been experimentally studied in numerous kinds of hydrocarbon cracking reactions.

2.5.1 Limitations of zeolites

Having said the above, there are limitations to zeolites as well which has diffusion shortcomings for branched molecules and mobility of reagents if they are of the same size as the micropores, as illustrated in Fig.12 (Feliczak-Guzik, 2018; Hartmann et al. 2016; Perez-Ramirez et al. 2008).

Diffusion of molecules that fit the size of the zeolite micropores (known as configuration diffusion) is often a stage which bounds the reaction being catalyzed due to the size of the molecules being the same as the size of the pores of zeolites. Molecular diffusivity immediately reduces to lower level than Knudsen diffusion (a frequent prevailing mechanism of diffusion in mesopores, 2-50nm sized pores) (Feliczak-Guzik, 2018).

This low diffusivity in micropores hinders the mobility of reagents from active sites, as seen in Fig. (12). the hindered transportation of reagents leads to the formation of these molecules into undesirable side products, which can establish the formation of coke during the process. Eventually the micropores will be blocked leading to the deactivation of the catalyst which lower its catalyst life, all of which leads to a point where the interiors of the catalyst remain inactive participant in the reaction where only outer part of the zeolite takes part in the catalytic reaction.

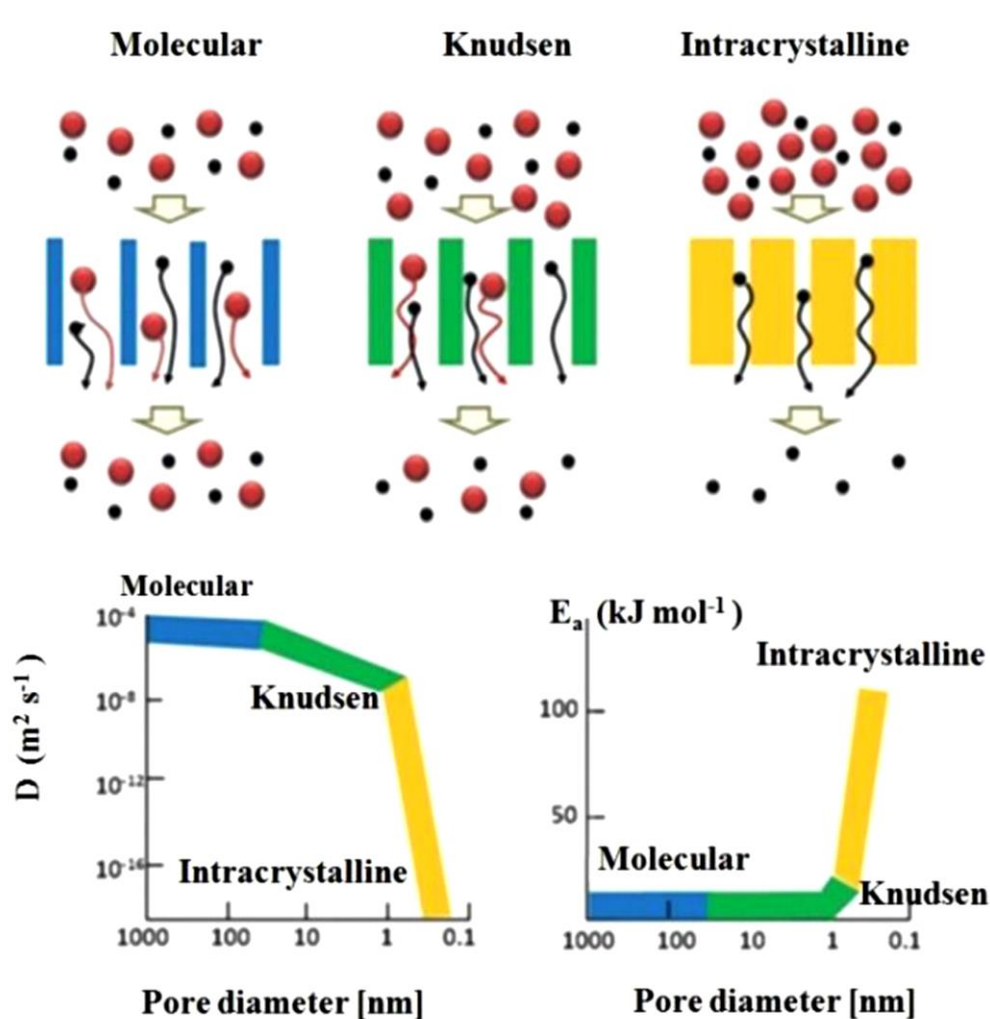


Fig. 12: Graphic depiction of the effect of pore size on the diffusion of large and small molecules and the effects of pore diameter on molecular diffusivity (D) and of the activation energy (E_a) on diffusion (Feliczak-Guzik, 2018; Li et al. 2014)

2.5.2 Acidity of zeolites

The activity in a catalytic reaction involving zeolites are due to its active acid sites tetrahedral framework with aluminum atoms. There occurs two kinds of active acid site one is bronsted acidity (proton donor) and other is lewis acidity (electron pair acceptor) as seen in Fig. (13). The acid sites in the structure are the result of the disproportionation that occurs within the lattice structure between silica and alumina. Where silica doesn't have any acidity associated with it, its aluminum atom that contributes in the

acidity. Hence, the number of acid sites are indicated by the number of aluminum in a zeolite. In any hydrocarbon transformation involving reactions where zeolites are involved, bronsted acidity are more of importance. This proton form of zeolite containing bronsted acid sites can easily be achieved by calcination of the zeolite at higher temperatures (Calemma et al. 2000; Jha and Singh, 2016; Kpere-Daibo, 2009).

Bronsted acid sites – donate protons

Lewis acid sites – accept electrons

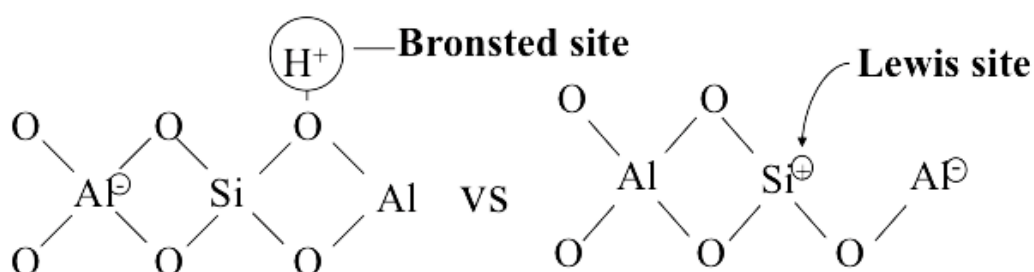


Fig. 13: Bronsted and Lewis acid sites in zeolite (Eser, 2018)

The presence of lewis sites gives the zeolite the presence of extra frame-work aluminum atom (EFAL), these EFAL can also be produced during the process of zeolite modification of dealumination where the alumina atoms are displaced and removed from the structure (Calemma et al. 2000; Jha and Singh, 2016; Kpere-Daibo, 2009).

Within the zeolite structure, a single silicon atom (Si^{4+}) has 3 valence electrons attached to it mostly by aluminum (Al^{3+}) which forms the Bronsted acid site of the zeolites. The resultant electron by the substitution is balanced by a proton which forms a bond between aluminum and silica with an oxygen atom to form a hydroxyl group i.e: $Si-O(H)-Al$, which is the proton donor. The strength and quantity of these acid sites can be

analyzed by many different methods like Temperature Programmed Desorption (TPD) of amines, Titration method, Calorimetry, Fourier Transform Infrared Spectroscopy (FTIR), alkane cracking, UV visible spectroscopy etc. This strength varies with different types and forms of zeolite. The strength of acid sites also varies with Si/Al ratio and substituted metal ions in zeolite structure. The trivalent cations substitution with the Si atoms result in the following acid strength order: $\text{B(OH)Si} < \text{In(OH)Si} \ll \text{Fe(OH)Si} < \text{Ga(OH)Si} < \text{Al(OH)Si}$. As of the effect of Si/Al ratio on the zeolite, increase in the ratio increases thermal stability, acid resistance, hydrophobicity, proton donor strength, temperature for degradation and decreases cation content and stability of zeolite in a solution, while decreasing the ratio increases hydrophilicity, ion exchange properties specially cations and decreases the size of the pore (as alumina has smaller atomic radius than silica) (Buca, 2017; Farneth and Gorte, 1995; Haag et al. 1984; Rybicki and Sauer, 2019).

2.5.3 Basic difference between ZSM-5 and BZ

In this research work, two types of zeolite catalysts i.e. ZSM-5 and BZ are employed for hydrocracking process.

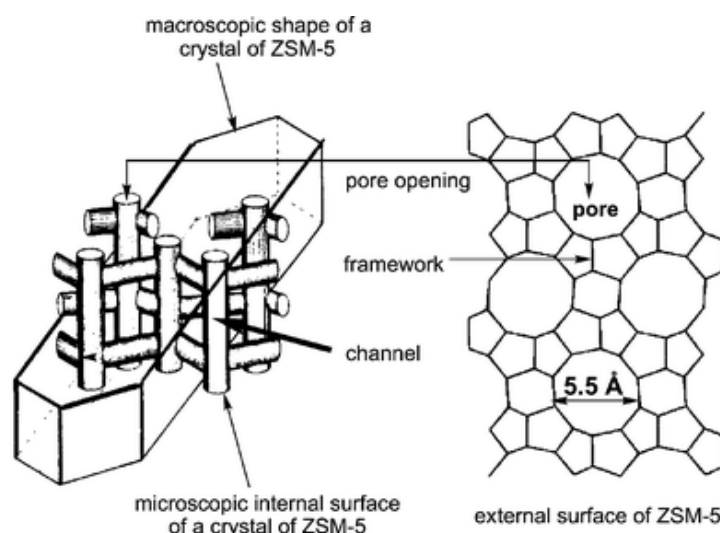


Fig. 14: Schematic diagram of ZSM-5 structure (Lei et al. 2003)

Zeolite Socony Mobil-5, very commonly known as ZSM-5 is an aluminosilicate zeolite which was found in 1967 and patented in 1975 with Si/Al ratio ranging between 12 to infinity, as seen in Fig. (14). It is widely employed in oil and gas industry as catalyst for various reactions. It has a high silica to alumina ratio, whenever an $(Al)^{3+}$ cation replaces a $(Si)^{4+}$ cation, an additional (positive charge or) proton is required to keep the material charge neutral making this material very acidic. It is microporous in nature with pores size falling in ‘medium pore size’ range from 5.4 to 5.6 Å, which has 10 ring straight channels running parallel as seen in Fig. (15) (Cejka and Van, 2005; Lei et al. 2003).

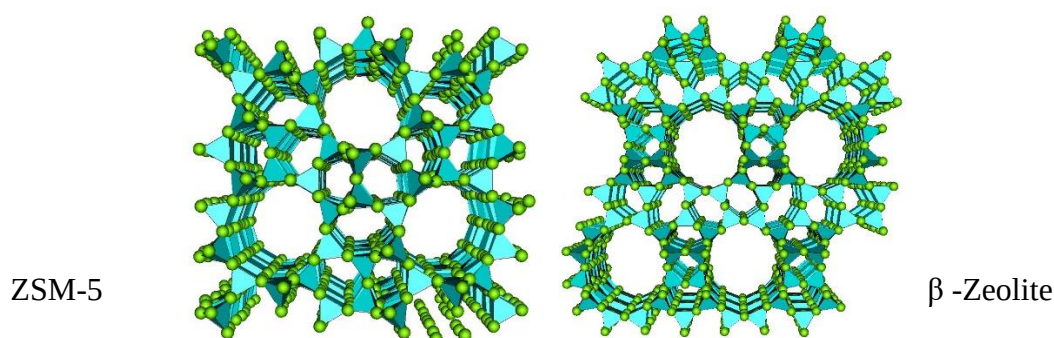


Fig. 15: Structural comparison between BZ and ZSM-5 (Chen et al. 2015)

On the other hand, BZ is relatively old that was discovered before ZSM-5. However, the interest in BZ is recently developed especially in the dewaxing operations. It has a framework type of BEA that has 12 rings as compared to MFI type which has 10 rings. BZ structure pore size falls in the large pores range about 7.5Å, which has 12 ring straight channels running parallel as seen in Fig. (17) (Zenonos et al. 2003).

2.6 Hierarchical zeolite catalysts

Due to the limitation faced by parent zeolites as mentioned in previous section, various researchers have been done for synthesis of zeolites with hierarchical porous structure i.e. micro-mesopores of which pore size range from 2-50nm based on IUPAC. This kind of solution tackles issues like mobility of larger molecules which are made easier due to presence of meso or macro sized pores while observing the acidity and crystallinity which shortens the diffusion path because of reduction of crystal size which intern increases the catalyst life span. Shortening the diffusion path also reduces the probability of catalyst deactivation (Feliczak-Guzik, 2018; Li et al. 2014). Hierarchical zeolites have found its applications in numerous catalytic reactions as seen in Fig. (16). It has been cited by numerous researchers that the hierarchical zeolites can significantly solve the shortcomings like low mass-transfer issue, deactivation of catalyst and low activity to large substrates in diverse chemical reactions.

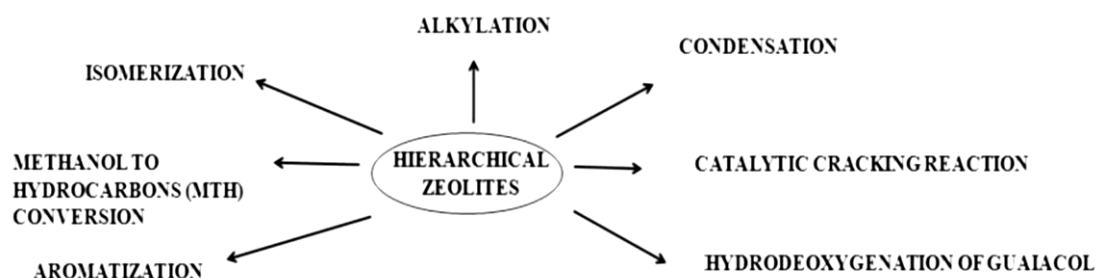


Fig.16: Application of hierarchical zeolites in catalytic reactions (Feliczak-Guzik, 2018)

Hierarchical zeolites can perhaps surge the extent of reactions in which zeolites are employed by letting adequate mass transfer of bulkier reactants or products, giving room for reactions which involve strong acidity catalyst to proceed on the mesopores surface and pore mouth. According to Feliczak-Guzik (2018), the research on the improvement of

new synthesis know-hows for the hierarchical zeolites has nearly got to the equilibrium state.

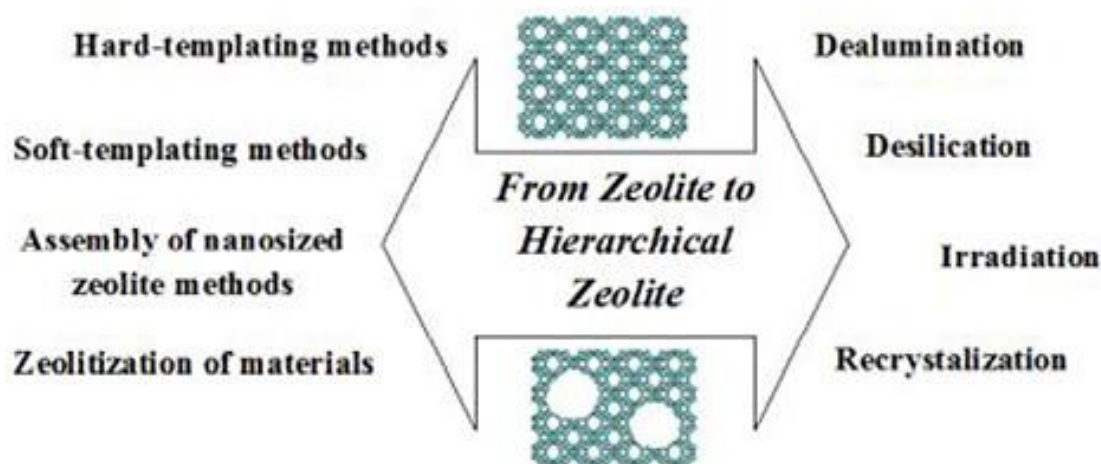
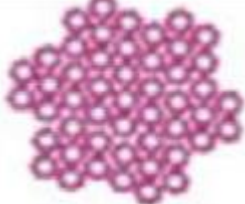


Fig. 17: Routes to transform zeolite to hierarchical zeolites (Feliczak-Guzik, 2018)

Increasing interest in hierarchical zeolites has led to numerous researches in this sector. With increasing researches and development, it becomes a challenge to categorize and classify them as seen in Fig. (17). Broadly based on the introduction of secondary porosity i.e: synthesis of hierarchical zeolites, they can be divided into 2 groups as seen in Table (6), namely (Feliczak-Guzik, 2018; Hartmann et al. 2016; Koohsaryan and Anbia, 2016; Li et al. 2014):

1. **Bottom-up (or Primary Syntheses):** which includes soft templating, hard templating and non-templating carried out during the synthesis of zeolites.
2. **Top-down (or Post Synthetic modification):** which includes demetallation like dealumination and desilication, recrystallization and irradiation carried out over post-synthetic modifications.

**Table (6): Routes for secondary porosity generation in zeolites
(Feliczak-Guzik, 2018; Serrano and Pizarro, 2013)**

Routes for secondary porosity generation			
Top-down approach		Bottom-up approach	
Desilication		Soft templating	
Dealumination		Hard templating	
Irradiation (<i>Desilication + recrystallization</i>)		Assembly of nanosized zeolite	
Surfactant templated or Recrystallization		Zeolitization of materials	

In this research work, post synthetic modification of demetallation is adopted to prepare hierarchical zeolites. This can be done through desilication or dealumination.

2.6.1 Dealumination

This method of ‘top-down’ approach is a method to remove aluminum from the zeolites structure (creating mesoporosity i.e. secondary porosity

in zeolites) which is a post synthesis approach and can be done through calcination, steaming (hydrothermal treatment), acid leaching or using chemical agents. The most often employed method is the elution of aluminum with an acid at high temperatures. Taken any scenario for dealumination (extraction of aluminum atom), it comes with partial breakdown of zeolite structure itself consequently leading to formation of vacancies which constitute added porosity in the range of mainly mesopores in the structure of zeolites. There are numerous approaches for dealumination, all involve hydrolyzation of Si–O–Al bonds to remove the aluminum content. The first step after preparation of the desired zeolite is calcination, in which some aluminum atoms are freed from the framework, subject to temperature and the kind of zeolite. It is observed by researchers that the different methods adopted for dealumination leads to serious changes in the acidic properties of the zeolite due to the changes in Si/Al ratio (Feliczak-Guzik, 2018; Hartmann et al. 2016; Koohsaryan and Anbia, 2016; Li et al. 2014).

Van et al. (2009) defined an approach of dealumination with the use of acid. Steps involved were, preparation and ageing of a solution which contained nanoparticles of BZ at temperature of 140°C, left to gradually cool, concentrated hydrochloric acid was then added followed by hydrothermal treatment at temperature of 150°C for 75 hours. As per the authors, the crucial step is the gradual cooling which leads to the formation of zeolite with greater crystallinity as well as additional porosity (ranging from 6-10nm).

Acid dealumination (AD) is a chemical process of using hydrogen atom to eliminate acid sites. If the dealumination is severe, it could cause the structural collapse of the zeolite at the entrance of the catalyst pore. In a study carried out by Zhang et al. (2017) in which ZSM-5 catalyst was

synthesized by chemical acid deposition and acid alumination in catalytic pyrolysis of pinewood, schematic shown in Fig. (18). Results indicated that chemical liquid deposition (CLD) by silica dioxide led to the handling of strong acid sites where as AD preferred the elimination of superficial acid sites. Furthermore, results indicated that both types of dealuminated ZSM-5 led to better BTX yield in comparison to the unmodified ZSM-5. Zhang et al. (2017) carried out the acid dealumination of catalyst in the following manner: leaching agent (phosphoric acid of 0.5-8mol/L) was used for dealumination where 10g of ZSM-5 and 200 ml of acid were placed in a flask which was heated with stirred in water bath at room temperature. Leaching agent was then removed by suction filtration. The sample was then dried for 2 hours in a drying oven at 80°C and then further dried at 110°C for another 2 hours. The samples were then calcinated at 600°C for 6 hours.

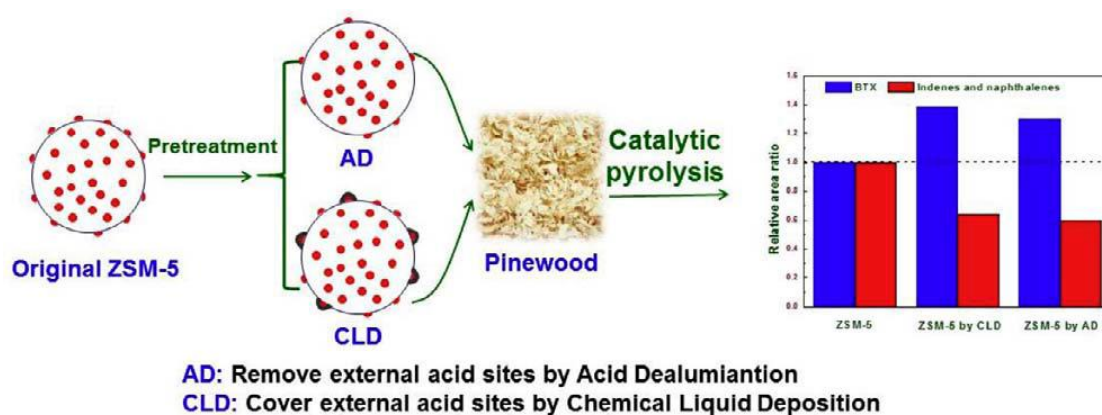


Fig. 18: Schematic for comparison of ZSM-5 catalysts for catalytic pyrolysis of pinewood (Zhang et al. 2017)

“Dealumination process was considered as one of the most preferred methods in introducing porosity into zeolites. However, due to the weak connection and penetration of the created pores along with severe damage to micropores and crystalline properties in adversarial treating

environments required looking for new approaches of mesoporosity generation” (Feliczak-Guzik, 2018).

Ibanez et al. (2017) dealuminated ZSM-5 catalyst by steaming at about 300-400-500°C and tested for conversion of 1-butene to propylene. The results showed that dealumination transformed specific strong acid framework tetrahedral alumina sittings located within the micropores to distorted extra-framework species. It was observed that the propylene selectivity was increased by 69%, coke deposition fell by 34% and the initial conversion only fell 6%.

Rostamizadeh and Yaripour, (2017) studied on dealumination of ZSM-5 for methanol to olefin conversion to tune the catalyst for it to have a long catalytic life of 384 hours. They synthesized the catalyst through hydrothermal technique and treated it by dealumination due to which the catalyst produced had large surface area of about 250 m²/g and high crystallinity i.e. over 97%.

To the best of our knowledge dealumination of zeolite-based catalyst hasn't been employed yet for its application in the degradation of mixed plastic wastes to fuel.

2.6.2 Desilication

Demetallation isn't just restricted to dealumination. Desilication (another 'top-down approach') is comparatively easier and employs economical materials like basic solutions sodium hydroxide (NaOH) to remove silica from the zeolite framework. Desilication is one of the most widespread approach for producing secondary porosity in zeolites which is centered on favored elimination of silicon from the zeolite structure in an alkaline environment. The hierarchical zeolite obtained is characterized with occurrence of secondary structure of mesopores in each grain while

instantaneously sustaining its microporous nature. Introduction of an additional system of pores by desilication affects the structural and acidic properties of the zeolites. These new properties influence the activity and selectivity as well as the life-span of zeolites in the catalysis (Feliczak-Guzik, 2018; Hartmann et al. 2016; Koohsaryan and Anbia, 2016; Li et al. 2014).

Bonilla et al. (2009) studied the desilication of a ferrierite sample using sodium hydroxide for porosity generation and improved effectiveness in polyethylene pyrolysis. Treatment of zeolite was carried out in parallel reactor system varying sodium hydroxide concentrations between 0.1 to 1 mol/L at temperature range of 333 to 363 K for varying time of 0.5 to 9 hours. 50cm³ reactor was filled with 10cm³ of sodium hydroxide aqueous solution, once desired temperature was attained 330g of zeolite in powdered form was added and stirred. Post treatment zeolite was cooled down using ice-water mixture and filtered and calcinated at 823K for 5 hours. These results show that sodium hydroxide induction in zeolite results in shedding, fracture and eventually opening of the ferrierite crystals which results in mesoporosity of combined inter/intracrystallinity in zeolite structure. The introduction secondary mesoporosity in the hierarchical zeolites improved the low density polyethylene degradation performance as compared to parent zeolite which is microporous in nature (Bonilla et al. 2009; Koohsaryan and Anbia, 2016)

Abello et al. (2009) prepared mesoporous ZSM-5 zeolite catalysts by desilication with organic hydroxides and compared with NaOH leaching. They concluded that by using strong organic bases as desilicating reagents like tetrapropylammonium (TPAOH) or tetrabutylammonium hydroxides (TBAOH) evaded the added step of ion-exchange required as in case of inorganic bases like NaOH. If inorganic bases are used then it is required

to do ion exchanging process with agent like NH_4NO_3 to produce protonic form of the mesoporous zeolite upon calcination). In liquid phase benzene alkylation with ethylene, high yield of 95% with TBAOH was achieved as compared to 62% with NaOH. Pictographic contrast of zeolite desilication by TBAOH and NaOH is shown in Fig. (19). Although TBAOH is used to give better yield and to avoid the ion exchange step but it bears much higher cost as compared to NaOH.

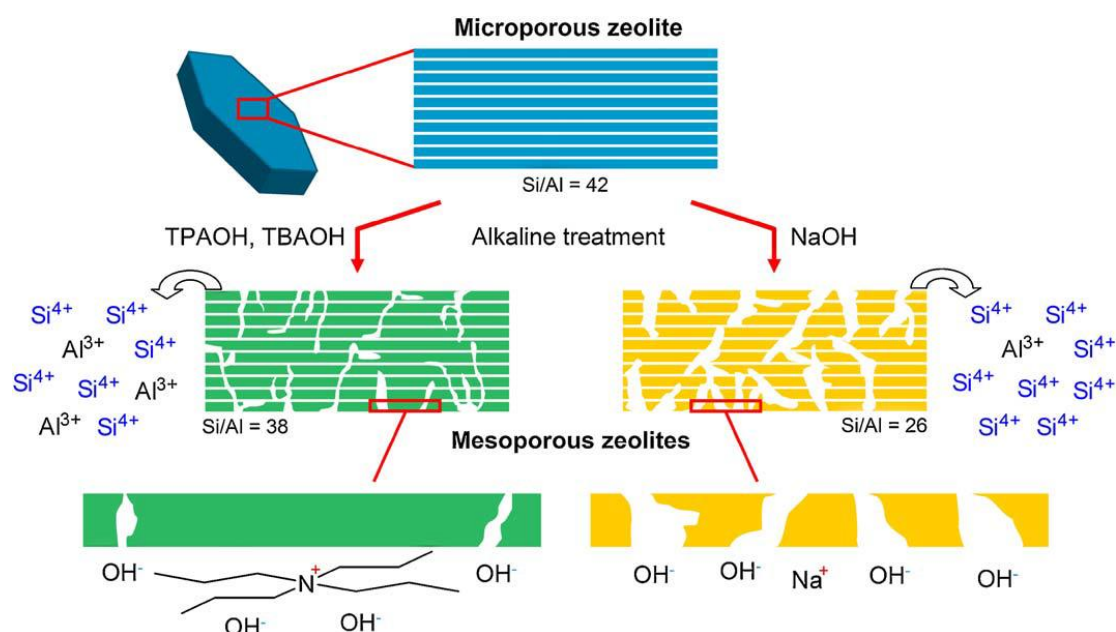


Fig. 19: Pictographic contrast of zeolite desilication by TBAOH and NaOH (Abello et al. 2009)

Recently, Feng et al. (2018) studied that the post-synthesis treatment (dealumination/desilication) is an effective approach to adjust the acidity and the pore structure of the ZSM-5 zeolites. Sodium hydroxide being a strong base for the desilication of ZSM-5 creating new mesopores and increased the ratio of Si/Al. Acid treatment (dealumination) of ZSM-5 enhanced the micropores surface area due to the removal of aluminum framework out of micropores channels. This dual approach played an important role in the n-heptane conversion that increased olefin selectivity as well as catalyst life-span as compared to parent ZSM-5.

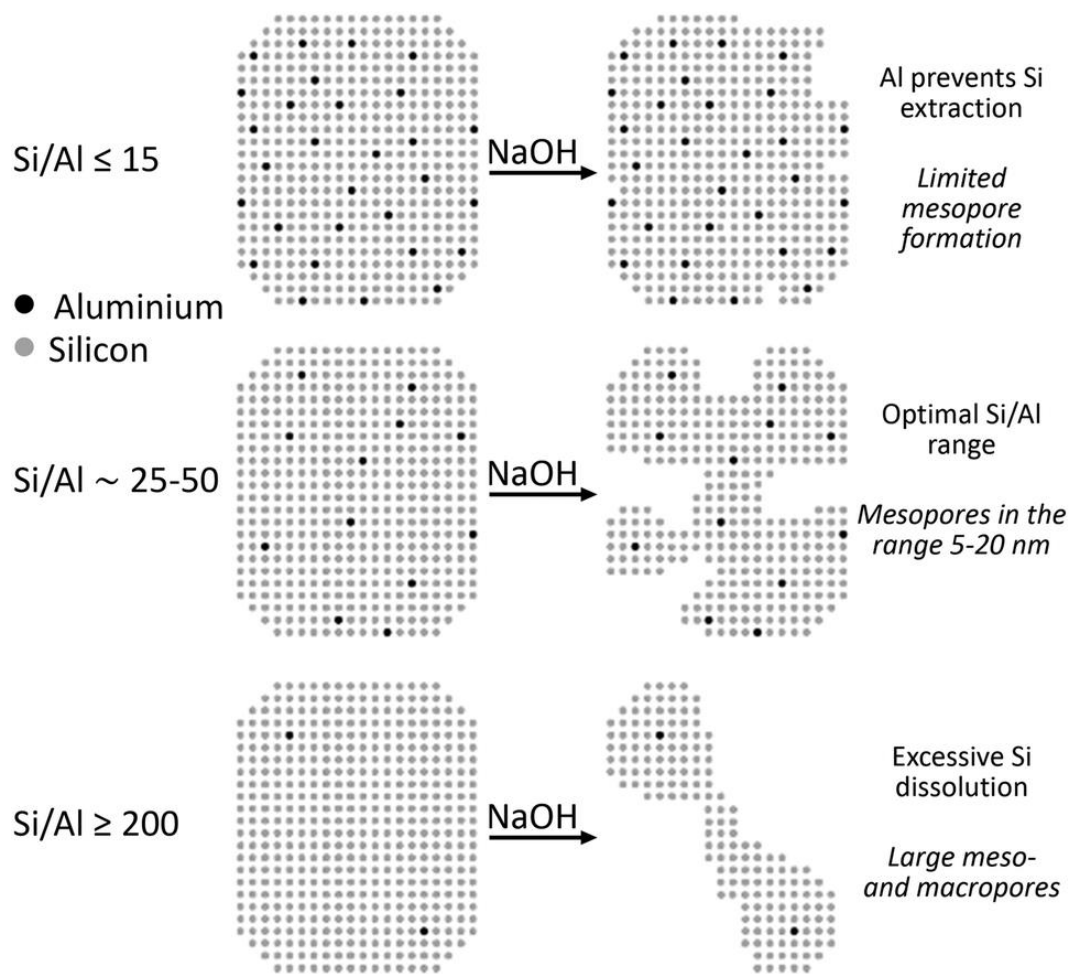


Fig. 20: Influence of NaOH on zeolite structure based on its Si/Al ratio (Groen et al., 2004; Schwieger et al., 2016; Zhang and Ostraat, 2016)

Besides common variables like temperature, concentration of the solution used for desilication (NaOH), and the time period of the treatment carried out; alumina (or Si/Al ratio) has a major effect on desilication process as seen in Fig. (20). Optimal value for the silica alumina ratio, for instillation of mesoporosity in the microporous natured zeolite structure is observed to be from 25 to 50 (Groen et al. 2004; Schwieger et al. 2016; Zhang and Ostraat, 2016).

The main pros of desilication is the easiness at which this can be attained and the requirement of inexpensive preparatory materials. However, the alkaline treatment must to be controlled precisely as

significant damage to the zeolite structure and loss of micropores can occur. Reasonable strategy to this issue can be tackled by pretreatment of zeolites or use of lower temperatures while calcinating zeolite with lesser damaged structures (Koohsaryan and Anbia, 2016).

Desilication method also leads to slight loss of micropores surface area due to the reduction of crystallinity and the aluminum atoms which are removed from the framework will hinder the micropores due to which the micropores volume will decrease causing fast deactivation of catalyst (Feng et al. 2018).

Although methods demetallation like desilication or dealumination causes the formation of mesoporosity in zeolite structure, the major shortcoming of these approach is the destructive impact it has on the zeolite structure during the processing, which is these approaches are also termed as destructive approach (while the methods of templating comes under constructive approach of secondary mesoporosity addition) (Feliczak-Guzik, 2018)

2.7 Influence of various process parameters on hydrocracking of plastic

Numerous researches (over 100 articles are cited in tabulated literature review in Appendix-1) have demonstrated and proven that plastic (in virgin or waste form) can be converted to useful chemical products that has potential to make its place in the market using catalytic or non-catalytic cracking. In literature, there are numerous process parameters that influence the product yield have been reported. These parameters include feed composition or the different types of plastics employed in the reaction, residence time or the time allowed for the reaction to run, reaction temperature, reaction pressure, type of catalyst, catalyst to feed ratio etc. There are some other factors that affect product yield such as catalyst particle size, reactor type, catalyst contact mode, ratio of hydrogen to nitrogen gas in hydrocracking reaction etc. The focus of this thesis involves the optimization of process parameters like the temperature, pressure and plastic-catalyst ratio. Here are few selected evaluated parameters in literature mentioned in Table (7) which are illustrated and cited in Appendix-1.

Table (7): List of selected literature review on process parameters and catalysts used in degradation of plastics

References	Feed	Temp. (°C)	Press. (atm)	Catalyst to plastic ratio	Catalyst
Ratnasari et al. 2017	HDPE	500	1.00	1:02	MCM-41, ZSM-5
Sebestven et al. 2017	PE, PP, PET	600	1.00	1:10	ZSM-5
Miteva et al. 2016a	PP, PS, PVC, PET	400-550	1.00	Varies	Al ₂ O ₃ and SiO ₂

Li et al. 2016	PE,PP	300-500	1.00	Varies	ZSM-5, MCM-41, KFS-16B, Al-SBA-15
Miteva et al. 2016b	HDPE, PP	350-480	1.00	1:20	ZSM-5
Chattopadhyay et al. 2016	HDPE, PP, PET	600	1.00	1:20	Cobalt based Alumina catalyst
Sonawane et al. 2015	PP	450	1.00	1:10 to 5:10	Natural Zeolite
Sakaki et al. 2014	HDPE, LDPE, PP	410-450	0.68	Varies	Al ₂ O ₃ and SiO ₂
Gao et al. 2014	LDPE, PP	350	1.00	1:90	MCM-49
Serramo et al. 2014	LDPE	310	19.73	1:30	Ni/Al-SBA-15
Fuentes-Ordóñez et al. 2015	PS	-10-300	1.00	Varies	Pt/Ferrierite and Pt/ITQ-6
Lee et al. 2014	PP, Seaweed	600	1.00	1:10	Al—SBA-15
Cleetus et al. 2013	PE	400-550	1.00	1:10	Y-Zeolite, etc
Jin et al. 2012	PS	410	1.00	Varies	MCM-41
Usman et al. 2012	LDPE	400	1.00	1:02	KIT-6
Sarkar et al. 2012	HDPE, LDPE, PP	200-400	1.00	1% Cat. by weight	Activated Carbon
Renzini et al. 2011	LDPE	500	1.00	1:02	ZSM-11
Lopez et al. 2011	Mixed plastic	440,500	1.00	1:25	ZSM-5
Panda et al. 2011	PP	400-550	1.00	1:02 to 1:10	Kaoline, Silica Alumina
Coelho et al. 2010	PE	550	1.00	Varies	NaY

2.7.1 Influence of catalyst employed

Catalyst employment has one of the most significant impact in the cracking of plastics for which a dual functional catalyst is required to serve this goal. The need for the existence of an acidic group which in this case it is bronsted acidic sites and hydrogenation dehydrogenation function on employment of which better conversion, higher liquid yield, greater quality of products and lower amount of coke is produced.

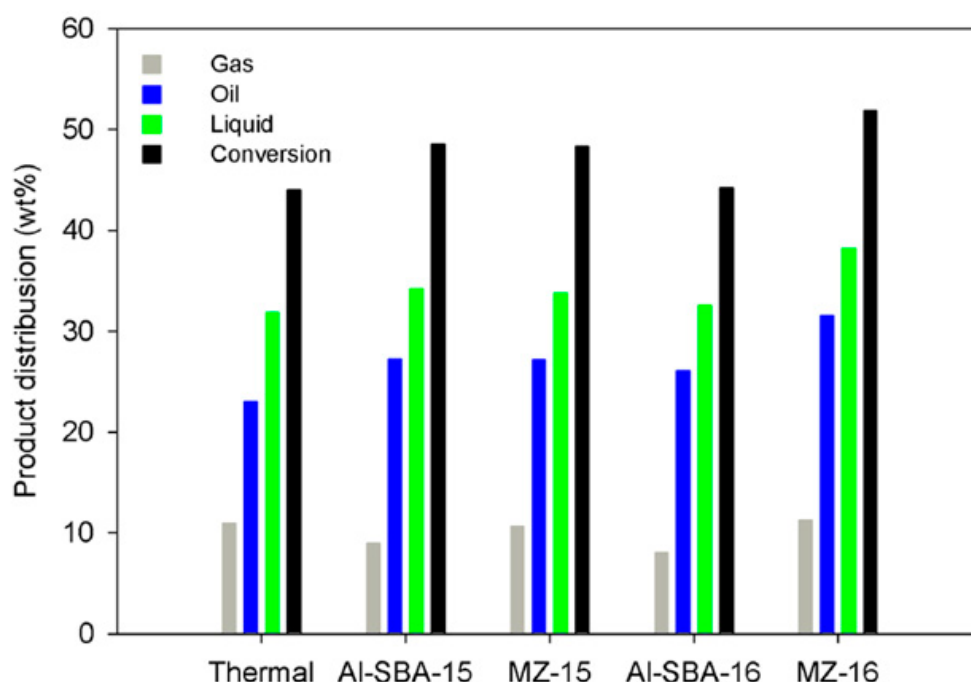


Fig. 21: Results of hydrocracking of model waste plastic carried out at 400°C, H₂ pressure of 20 bar, reaction time of 60 min, feed to catalyst ratio equal to 20:1 (by wt) (Munir et al. 2017)

Munir et al. (2017) carried out experiments using model plastic feed that contained a mixture of HDPE, LDPE, PP and PS at different temperatures of 375, 400 and 425 °C under H₂ pressure of 20 bar, reaction time of 60 min, feed to catalyst ratio of 20:1 (by wt.). They used bottom-up approach i.e. zeolitization of materials and assembly of nano sized zeolites for the secondary porosity addition or hierarchical zeolites preparation. They obtained a maximum liquid yield of about 39% over

MZ-16 at 400 °C as shown in Fig. (21). At higher reaction temperatures, the thermal run is found to be the most active and produces high liquid yield. This may occur due to the increased formation of coke which may result over an active catalyst especially with large pores and at relatively high temperature (Munir et al. 2017).

Reactions involving catalyst are essential in reducing the reaction temperature as well as the residence time of the reaction. Involvement of suitable catalyst also gives the user leverage to alter the yield as well as selectivity. For a hydrocracking reaction to take place at lower temperatures, it is essential for a catalyst to have a strong acidic function like zeolites or amorphous Si-Al along with strong hydrogenation-dehydrogenation function like platinum. Increased gas yields are reported where strong acidic function are employed. A catalyst with good cracking abilities can increase the number of aromatics by cyclization reactions. Reduced coke deposits or formation, higher amount of liquid yield occurs on using strong hydrogenation-dehydrogenation function. Reduced olefins and increased branched chain hydrocarbons are reported on using strong acidic function. Higher loading of the catalyst increases the depolymerisation and gas yield (Dermirbas, 2004; Ding et al. 1997; Lopez et al. 2017; Miandad et al. 2017; Munir et al. 2018; Panda et al. 2010; Al-Salem et al. 2017).

2.7.2 Influence of using different types of plastics

There has been numerous researches that has been carried on individual plastic types. In regards with the ease at which respective plastic material degrades in presence of hydrogen, they can be ranked as Polyisoprene (PIP) > PS > PET > PP > LDPE > HDPE. Lower amounts of gas yields, higher amounts of liquid yield, product in gasoline range and higher concentration of branched hydrocarbons are obtained on PP

degradation in comparison to HDPE; as seen in Fig. (22). On comparing the above mentioned plastics, degradation of PS gives the highest liquid yield where LDPE and HDPE give the lowest. As for the gas yield is concerned, the opposite is true. On analyzing liquid oil fractions, it is noted that LDPE and HDPE usually comprise of alkane, branched alkanes and fewer amounts of aromatics. Whereas PP degradation yields greater amounts of isoalkanes and PS degradation yields alkyl benzene and phenyl alkanes in comparison.

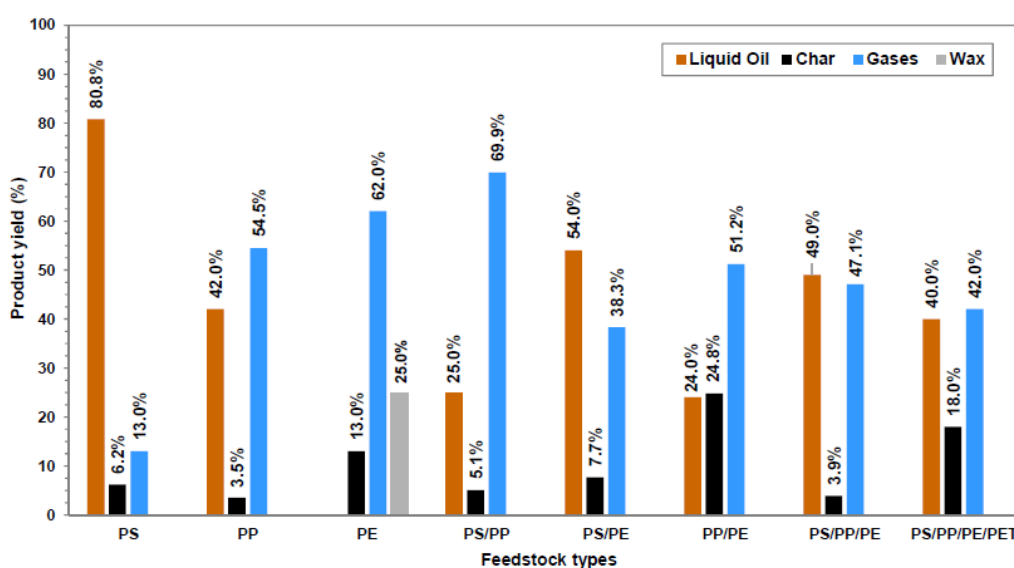


Fig. 22: Influence of various types of plastics on product yield (Miandad et. al. 2017)

Usually in a cracking reaction that involves mixture of plastics, polyethylene favors formation of paraffins, on increasing the PS or PP ratio in the blend yields higher aromatics and alkenes. Noteworthy interaction between respective types of plastics is seen when a blend of these individual plastic materials is employed in hydrocracking reaction. By altering the structure of a plastic blend the coveted nature of the oil created might be acquired. A waste plastic blend may altogether influence the performance of the catalyst because of the contaminations present in the

waste blend (Dermirbas, 2004; Ding et al. 1997; Lopez et al. 2017; Miandad et al. 2017; Munir et al. 2018; Panda et al. 2010; Al-Salem et al. 2017).

2.7.3 Influence of process reaction time

Reaction time or residence time is another important factor that has significant influence on the process of hydrocracking plastic to fuels and it is an important deciding factor on the extent of degradation and quality of liquid and gas yields. Increasing the reaction time, increases the plastic conversion as well as the gas yield as seen in Fig. (23). However, it is also reported that in degradation of plastics, maximum gas yields are attained even after reaction completion. Furthermore, it has been reported that light gases, naphthalene, benzenes and alkyl benzenes increase with residence time whereas heavy liquid yields, diphenylalkanes and triphenylalkanes decrease with time, which eventually may end up in the gaseous phase on longer reaction time.

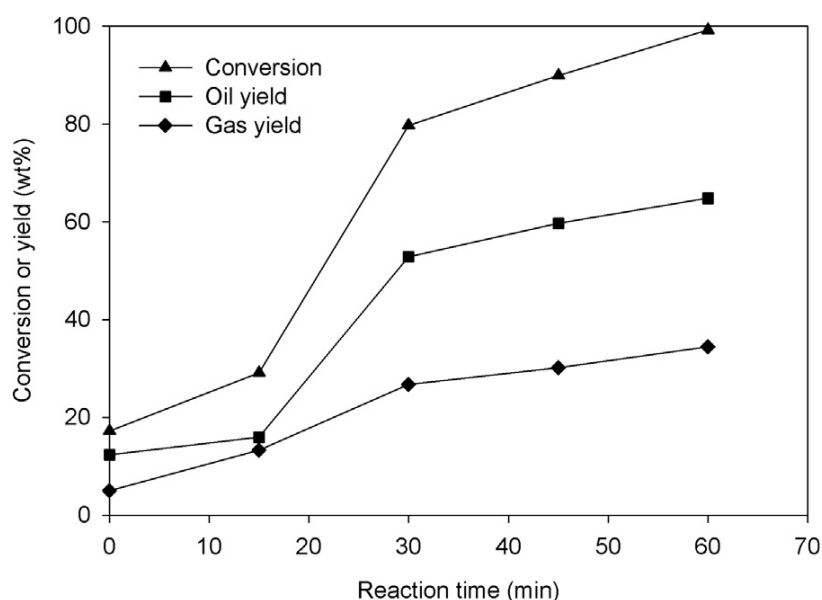


Fig. 23: Influence of reaction time on hydrocracking of plastic waste, on liquid yield, gas yield and conversion (Ding et al. 1997)

For usual residence time at relatively higher temperatures the liquid yield increases with time and after a point remains constant. The time at which maximum liquid yield is achieved depends on various other parameters involved like catalyst involved, temperature, pressure, plastics used etc. On employment of a catalyst, reaction time from 30 to 60 min has been widely reported. (Dermirbas, 2004; Ding et al. 1997; Lopez et al. 2017; Miandad et al. 2017; Munir et al. 2018; Panda et al. 2010; Al-Salem et al. 2017).

2.7.4 Influence of process reaction temperature

The temperature at which the hydrocracking of waste plastics is carried out is amongst the most important factor that has major influence on the product yield, conversion and quality of the product. Normally, with the increase in temperature of the reaction the conversion increases as well, but it also increases the coke formation. Gas yield increases with temperature while liquid yield decreases at higher temperature due to more cracking at higher temperature i.e. liquid of heavy hydrocarbons are converted into gaseous light hydrocarbons. The general trend on employment of not so active catalyst is that with increase in temperature, degradation of plastic occurs rapidly which then slows down at higher temperature as it reaches reaction completion. Liquid yield increases with increase in temperature, then slows down at higher temperature as products are mainly converted to lighter hydrocarbons and coke. For active catalyst involved in hydrocracking of plastics, reaction temperature ranges between 370-410°C (Dermirbas, 2004; Ding et al. 1997; Lopez et al. 2017; Miandad et al. 2017; Munir et al. 2018; Panda et al. 2010; Al-Salem et al. 2017).

2.7.5 Influence of process reaction pressure

The influence of reaction pressure on degradation of plastic waste to fuel is something that has been not very much explored. Majority of the researches in this area are carried out at atmospheric pressure. This parameter is something that needs to be studied and evaluated that represents a major research gap. In literature, pressure parameter has not been evaluated for the conversion of mixed waste plastics to fuel using hierarchical zeolites (dealumination/desilication), hence this research focuses on evaluating this parameter for novelty. Introducing pressure through hydrogen gas can decrease the formation of free radicals in the cracking of hydrocarbons. Introduction of hydrogen also increases the amount of saturated products and also reduces coke formation.

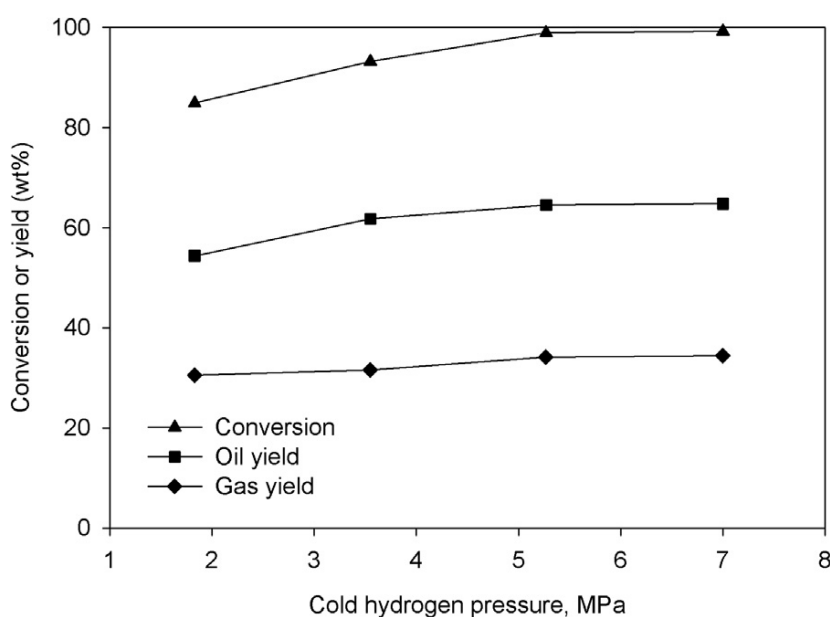


Fig. 24: Influence of hydrogen pressure on the reaction (Ding et al. 1997)

It may also increase the activity of catalyst during the reaction period by re-activating the active sites of the catalyst. Hence it's an essential factor in determining the quality of the products. Based on literature, it can be

said that lower pressure has no influence on the reaction, however the situation may change at higher pressure. However, the quality of the products is enhanced due to the presence of hydrogen in the reaction as seen in Fig. (24). Impurities removal and coke formation also decreases in presence of hydrogen pressure in a reaction. Based on literature, 20-60bar pressure is found be ideal for this application (Dermirbas, 2004; Ding et al. 1997; Lopez et al. 2017; Miandad et al. 2017; Munir et al. 2018; Panda et al. 2010; Al-Salem et al. 2017).

2.8 Concise summary of literature review

Waste has just been dumped and overlooked. The selection of approach to waste management depends on various factors, some of the prominent ones include the economy of the country itself, awareness etc. Nonetheless, with an increment in the amount of waste and decrease in the land accessible for dumping or landfill purpose, and the combination of toxic matter like pesticides in landfills are more poisonous than ever before. The eventual fate of waste must be based on sustainable development and green methods to tackle wastes. Majority of the waste are biodegraded with time, except plastics. It is absolute waste of resources as plastics are petroleum derived products which can be recycled. Here are few summarized major highlights from the previous sections:

- There are numerous types of plastics broadly categorized as thermoplastics and thermosets. However, majority of the plastics produced are thermoplastics. Most commercially used plastics are PP, LDPE, HDPE, PS, PET and PVC. However, for plastics degradation purpose PET and PVC are undesired as for PVC chlorine is to be taken care of and as for PET oxygen is to be taken care of. All these plastics fall in the melting temperature range of 160-300°C
- Plastic wastes can be of either municipal origin or industrial origin. The interest of this thesis lies in the municipal originated mixed plastic wastes which comprises of PE, PP, PS, PET and PVC.
- There are so many ways plastic waste can be managed. Mostly they are landfilled. The interest of the thesis work lies in the chemical recycling, as it is the sector where majority of the research and development happens.

- Chemical recycling falls in the category of tertiary recycling. The word ‘chemical recycling’ is also sometimes called feedstock recycling or advanced recycling technologies which intends to convert waste plastics which are originally long chain polymers into smaller monomers as chemical intermediates via heat with or without chemical treatment. There are many ways this can be done, by thermal pyrolysis, catalytic pyrolysis, Hydrocracking, gasification or depolymerization. The interest of this thesis work lies in the Hydrocracking with the influence of a catalyst i.e: catalytic hydrocracking.
- Zeolites are crystalline aluminosilicate of basic origin with well-defined porous structures and pore sizes (between 0.3-2nm) that are extensively employed in catalysis due its various properties. However, in its application for cracking long chain hydrocarbons has a hurdle of it being microporous in nature and anything above that size will block the pores of the catalyst leading to quick deactivation of catalyst and contributing to coke formation as well. This very issue can be tackled by modification in properties of zeolite in preparation of Hierarchical zeolites.
- Due to the limitation faced by parent zeolites, various researches have begun in synthesis of zeolite with hierarchical porous structure which shows the presence of more than one pore system usually mesopores (2-50nm). Hierarchical Zeolites can be broadly prepared by 2 approaches, Primary Syntheses or Post Synthetic modification. The interest of this thesis lies in exploring 2 of top down approach which are desilication and dealumination. The applications of hierarchical zeolites have not yet been explored in the application of

degradation of mixed plastic waste, which is the focus of this research work.

- On studying the literature in terms of influence of process parameters, it can be deduced that (a) catalyst employment had a major impact on the yield in terms of quality as well as quantity (b) mixed plastic waste like PS/PP/PE/PET together on employment gives lowest product yield as compared to degrading them individually, and has not been extensively researched (c) Optimum reaction time ranges between 40-60 minutes. (d) For catalytic reactions involving plastic degradation, temperature ranges between 370-410°C. (e) Pressure parameter has not been explored extensively in literature. Based on literature review, it is deduced that lower pressure has no influence on the reaction, however the situation may change at higher pressure. However, the quality of the products is enhanced due to the presence of hydrogen in the reaction. Impurities removal and coke formation also decreases in presence of hydrogen pressure in a reaction; 20-60bar pressure is ideal for this application.

Based on the above-mentioned highlights of the literature review. Preliminary experiments will be carried out first to evaluate the modified hierarchical zeolite's application in degradation of waste plastic mixture. Following which optimization of catalyst preparation will be done to maximize the liquid yield, after which optimization of the process parameters will be carried to further maximize the product yield. The catalyst characterization will be carried out to evaluate its physical and chemical characteristics which are responsible for its performance in a reaction. GCMS of product will also be done to identify and quantify the analytes.

Chapter 3

Methods and procedures

Table of contents

Subject	Page Number
Chapter Three Methods and Procedures	
3.1 Optimization methodology	74
3.2 Kinetic Studies approach	79
3.2.1 Differential isoconversional approach	82
3.2.1.1 Friedman method	82
3.2.1.2 Ozawa method	82
3.2.1.3 Freeman and Carolls method	83
3.2.2 Integral isoconversional approach	83
3.2.2.1 Doyles approximation method	83
3.2.2.2 Coats Redfern method (CR)	84
3.2.2.3 Modified Coats Redfern method (MCR)	85
3.2.2.4 Flynnne Walle Ozawa (FWO) method	84
3.2.2.5 Kissinger Akahirae Sunose (KAS) method	84
3.2.2.6 Distributed Activation Energy Model method (DAEM)	84
3.3 Experimental methodology	87
3.3.1 Materials used	87
3.3.2 Catalyst modification methodology	90

3.3.2.1 Desilication method	91
3.3.2.2 Dealumination method	92
3.3.2.3 Alumina Impregnation method	93
3.3.3 Experimental procedure for atmospheric setup	93
3.3.4 Experimental procedure for pressure setup	97

3.1 Optimization methodology

There are numerous well-known methods for the efficient design of experiments to gather the most amount of information for little amount of efforts (DeCoursey, 2003). Orthogonal experimental design for instance Taguchi allows to reduce the number of experiments at the misfortune in trial resolutions inferable from their powerlessness to catch higher request associations because of the impact of perplexing signs amongst factors (Yang et al. 2003). The full factorial design of experiments retells all probable combinations within the experimental space. Full factorial designs are usually expensive but when few number of variables are studied like in our setup here, the full factorial design of experiment is a practical option that enables us to capture second order interactions with greater detail.

In contrast to ‘one factor at a time’ type experiments which if used ends up in huge number of experiments to be carried out for optimization, factorial design fundamentally lessens the large number of runs required to decide the impact of a factor, particularly when large number of factors to be investigated. Notably, factorial design is an excellent way to distinguish the presence of interaction between factors. Many analyses include the investigation of the impacts of at least two variables. In general, factorial outlines are most effective for this kind of trial. By a factorial design, it is implied that in each total trial or replication of experiment every conceivable mix of the levels of the variables are researched like for instance if there are “a” levels of factor A and “b” levels of factor B, each replicate contains all “ab” combinations (Gosh and Rao, 2003).

To perform a full factorial central composite design (CCD), 81 experiments would be required to be done for 4 factors whereas in

comparison on the other hand only 25 would be required in Box-Benkh design (BBD). It is often stated that BBD is complimentary to CCD as BBD targets the points where CCD misses as it can be seen in Fig. (25). In a scenario where few factors are there, in such experimental scenario BBD gives a good fit quadratic model to gather data in the form mentioned below (Gosh and Rao, 2003).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j}^k \beta_{ij} x_i x_j + \varepsilon \quad (3.1.1)$$

where Y indicates the responses or the dependent variables, β_0 is the constant coefficient or the offset term, β_i is the coefficients for the linear effects, β_{ii} is the term for quadratic effects, β_{ij} represents interaction effects, x_i and x_j factors are the independent variables and ε is the residual associated with the experiment.

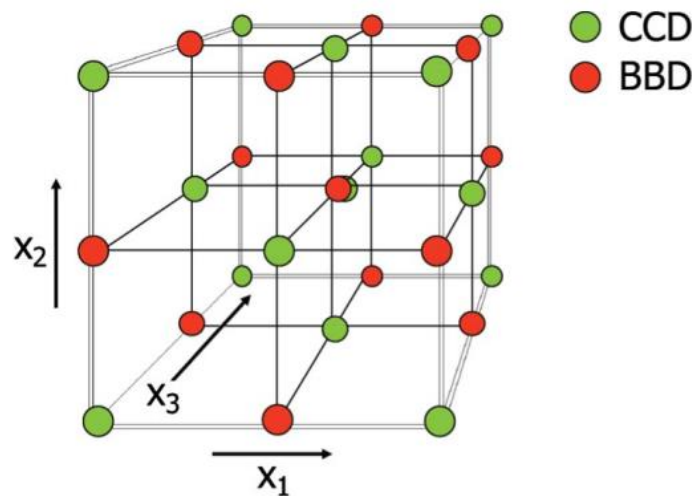


Fig. 25: Comparison of 3-level BBD (red) with CCD (green).

Due to the design being orthogonal, it is conceivable to fractionate the impacts of each factor and find the interaction between the factors. In case of Box-Benkh design, the control variables can be set to only 3 levels compared to CCD's 4, in the coded format 0,1 and -1 (these coded values

indicate middle, higher and lower setting), where CCD has additional (Gosh and Rao, 2003).

Diverse varieties of factorial designs have been effectively connected to numerous modern applications. Chen et al. (2003) utilized a statistical factorial design to distinguish variables and their interactions for the chemical and physical cleaning of UF (ultrafiltration) and RO (reverse osmosis) frameworks in municipal wastewater recovery. Somidi et al. (2017) used factorial design for conversion of epoxidized oils to O-propylated biolubricants interpreting the interaction of factors like temperature, epoxy to 1-propanol molar ratio, catalyst loading and reaction time. In this project, the interaction of plastic to catalyst ratio, temperature, pressure and reaction time are to be studied and optimized.

Table (8): CCD coded values for 2 factors

Run	Factor-1	Factor-2
1	-1	1
2	1	1
3	1.414	0
4	0	1.414
5	-1	-1
6	0	0
7	0	0
8	-1.414	0
9	0	0
10	1	-1
11	0	0
12	0	-1.414
13	0	0

Before the experimental process parameters optimization is carried out. Catalyst optimization is also carried out using 2 factor CCD design,

which has 8 corner points and 5 center points as seen in the Table (8). This approach was chosen as only 2 parameters was required to be assessed hence CCD had to be the choice as BBD starts from 3 factors and doesn't exist for 2 factors. The coded values for the experimental runs of 2 factor CCD can be seen in the above Table(8) (which is produced from Minitab software).

Table (9): BBD coded values for 3 factors

Run	Factor-1	Factor-2	Factor-3
1	1	0	1
2	-1	0	-1
3	1	1	0
4	0	1	1
5	0	1	-1
6	1	0	-1
7	0	0	0
8	1	-1	0
9	-1	0	1
10	0	-1	-1
11	0	0	0
12	0	-1	1
13	-1	-1	0
14	-1	1	0
15	0	0	0

Initially BBD-3-factorial design was chosen, as CCD has 20 experimental runs as compared to BBD which has just 15, as seen in Table (9) and (10). Prior to conducting the set of experiments as per DOE, early tests are done to evaluate the range or limits of various control parameters at each load. After which the relevance of the factors are to be evaluated and decided upon the number of factors to be used for the design based on which the final Table of experiments are to be carried out. After analysis

of initial data, it can be deduced that it is essential to evaluate more levels in temperature, pressure and catalyst to plastic ratio and hence finally it is decided to stick to 3-factorial CCD design with axial points as well as to evaluate and incorporate extreme points as shown below in Table(10).

Table (10): CCD coded values for 3 factors

Run	Factor-1	Factor-2	Factor-3
1	1	1	1
2	1	1	-1
3	1	-1	-1
4	-1	1	1
5	0	0	0
6	0	0	0
7	-1	-1	1
8	-1	-1	-1
9	1	-1	1
10	0	0	0
11	0	0	0
12	-1	1	-1
13	0	0	1.633
14	0	0	-1.633
15	0	0	0
16	0	0	0
17	1.633	0	0
18	-1.633	0	0
19	0	1.633	0
20	0	-1.633	0

3.2 Kinetic Studies approach

Thermogravimetric analyzer (TGA) is a high temperature furnace which measure the weight loss of a sample that can be done at different heating rates and temperatures. TGA data is extensively used for kinetic studies.

The data that would be received from TGA will be used in various models for finding the parameters related to kinetics. The kinetic parameters and the activation energies are evaluated at heating rate of 10 °C/min from ambient temperature to high temperatures of 600°C. The TGA takes record for the data at each 0.1s, while the data obtained are used for different kinetic models. Samples of less than a gram is used in TGA so that heat and mass transfer barriers can be considered negligible. Due to this very reason rate of reaction can be calculated by TGA more accurately compared to other methods (Khedri and Elyasi, 2016; Powell, 1957).

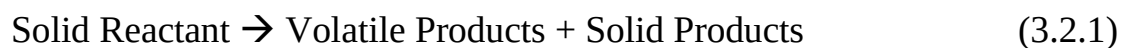
The TGA process can be run in two different modes; isothermal and non-isothermal, the later taking lesser time and hence being much more appealing for quick results. It is said that isothermal approach's data is more reliable. Furthermore, it is recommended that this approach be employed in degradation of plastics. (Khedri and Elyasi, 2016; Newkirk, 1960; Waters and Paddy, 1988)

Two approaches can be adopted to analyze the dataset received from TGA, isoconversional (model-free/model fitting) and non-isoconversional approaches. In the later approach, the kinetic parameters are constant through out the course of reaction, on the other hand, in the former approach the kinetic parameters can be calculated as function of the extent of reaction. Since degradation of plastics is not a single step reaction and produces intermediate, due to this reason researchers employ

isoconversional approach in this application. In this approach, the best fit models are chosen as they give appropriate statistical fit of data, from which kinetic parameters can be calculated. It is noteworthy that the estimated kinetic parameters from non-isothermal TGA are not applicable for isothermal measurements. Majority papers in similar line of work have affirmed that pyrolysis reactors work under constant temperature, few have studied isothermal TGAs of waste plastics. The common methods to analyze isothermal TGAs are the conventional method which generates constant kinetic parameters over the entire decomposition, and the isoconversional model-free method which is highly recommended in different works. Kinetic models are all based on the basic rate of conversion equation for thermal degradation (Aboulkas and Bouadili, 2010; Arkhangel'skii et al. 2013; Khedri and Elyasi, 2016; Miteva, et al. 2016; Yan et al. 2015).

Although there exist plenty of researches on the study of plastic decomposition, it is yet difficult to find a model to design an industrial scale reactor as the precision of predicting the kinetic parameters are in question. Furthermore, for the kinetic study purpose, degradation of mixed plastic waste by hydrocracking using hierarchical zeolites hasn't been evaluated to the best of our knowledge. In this study, TGA is carried out to evaluate the kinetic parameters which are calculated using various isoconversional methods like Coats-Redfern, the modified Coats-Redfern, Friedman, Ozawa, Kissinger Akahiraie Sunose (KAS), Flynn-Wallace Ozawa (FWO) and Distributed Activation Energy Model (DAEM).

The concentration of the reactants is assumed to be constant through the course of reaction. The decomposition of the reactants can generally be expressed as:



The kinetics of solid-state reactions can be expressed as:

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (3.2.2)$$

Where α is the extent of conversion equated as:

$$\alpha = \frac{m_o - m_t}{m_o - m_f} \quad (3.2.3)$$

Where ‘m’ (mg) is the mass of sample, m_o , m_t , and m_f being initial, actual and final mass of the sample, respectively. The function for the decomposition reaction is expressed as follows where ‘n’ is the order of reaction:

$$f(\alpha) = (1 - \alpha)^n \quad (3.2.4)$$

The activation energy from the Arrhenius equation is expressed as:

$$k = A * \exp\left(-\frac{E}{RT}\right) \quad (3.2.5)$$

Where ‘A’ is the pre-exponential factor (K^{-1}), ‘R’ is the universal gas constant (kJ/mol.K), ‘E’ is the activation energy (kJ/mol), ‘T’ is the reaction temperature (K). Substituting equation (3.2.4) and (3.2.5) in (3.2.2), for $n=1$:

$$\frac{d\alpha}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1 - \alpha) \quad (3.2.6)$$

The heating rate β (K/min) constant can be expressed as $\beta = \frac{dT}{dt}$, then for non-isothermal TGA experiments equation (3.2.6) is expressed as, for $n=1$:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot \exp\left(-\frac{E}{RT}\right) \cdot (1 - \alpha) \quad (3.2.7)$$

Based on above equations, various methods are categorized as differential approaches and integral approaches as enlisted below:

3.2.1 Differential Isoconversional Approaches

This approach employs instantaneous rate values, it is very sensitive to experimental noise and tends to be numerically unstable. Use of incremental methods can obviate this trouble. For the linear heating program, it is integrated within conversion. Due to the integration, the influence of experimental noise is eliminated to a great extent. For an infinitely small increment, the differential isoconversional method that accounts for variation in the activation energy is obtained. This approach is a reasonable compromise between the stability of calculations and obtaining good estimates of actual values of activation energy (Simon, 2004).

3.2.1.1 Friedman method

This method of differential isoconversional approach is more accurate than integration method as it doesn't require approximation, it is based on equation (3.2.6) directly:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta \frac{d\alpha}{dT}\right) = \ln(A) + \ln(1-\alpha) - \frac{E}{RT} \quad (3.2.8)$$

The 'E' and 'A' can easily be obtained by plotting $\ln\left(\beta \frac{d\alpha}{dt}\right)$ v/s $1/T$ (Friedman, 1964; Khedri and Elyasi, 2016).

3.2.1.2 Ozawa method

This method is also a differential isoconversional approach which is also based on equation (3.2.6):

$$\ln(\beta) = \ln\left(\frac{d\alpha}{dT}\right) + \ln(A) + \ln(1-\alpha) - \frac{E}{RT} \quad (3.2.9)$$

The ‘E’ and ‘A’ can be obtained by plotting $\ln(\beta)$ v/s $1/T$ which is a straight line (Khedri and Elyasi, 2016; Ozawa, 1965).

3.2.1.3 Freeman and Carroll’s method

This method is a differential isoconversional approach which is based on equation (3.2.6):

$$\frac{\ln\left(\frac{d\alpha}{dt}\right)}{\ln(1-\alpha)} = -\frac{E}{2.303*RT} \frac{\left(\frac{1}{T}\right)}{\ln(1-\alpha)} + n \quad (3.2.10)$$

Plotting $\frac{\ln\left(\frac{d\alpha}{dt}\right)}{\ln(1-\alpha)}$ v/s $\frac{\left(\frac{1}{T}\right)}{\ln(1-\alpha)}$ gives the activation energy as the slope and the intercept represents the order of the reaction (Freeman and Carroll, 1958).

3.2.2 Integral Isoconversional Approaches

The integral isoconversional methods with linear heating program average values of activation energy over the region. Even for the simplest case of a linear dependence of activation energy on conversion, the kinetic equation is not separable. The treatment of experimental data using integral isoconversional methods gives values of activation energy which, obviously, are again averaged over the whole conversion range. However, the way of averaging entirely differs for the isothermal and non-isothermal methods. This is obviously the reason of inconsistency between the activation parameters derived from isothermal and non-isothermal experiments. Since the activation parameters are averaged in both methods, their values cannot reproduce the actual rate of the process at the fixed conversion (Simon, 2004).

3.2.2.1 Doyle’s approximation method

This approach is derived from integral isoconversional approach:

$$\ln(-\ln(1-\alpha)) = \ln\left(\frac{AR}{\beta E}\right) - 5.33 - 1.052 \frac{E}{RT} \quad (3.2.11)$$

The activation energy can easily be obtained by plotting $\ln(-\ln(1-\alpha))$ v/s $1/T$ for a value of conversion ' α ', the slope of this graph will be $(-1.052 \frac{E}{R})$ and the intercept represented as $(\ln(\frac{AR}{\beta E}) - 5.33)$ (Doyle, 1961; Rocha et al. 2018).

3.2.2.2 Coats Redfern method (CR)

This approach is often used to determine the kinetic parameters of solid fuels and is based on the integral approach which includes a thermal degradation mechanism to the equation:

$$\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (3.2.12)$$

The Coats-Redfern curve is plotted for $\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right)$ v/s $1/T$, the slope of this graph will be $(\frac{E}{R})$ and the intercept represented as $\ln\left(\frac{AR}{\beta E}\right)$ (Fischer et al.1987; Rocha et al. 2018).

3.2.2.3 Modified Coats Redfern method (MCR)

This is based on the integral approach and includes a thermal degradation mechanism to the equation like 'Coats Redfern method':

$$\ln\left(\frac{\beta}{T^2(1-\frac{2E}{RT})}\right) = \ln\left(-\frac{AR}{E\ln(1-\alpha)}\right) - \frac{E}{RT} \quad (3.2.13)$$

Assuming $\left(1 - \frac{2E}{RT}\right) \ll 1$ which is always true, plotting $\ln\left(\frac{\beta}{T^2}\right)$ v/s $1/T$ and applying a linear fit the 'A' and 'E' can be obtained. The slope gives 'E' and the intercept 'A' can be calculated accordingly (Fischer et al. 1987; Rocha et al. 2018).

3.2.2.4 Flynne Walle Ozawa (FWO) method

This approach is derived from integral isoconversional approach using Doyle's approximation method, at constant conversion and varying heating rates. It is represented by expression:

$$\ln(\beta) = \ln\left(-\frac{AE}{R\ln(1-\alpha)}\right) - 5.331 - 1.052\frac{E}{RT} \quad (3.2.14)$$

The activation energy 'E' and pre-exponential factor 'A' can be obtained by plotting $\ln(\beta)$ v/s $1/T$ which is a straight line, for a value of conversion ' α ' (Flynn and Wall, 1966; Flynn, 1983; Khedri and Elyasi, 2016; Ozawa, 1965).

3.2.2.5 Kissinger Akahiraie Sunose (KAS) method

KAS method is very similar to Kissinger method. KAS and FWO belong to the same group which is founded from 'Coats-Redfern approximation method' in equation (3.2.12):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(-\frac{AR}{E\ln(1-\alpha)}\right) - \frac{E}{RT} \quad (3.2.15)$$

Plotting $\ln\left(\frac{\beta}{T^2}\right)$ v/s $1/T$ is a straight line, for a value of conversion ' α ' (Akahira, 1971; Kissinger, 1957; Khedri and Elyasi, 2016).

3.2.2.6 Distributed Activation Energy Model method (DAEM)

The distributed activation energy model (DAEM) is believed to be proposed first by Pitt, 1962, which is presented by a series of parallel first-order reactions with different 'E' values but the same 'A' factor. The nth-order DAEM was latter developed by Braun and Burnham, 1987. This approach is often used to analyze complex reaction process such as fossil fuel pyrolysis and thermal regeneration of activated carbon. Using

statistical modifications and simplifications proposed by Miura and Maki (1998), the equation is represented as:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT} \quad (3.2.16)$$

Plot $\ln\left(\frac{\beta}{T^2}\right)$ v/s $1/T$ is a straight line, where ‘E’ and ‘A’ can be calculated using equation (3.2.16) (Miura, 1995; Miura and Maki, 1998; Perera and Narayana, 2018)

3.3 Experimental methodology

3.3.1 Materials used

The basic materials required in this project is the waste plastics that are found in the store of lab 27-123 have been supplied by al-Taj plastic company. The plastics as seen below in Fig. (26), were used in the ratio 10.57% PP, 34.82% PS, 24.76% LDPE and 29.85% HDPE. Furthermore, the selected plastic types are more common and represent over half of the total plastic wastes (Silvarrey and Phan, 2016).



Fig. 26: Sample of waste plastics used

Two types of zeolites were used as catalyst, namely ZSM-5 (CBV2314) and Beta-Zeolite 300 (CP811C-300) which are products of Zeolyst International. For the material safety data sheets of the catalysts used, please refer to Appendix-II(A). The results of N_2 -adsorption/desorption measurement and micropore volumes of zeolites are shown in Table(11). Values shown in Table(11) indicate that BZ has high surface area and pore volume as compared to ZSM-5 catalyst. This shows that BZ is more porous than ZSM-5. For N_2 -adsorption/desorption

isotherms of BZ used, please refer to Appendix-II(B). From the isotherms of each catalyst, there observed a steep increase in the adsorption branch of the isotherm in the area of higher relative pressures. They both show typical type IV isotherms. This attributes to the multilayer adsorption of N₂ in the mesopores of these catalyst (Li et al. 2013). In addition, Si/Al ratio of BZ is also high as compared to ZSM-5. This indicates that BZ is more siliceous and less acidic than ZSM-5. Besides the various materials used, some materials are seen in Fig. (28) that were used for catalyst modifications. For the list of chemicals used, please refer to Appendix-II(C).

Table (11): Details of zeolites used (Zeolyst, 2018)

Zeolite Type	Zeolyst Product ID	Si/Al Ratio	Nominal Cation Form	Surface Area (m ² /g)	Micropores Volume (cm ³ /g)
ZSM-5 (Zeolite Socony Mobil-5)	CBV2314	23	Ammonium	425	0.127
Beta Zeolite (BZ)	CP811C-300	300	Hydrogen	620	0.210

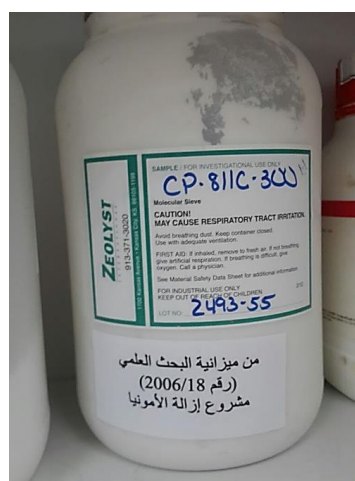
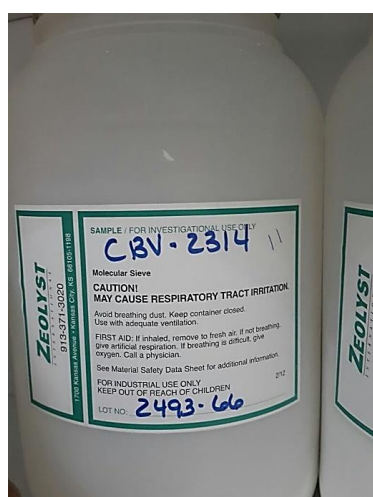
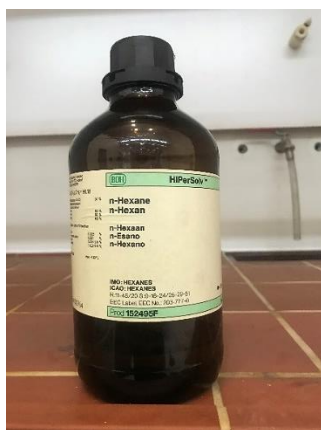


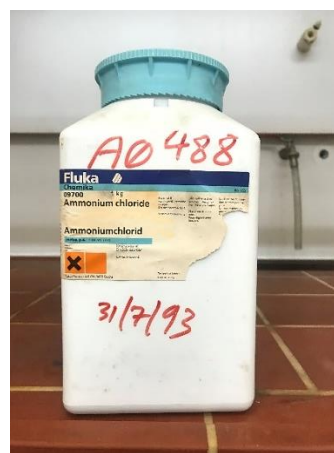
Fig. 27: Zeolyst International's ZSM-5 and BZ stock



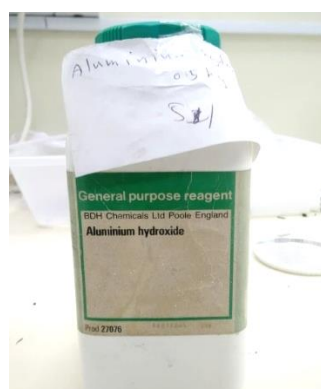
(a)



(b)



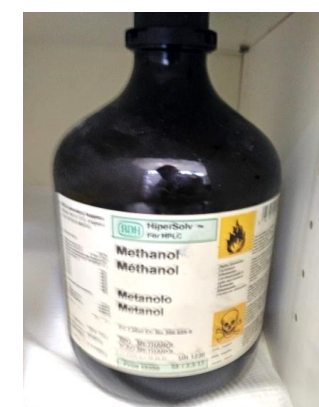
(c)



(d)



(e)



(f)



(g)



(h)



(i)

Fig. 28: Various material used: (a) n-hexane, (b) silica gel coarse (c) ammonium chloride, (d) aluminum hydroxide, (e) whatman paper, (f) methanol, (g) sodium hydroxide, (h) silica gel (for column chromatography), (i) activated carbon

Some of the materials used are; sodium hydroxide (Research Lab-Fine Chemical Industries, extre pure), hydrochloric acid (Research Lab-Fine Chemical Industries, purity 34-37%), ammonium chloride (Fluka, purity 99.5%), nitric acid (BDH, purity 68-70%), and aluminium hydroxide (BDH, purity 47%). Silica gel (BDH, coarse type) and activated carbon (BDH, fine type) are used to absorb moisture from the liquid samples before its analysis in GCMS. Chemicals like n-Hexane (BDH, purity 98.5%), Tetrahydrofuran (BDH, purity 99%) and Methanol (BDH, purity 99.8%) are used to form a mixture with waxes samples. Hydrogen and nitrogen gases of purity 99.99% are used. Whatman filter paper of 0.8 micrometer are used to filter catalyst as well as oil samples before its use in GCMS to avoid solid residues being stuck in the column.

3.3.2 Catalyst modification methodology

3.3.2.1 Desilication method

The as-synthesized ZSM-5 zeolite (Zeolyst International's CBV2314) was first calcinated in static air at 550°C for 4 hours in glass tube reactor (Thermo Scientific Lindberg/Blue M). 5g of ZSM-5 sample was introduced to 150ml of 1M sodium hydroxide solution and stirred at 500 rpm while heating at 90°C for 45 minutes. The sample was then vaccum filtered and thoroughly washed with deionized water until pH 9 is reached. The sample was then dried in an oven over night at a temperature of 100°C. Subsequently, an acid washing was performed using 50ml of 0.1 M hydrochloric acid for 30 minutes at 90°C to decrease the extra framework aluminum species. The obtained zeolite was then rinsed with deionized water until pH 5. Following the acid treatment, samples were ion exchanged to remove the sodium ions and replace them with ammonium ions (that can be changed to proton form on calcination); this is done by subjecting

the catalyst sample with 100ml of 1M ammonium nitrate for 2 hours at 90 °C, the sample was treated with fresh solution every 2 hours period which was done 3 times (Hoff et al. 2017). The resulting zeolitic material was filtered, washed with deionized water and dried at 100 °C overnight as seen in Fig. (29) and (30). Fig. (29a) depicts the catalyst being stirred at a desired temperature with the additive to prepare hierarchical zeolites. It is then vacuum filtered as seen in Fig. (29b) after which it looks like as seen in Fig. (29c). It is then dried in an oven shown in Fig. (30), after which it looks like as seen in Fig. (29d). Finally, the resultant sample was calcinated in air at 600 °C for 2 hours before use to thermally decompose ammonium ions and to obtain acidic proton form. The desilicated Beta zeolite (DBZ) was also prepared in a similar manner. For DBZ, varying strength of sodium hydroxide was attempted such that the BZ structure doesn't collapse.

3.3.2.2 Dealumination method

The as-synthesized ZSM-5 zeolite (Zeolyst International's CBV2314) was first calcinated in static air at 550°C for 4 hours in glass tube reactor (Thermo Scientific Lindberg/Blue). Then add 3g of zeolite to 50 mL of 1M hydrogen nitrate solution. The mixture was stirred for one hour at a temperature of 65°C after which it was followed by filtrated and washed with warm deionized water until neutral pH was obtained (Reule et al. 2017). The resulting zeolitic material was filtered, washed with deionized water and dried at 100 °C overnight as seen in Fig. (29) and (30) Finally, the resultant samples was calcinated in air at 600 °C for 2 hours before use to thermally decompose ammonium ions and to obtain acidic proton form.

3.3.2.3 Alumina Impregnation method

Alumina is impregnated over DBZ at various loading amounts. A calculated amount (0.5g, 1g, 2g, 3g and 5g i.e. 4.56, 8.74, 16.07, 22.3 and 32.38 wt.% of Al₂O₃ loading per zeolite, respectively) of aluminum nitrate

was added in 40ml of water. 5g of the DBZ was mixed with this solution and allowed to stir vigorously for 1 hour at varied temperature (50, 60, 70, 80 and 90°C). The solution was then equilibrated for further 24 hours at room temperature. The final alumina impregnated zeolite catalyst was dried in an oven at 100°C overnight. Finally, the resultant samples was calcinated in air at 600 °C for 2 hours.



(a)



(b)



(c)



(d)

Fig. 29: (a) Zeolite samples being heated while magnetically stirred (this apparatus has a maximum attainable temperature of only 80°C), (b) Vacuum filtration setup of the synthesised zeolite, (c) Hierarchical zeolite samples after filtration, (d) Samples after over night oven drying at 100°C.



Fig. 30: Drying oven, used for drying the catalyst samples

3.3.3 Experimental procedure for atmospheric setup

Before the experimental procedure starts, the prepared catalysts were calcinated at 600°C for 2 hours in air. Then preliminary experiments were performed to evaluate the catalyst in the catalytic hydrocracking of plastic waste under atmospheric pressure. The essential factors here are the reaction temperature, hydrogen and nitrogen flow and the plastic/catalyst ratio used. The reaction temperature is 400°C and the heating rate is set at 10°C/min. The catalyst to plastic ratio used is 1:20 and the hydrogen/nitrogen flow set at flowrate of 0.01L/min.

The setup is such that there is a quartz glass tube reactor (Thermo Scientific Lindberg Blue M) as seen in Fig. (31), with connections on both side of the tube. The quartz tube has dimensions of 600 mm length, 20

mm diameter and thickness of 2 mm. The schematic of the setup can be seen in Fig. (32).



Fig. 31: Glass tube furnace with single set point controller.

The right side of the reactor is connected to the gas inlet with a cork, where hydrogen and nitrogen coupled flow (ratio 1:25) comes in and the left side is connected through a pipe to a stainless steel bolted condenser which is placed in an ice bath cooler.

The cracking reaction takes place inside the tube which can be looked at as a semi-batch reactor where the mixed municipal plastic waste along with the catalyst is placed. The process is such that the hydrogen and nitrogen flows from the right end while the produced vapor leaves from the left. Please refer to Appendix-VIII for the characterization of catalyst and liquid products.

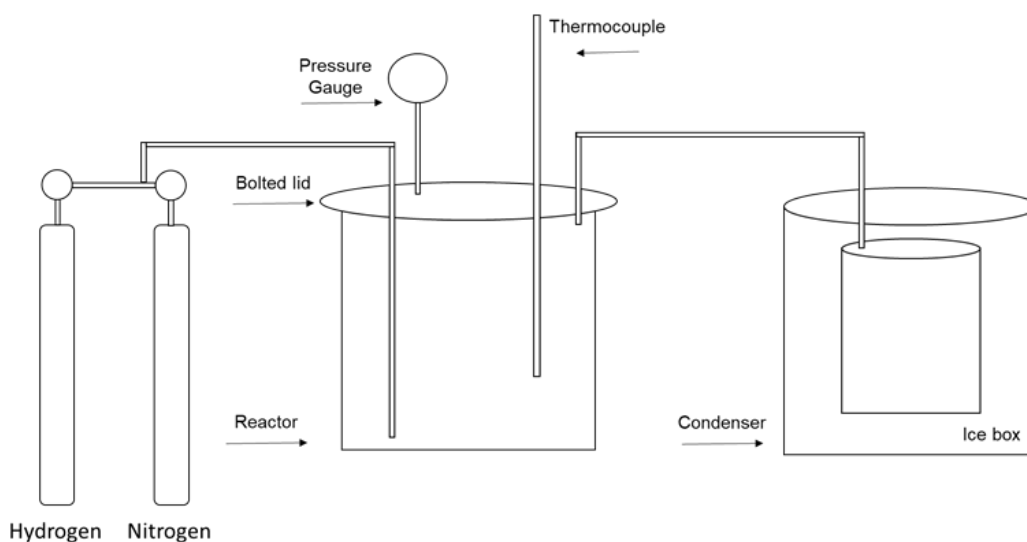


Fig. 32: Schematic diagram of the setup

The hydrogen is necessary for the reaction as it is a catalytic hydrocracking reaction process, while the nitrogen is acting as a carrier gas. Only after reaction temperature is reached hydrogen is introduced to the reactor. Both cylinders are connected to flowmeter device in which the ratio of the inlet gases are maintained constant at 1.25 during the reaction.

The bolted stainless steel condenser is connected to another small sized glass capped bottle connected through a ball valve that is placed on top of the condenser where the vapors that are not condensed which are mainly nitrogen and unreacted hydrogen and light hydrocarbons overflows out of the bolted stainless steel condenser. The cylindrical shaped bolted stainless-steel condenser can be opened from the top which has eight screw bolts onto it. This setup is immersed in an ice bath where the temperature is set approximately 0°C (the temperature remains below 0°C however the ice bath temperature fluctuates which may be due to the inlet of hot vapors)

Firstly, N_2 is passed through the tube to remove any air inside, after which the temperature is increased step wise from room temp to the desired temperature, once temperature is reached H_2 is also added with H_2/N_2 ratio of 1:25 and the reaction is allowed to run for 45 min. On reaction completion, the H_2/N_2 gas flow is stopped after which the stainless-steel condenser is unbolted and the liquid yield is collected through a pipette, which is then moved to capped bottle after which it is weighted as seen in the Fig. (33). In this setup the solid remains in the glass tube reactor cannot be weighted as they tend to be waxy and sticky in nature, for this to be removed the glass tube reactor is heated up to over $700^\circ C$ so it can be melted away and easily cleaned. The liquid produced from the experiments of the selected catalyst is then analysed by GC-MS to determine the gasoline fraction of each sample. Before liquid samples can be used in GC-MS, it is filtered using whatman filter paper, to filter out any solid that may cause issues in GC-MS equipment and passed through silica gel to remove moisture.

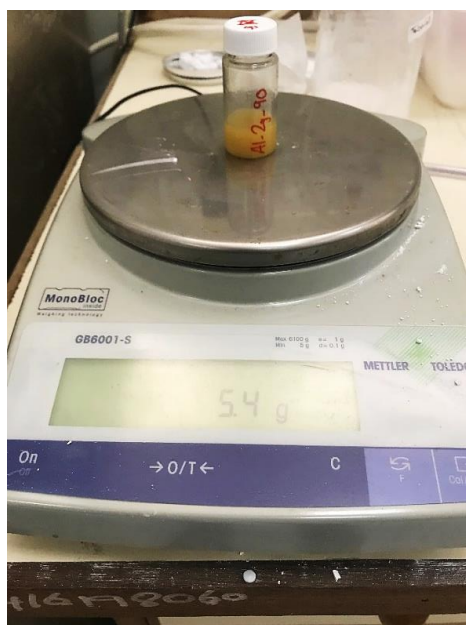


Fig. 33: Weight of liquid yield produced

3.3.4 Experimental procedure for pressure setup

A different setup is used for evaluating pressure parameter. (This setup is based in Sultan Qaboos University, Oman which was used in collaboration for this research). The setup as seen in Fig. (34a) comprises of 300ml vessel with an inlet and outlet valves as seen closely in Fig. (34b) which are pressurized using hydrogen and nitrogen connected to it (Munir et al. 2017). It has a pressure gauge and a thermocouple mounted to it as seen in Fig. (34d).



(a)



(b)



(c)



(d)

Fig. 34: (a) High pressure parr autoclave vessel setup, (b) close-up of the pressure setup, (c) gas collecting bag of 1000 ml volume, (d) 300 ml vessel of the pressure setup

The procedure begins with the cleaning and drying of the autoclave. It was then loaded with weighed amounts of plastic and catalyst mixture. The hydrogen was filled in the autoclave. Before increasing the temperature, the initial pressure of the autoclave was recorded and leak test was conducted for at least 30 min prior to start all experiments. Desired value of initial pressure was used depending upon the experimental conditions as per DOE. The temperature of the autoclave was then raised up to desired temperature using intact furnace. The temperature was raised in steps with an incremental value of 20°C. Pressure was recorded at different attained temperatures. Maintain the autoclave temperature and pressure for 60 minutes. The pressure was noted at every 10 min interval. After completion of experiment, the furnace was separated by moving it away from the autoclave and it was left to drop the autoclave temperature to 200°C then to 50°C. The autoclave was left for few hours to let it cool down. The final autoclave pressure was recorded in order to have an idea about the volume of generated gasses. The gases were carefully collected using gas bag as seen in Fig. (34c) and the number of filled gas bags were recorded in order to calculate the volume of produced gases. The autoclave was dismantled and 10g of n-heptane was added to extract the dissolved fractions using pre-weighted filter paper. The mixture was filtered using the weighted filter paper and weigh the filtrate (n-heptane soluble). The filter paper was dried for about 30 min to remove n-heptane at room temperature. The dried contents over the filter paper were transfer into another conical flask, to which add 5g of THF (Tetrahydrofuran) and mixed. Using the same filter paper to extract the THF solubles, the filtrate is weighted out. N-heptane is known to be an excellent solvent to dissolve about C5-C18 range of hydrocarbons which is about the same as useful fuel's range (e.g. gasoline, kerosene, diesel etc.) Hence, this is done to determine that how

much of the liquid yield is in the useful fuel's range. THF is used to dissolve the rest of the liquid which is in the range of C₁₈-C₂₅. The filter paper was kept with the residue over it in an oven at 105 to 110°C to dry the contents and then the dried filter paper with coke and catalyst were weighted. The rest of the experiments were carried out in similar manner by varying temperature, pressure and catalyst to plastic ratio. Solid, liquid, oil, gas yields and conversion are then calculated by using the following equations:

$$\text{Oil yield (\%)} = \frac{\text{weight of } n\text{-heptane solubles}}{\text{weight of plastic}} \times 100 \quad (3.3.4.1)$$

$$\begin{aligned} \text{Liquid yield (\%)} = & \\ & \frac{\text{weight of total THF solubles} + \text{weight of } n\text{-heptane solubles}}{\text{weight of plastic}} \times 100 \\ (3.3.4.2) \end{aligned}$$

$$\text{Solids yield (\%)} = \frac{\text{weight of dried solid residue}}{\text{weight of plastic}} \times 100 \quad (3.3.4.3)$$

$$\text{Gas yield (\%)} = 100 - (\text{liquid yield} + \text{solid yield}) \quad (3.3.4.4)$$

$$\begin{aligned} \text{Conversion(\%)} = & \\ & \frac{\text{weight of the plastic fed} - \text{weight of the dried solids residue}}{\text{weight of plastic}} \times 100 \\ (3.3.4.5) \end{aligned}$$

Chapter 4

Results, Discussion and Recommendation

Table of contents

Subject	Page Number
Chapter Four Results, Discussion and Recommendation	
4.1 Preliminary results	101
4.1.1 Preliminary experiments and analysis on ZSM-5	102
4.1.2 Preliminary experiments and analysis on BZ	107
4.2 Catalyst optimization results	115
4.3 Process parameters optimization results	132
4.4 Kinetic studies	149
4.5 Conclusion	156
4.6 Future recommendations	159
4.7 Economic prospects of plastic recycling	162

4.1 Preliminary results

As per the experimental procedure mentioned in section 3.3.3 and catalyst preparation methods in section 3.3.2, the catalysts were accordingly prepared using parent ZSM-5 and BZ. Steps to prepare hierarchical zeolites were carried out to prepare catalyst which were then employed in the reaction process of conversion of mixed municipal waste plastic to fuel.

Preliminary experiments were carried out using desilicated ZSM-5 and dealuminated ZSM-5 along with an experiment carried out on parent ZSM-5 zeolite catalyst to evaluate the product yield. Similar experiments were also carried out on parent BZ. These experiments were carried out at conditions illustrated in a Table (12).

Table (12): Reaction process conditions.

Sr. No	Process Parameters	
1	Temperature	400 °C
2	Pressure	Ambient
3	Heating Rate	10 °C/min
4	Reaction Time	45 minutes
5	Plastic to catalyst ratio	20:1
6	Nitrogen to Hydrogen ratio	25:1

4.1.1 Preliminary experiments using ZSM-5

The details of parameters and specification involved to prepare the catalyst using ZSM-5 zeolite are mentioned in Table (13).

Table (13): Parameters involved in catalyst preparation for preliminary experiments

Sr. No.	Parameter	Desilcated ZSM-5	Dealuminated ZSM-5
1	Chemical Used	Sodium Hydroxide	Hydrochloric acid
2	Dilution Ratio	1g in 30ml water	1g in 20ml water
3	Molarity	1M	1M
4	Temperature	90 °C	60 °C
5	Mixing Residence time	45 minutes	45 minutes
6	Mixing rate	500 rpm	500 rpm
7	Drying time (at 100°C)	Overnight	Overnight

SEM images of all zeolites at the same magnification level are shown in Fig. (35) where Fig. (35a), Fig. (35b) and Fig. (35c) show SEM images of parent ZSM-5, desilicated ZSM-5 and dealuminated ZSM-5 catalysts, respectively. From these SEM images it can be deduced that the resultant hierarchical zeolites are mesoporous in nature with about quasi spherical morphologies with larger pore sizes. It can also be observed from the SEM images that very tiny particle with unclear shapes, within a few nm sizes ranges, agglomerate with each other to form irregular clusters of different morphologies. In order to observe the clear morphologies and confirm the mesoporosity of the zeolite catalyst, a high-resolution transmission

electron microscopy analysis must be performed. The results indicate that most of the crystals keep their shapes after treatments. However, some surface roughness was observed in the SEM images. These results match well with the results of the literature (Smail et al. 2019; Song et al. 2018; Zahara et al. 2018). The SEM images shows that all the ZSM-5 zeolite particles have quasi spherical shape that are specific characteristic of ZSM-5 zeolites.

Fig. (36) shows XRD patterns of all zeolites that include parent ZSM-5, dealuminated ZSM-5 and desilicated ZSM-5. All zeolites show the typical patterns of the ZSM-5 structure at 2θ values of 23.27° and 23.86° which correspond to the crystal planes at (501) and (422), respectively (Pérez-Page et al. 2016) and these peaks are designated by the star symbol in Fig. (36). Diffraction patterns of modified ZSM-5 catalysts show that the crystal structure of the zeolite is maintained even after desilication and dealumination treatments. However, intensity of the major peaks for the desilicated ZSM-5 are observed to be low (Ni et al. 2011). Additionally, narrow peaks of all zeolites indicate that they are all crystalline in nature.

Demetallation is known to be a destructive process as it leads to partial break down of the zeolite framework, breaking the Si-O-Si and Si-O-Al bonds into active forms i.e. Si-O and Al-O. Therefore, the tetrahedral structures of Si-O and Al-O are damaged, and their structural shapes are no longer intact (Li et al. 2017; Rohayati et al. 2017). The results of EDS analysis giving Si/Al ratios of all ZSM-5 samples are shown in Table (14). Upon desilication the Si/Al ratio decreases and upon dealumination, the ratio increases, due to elimination of Si from the former sample and Al from latter sample. Desilicated ZSM-5 has higher acidity in comparison to the untreated ZSM-5 due to lower Si/Al molar

ratio. Furthermore, the Si/Al ratio of untreated ZSM-5 and dealuminated ZSM-5 did not change significantly much as compared to untreated ZSM-5 and desilicated ZSM-5. The reduction in the ratio in desilicated ZSM-5 is an indication that the modification lead to extraction of many atoms from the zeolite structure as well as change in the crystal structure. The crystallite size also appears to be bigger in hierarchical ZSM-5.

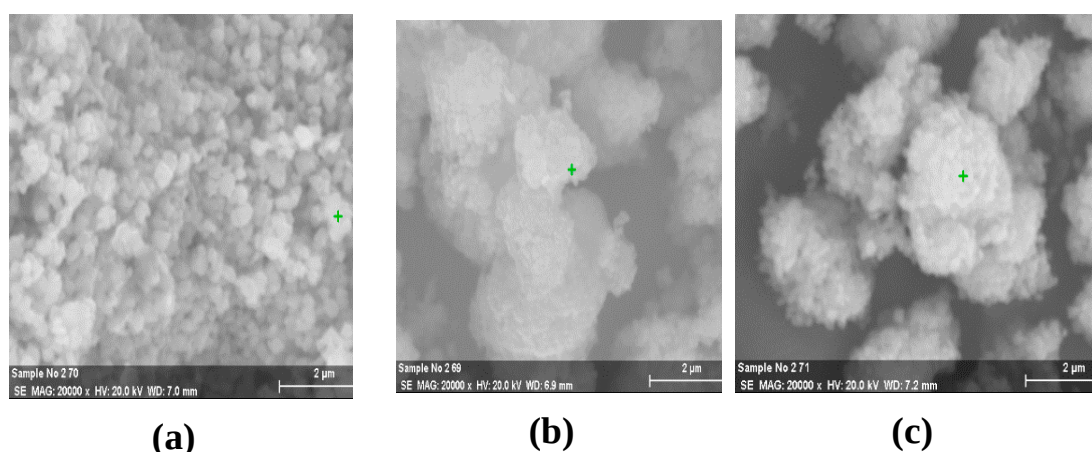


Fig. 35: SEM images of (a) Parent ZSM-5 (b) Desilicated ZSM-5 (c) Dealuminated ZSM-5

Table (14): Ratio of Si/Al and crystallite size of modified ZSM-5

Catalyst	Parent ZSM-5	Desilicated ZSM-5	Dealuminated ZSM-5
Si/Al Ratio	23	7.85	25
Crystallite size (nm)	15.89	31.79	19.87

Crystallite sizes were calculated using the Debye Scherrer's formula. It is found that the crystallite size for parent ZSM-5 is 15.89nm, 31.7nm for desilicated ZSM-5 and 19.87nm for dealuminated ZSM-5. Smail et al. (2019) reported the same Zeolyst ZSM-5 having a crystallite size of 22nm as compared to our results where unmodified ZSM-5 has a crystallite size of 15.89nm. However, the crystallite size of unmodified ZSM-5 reported

by Song et al. (2018) is 15nm, which is quite close to present research's findings. It is also established from recent literature findings that desilicated catalyst has bigger pore sizes as compared to dealuminated catalyst. It is reported by Zhang et al. (2017) that the desilicated catalyst size ranges between 20-30nm and as for dealuminated catalyst it is 12-20nm. The reported crystallite size of hierarchical zeolite in this research falls in line with the findings from literature.

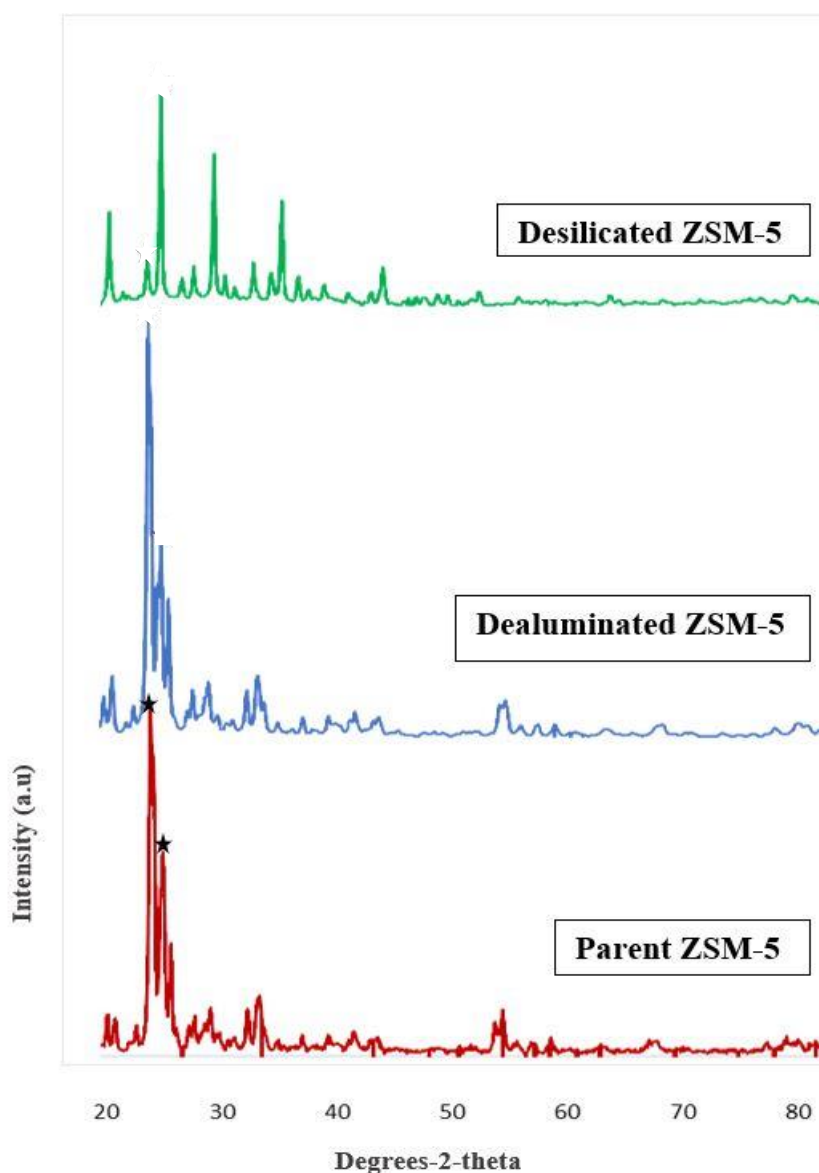


Fig. 36: XRD compairson of ZSM-5 with hierarchical ZSM-5

Fig. (37) illustrates the difference of product distribution on using parent ZSM-5 catalyst in comparison to catalysts that are desilicated and

dealuminated. These values are derived from the GCMS analysis of the liquid yield achieved according to which they are categorized as ‘aromatics, olefins (alkene and alkyne), saturated aliphatic (alkanes)’ which make up 100%. Gas, liquid and solid also makeup 100% and they are categorized based on the ranges of carbon atoms i.e. C₁-C₄, C₅-C₁₈ and C₁₉ plus, respectively. Amongst which gasoline is separately categorized based on range of carbon atoms falling from C₅ to C₁₂ (Munir et al. 2017). For further details of the GCMS data, please refer to Appendix-X.

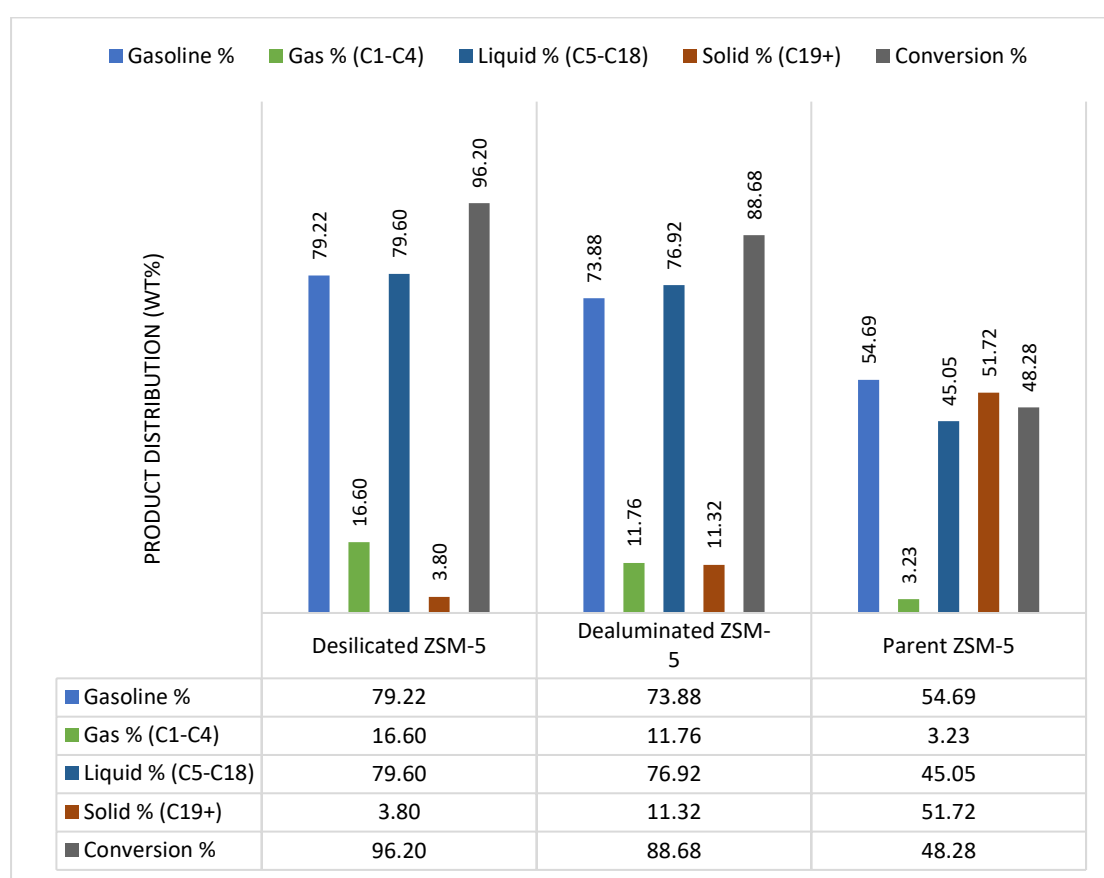


Fig. 37: Graphical and tabulated representation of preliminary experiments

For details of Fig. (37), please refer to Appendix-III. From Fig. (37), it can be seen clearly that the zeolites prepared by using dealumination and desilication processes give much higher liquid yield and conversion in comparison to the parent ZSM-5. Dealuminated ZSM-5 gives a liquid

yield of 76.92% and conversion of 88.68%, both are less than desilicated ZSM-5. Desilicated ZSM-5 gives a liquid yield of 79.60% and conversion of 96.20% in comparison to unmodified ZSM-5 which gives a liquid yield of 45.05% and conversion of 48.28%. This increase in liquid yield maybe due to increase in the mesoporosity of the modified catalyst. The long hydrocarbon chains may not be able to access the active site of the microporous catalyst due to their size and hence reducing the access to the catalyst active sites. This result may contribute to lower liquid yield which is observed in Fig. (37). Desilicated ZSM-5 gives highest liquid yield and highest percentage in the gasoline range too, besides conversion. ZSM-5 has excellent catalytic efficiency in cracking due to its strong acidic properties and its microporous crystalline structure. It has a 3D pre-channel structure with pore size of 5.4-5.6 Å, which allows an increased cracking of molecules (Ji et al. 2017). Mesoporous materials allow the diffusion of the heavy molecules and hence produce more liquid quantity compared to the gaseous product, as seen in Fig. (36) of desilicated and dealuminated ZSM-5 that demonstrated much higher liquid in comparison to parent ZSM-5. The results indicated can surely be further improved by optimizing the process parameters and catalyst preparation parameters.

4.1.2 Preliminary experiments and analysis using BZ

BZ's silica to alumina ratio is about 300 as compared to ZSM-5 which has a ratio of 23. Hence dealumination isn't carried out as there is barely any alumina in BZ. Regarding catalyst optimization, alumina impregnation coupled with desilication of BZ is carried out, as desilication would reduce the amount of silica in the BZ along with the mesopores creation and alumina impregnation would improve the acidity of the catalyst. Hence, to assess this argument, preliminary experiments were carried out using unmodified BZ and desilicated BZ that on which alumina is loaded.

Parameters involved in preparation of the catalyst are mentioned in Table (15).

On performing the desilication of BZ, it would immediate dissolve out or in other words dissolution of the silica in the zeolite structure occurs where much of the lattice structure has collapsed. Desilication using sodium hydroxide in this case lead to excessive silica dissolution and very little or nothing of the zeolite structure is left. Experiments were carried out on desilication of BZ (Si/Al = 300) using sodium hydroxide to find out appropriate parametric ranges such that zeolite structure does not collapse as elaborated in detail in Appendix-VI. The range of dilution ratio of 1g BZ in 5ml sodium hydroxide (1/5) to 1g BZ in 70ml sodium hydroxide (1/70) were explored. For exploring the ratio, concentration and temperature were fixed at 0.5M and 65°C, respectively. As of BZ to solution ratio is concerned, following different ratios (1/5, 1/10, 1/15, 1/20, 1/30, 1/40, 1/50, 1/60 and 1/70) were selected and test runs were carried out. Out of which all ratios lead to dissolution of the BZ except 1/5 and 1/10. Synthesis temperature (65, 75, 85°C), BZ to solution ratio (1/5, 1/7 and 1/10) and concentration (0.1, 0.3 and 0.5M) were selected and experiments were carried out to prepare desilicated BZ. Based on the results obtained from EDS, a configuration was chosen to prepare DBZ.

After going through the process of finding the parametric setting such that the structure does not collapse, the values mentioned in Table (15) were used to prepare DBZ, after which alumina was impregnated on it accordingly. From here on alumina impregnated on desilicated BZ is abbreviated as 'DBZA'.

Table (15): Parameters involved in catalyst preparation of DBZA

Sr. No.	Parameter	Desilication	Alumina Impregnation
1	Chemical Used	Sodium Hydroxide	Aluminum Nitrate
2	Molarity	0.1M	1M
3	Dilution Ratio	1g per 30ml water	1g per 80ml water
4	Temperature Synthesized	75 °C	60 °C
5	Mixing Residence time	45 minutes	60 minutes
6	Mixing rate	500 rpm	500 rpm
7	Drying time (at 100°C)	Overnight	Overnight

Fig. (38) shows XRD patterns of both unmodified BZ and DBZA. XRD patterns show both broad and sharp peaks simultaneously indicating the disordered structure present in BZ samples (Mostowicz et al. 1997). The characteristic peaks observed at 2θ of 7.8° and 22.5° are assigned to (001) and (302) planes, respectively (Perez-Pariente et al. 1987). The broad peak at 7.8° (shown as square symbol in the figure) is related to the defect structure, while the sharp peak at 22.5° (shown as star symbol in the figure) is attributed to the crystallinity of the samples (Gonzalez et al. 2013). From XRD patterns it seems that DBZA is more crystalline as compared to parent BZ.

Table (16) shows Si/Al ratios obtained from EDS analysis of both unmodified BZ and DBZA samples. Si/Al ratio of unmodified BZ decreases upon desilication i.e. DBZ. The prepared DBZ catalyst ratio is

found to be 32.42 which becomes 6.43 upon alumina impregnation. Fig. (39) shows SEM images of all BZ samples (parent BZ, DBZ and DBZA) at the same magnification level. From these SEM images, it can be deduced that all zeolites show uniform spherical morphologies indicating that structure does not change considerably even after desilication and alumina impregnation treatments. However, the surface appears to be rough, porous and particles seem to be more conglomerated as compared to the parent BZ. This conglomeration of particles may be due to the alumina impregnation. Crystallite sizes were also calculated for parent BZ and DBZA using the same Debye-Scherrer's formula as shown in Table(16). No significant difference in crystallite sizes were observed in both zeolite samples indicating that surface properties are not changed considerably. BET is needed to be carried out to know the volume and surface area of the zeolite, which unfortunately couldn't be carried out.

Table (16): Si/Al ratio and crystallite size of all BZ catalysts

Catalyst	BZ	DBZ	DBZA
Si/Al Ratio	300	32.42	6.43
Crystallite size (nm)	34.4	-	35.1

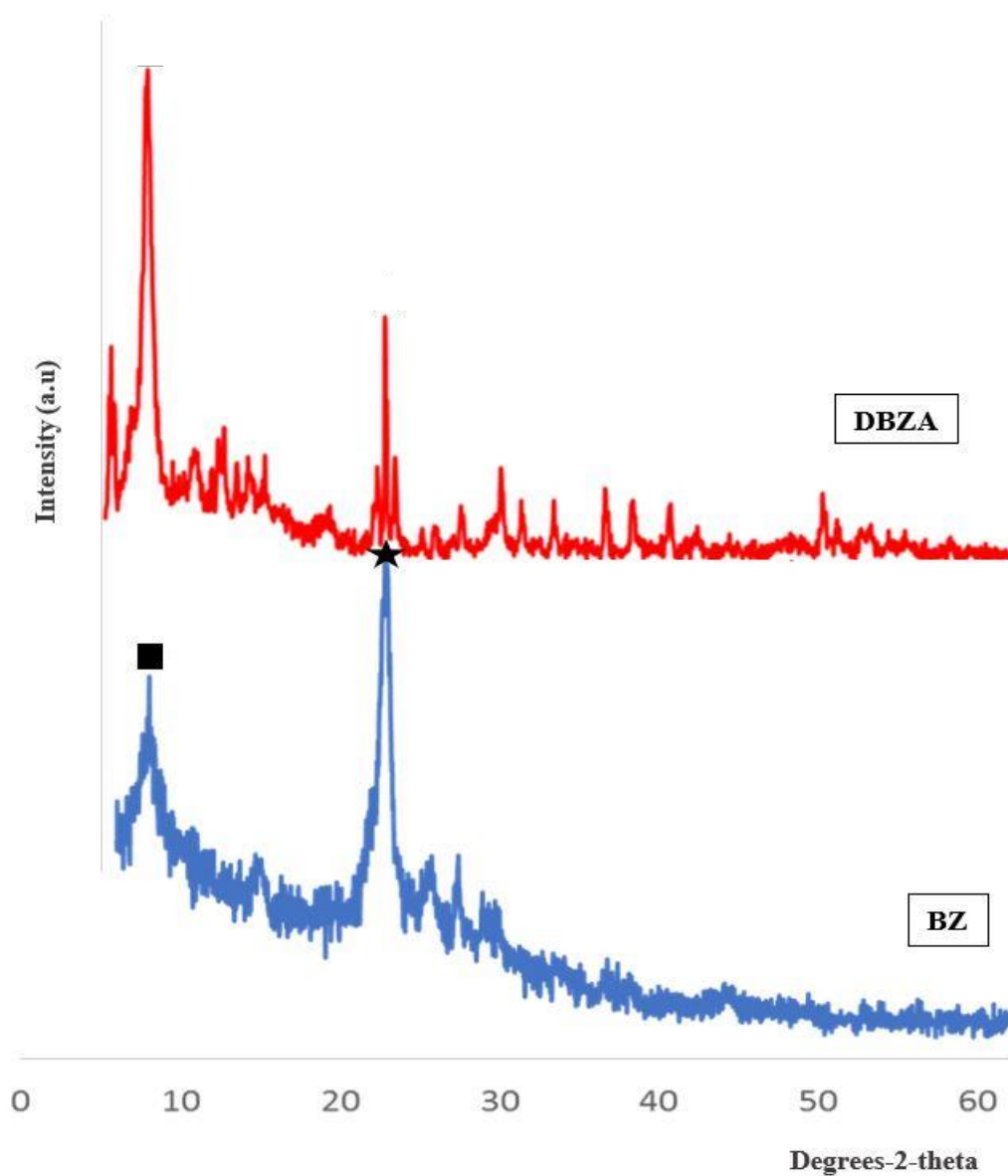


Fig. 38: XRD of BZ and DBZA

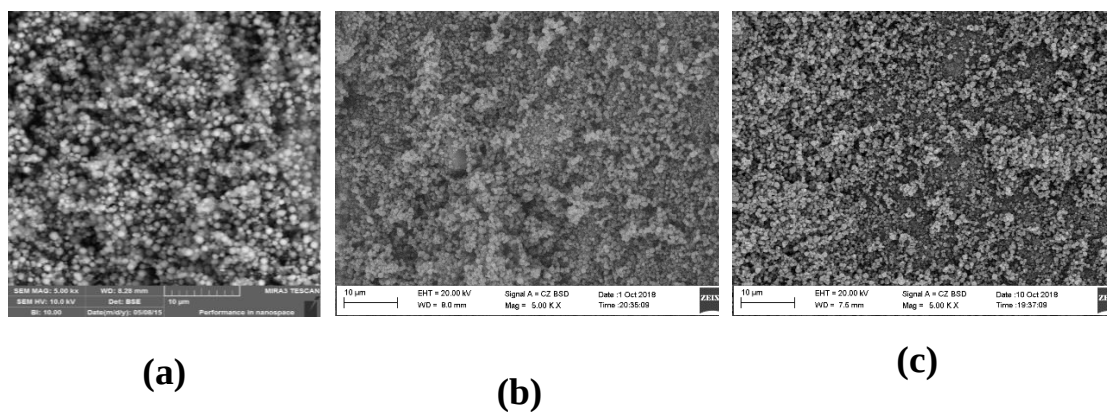


Fig. 39: SEM images of (a) Parent BZ (b) DBZ (c) DBZA

The data shown in Fig. (40) are derived from the GCMS analysis of the liquid yield achieved according to which they are categorized as ‘aromatics, olefins (alkene and alkyne), saturated aliphatic (alkanes)’ which make up 100%. Gas, liquid and solid also make 100% and they are categorized based on the ranges of carbon atoms i.e. C₁-C₄, C₅-C₁₈ and C₁₉ plus, respectively. Amongst which gasoline is separately categorized based on range of carbon atoms falling from C₅ to C₁₂ (Munir et al. 2017). Please refer to Appendix-X for details of Fig. (40). According to the illustrated data, based on initial findings, it can be seen that DBZA gave better liquid yield (*c.a.* 83%) than unmodified BZ (*c.a.* 78%) and desilicated ZSM-5 (*c.a.* 79%). However, the overall conversion seemed to be more or less the same. In addition, liquid percentage obtained using DBZA is all in the gasoline range (useful fuel) as compared to mere 68% and 79% on employing unmodified BZ and desilicated ZSM-5, respectively. For details of Fig. (40), please refer to Appendix-IV. High conversion and liquid yield for unmodified BZ as compared to unmodified ZSM-5 can be attributed to their surface properties such as pore volume and surface area. ZSM-5 has lower surface area (425m²/g) and pore size (5.5Å) as compared to BZ which has high pore size (7.5Å) as well as surface area (620m²/g). This also indicates that ZSM-5 has more diffusion limitations for this application in comparison to BZ.

It can be understood from literature that lower pore size results in increased coking and early catalyst deactivation which in turn may contribute to lesser liquid yield (Cejka and Van, 2005; Lei et al. 2003; Zenonos et al. 2003). This is what exactly reflected in this study as well. High amount of liquid yield for the DBZA may be due to its high surface area, large pore size and high acidity as compared to rest of catalysts. DBZA catalyst containing a crystallite size of 35.1nm compared to

desilicated ZSM-5 that has crystallite size of 31.79nm gave higher liquid yield, probably because of combination of more available acid sites arising from a higher surface area and the more mesopores of the bigger crystallite size zeolite (Cui et al. 2012). (To confirm, acidity tests need to be done, unfortunately it has not been done because of the unavailability of the facility).

Moreover, the catalyst had greater middle distillate selectivity, which could be attributed to the higher hydrogenation activity in the larger pore channel of the crystallite reducing diffusion limitation. This may be one of the justifications for the fact that on desilication of ZSM-5 and BZ, BZ led to higher liquid yield. This is supported by a very recent study done by Mayorga et al. (2019) for the application of hydrotreatment of soya oil to produce bio-kerosene using BZ (same Zeolyst BZ as ours) and ZSM-5. They observed that BZ are more promising and presenting good selectivity towards medium products as compared to ZSM-5.

As DBZA gave better liquid yield and that liquid yield was in the useful fuel range, hence DBZA is selected for catalyst optimization, where catalyst preparation parameters are accessed to maximize the liquid yield of the catalyst at a given set of process parameters. This is done to further improve the catalyst to bring out the best from the catalyst at given conditions of a process, before process optimization is carried out.

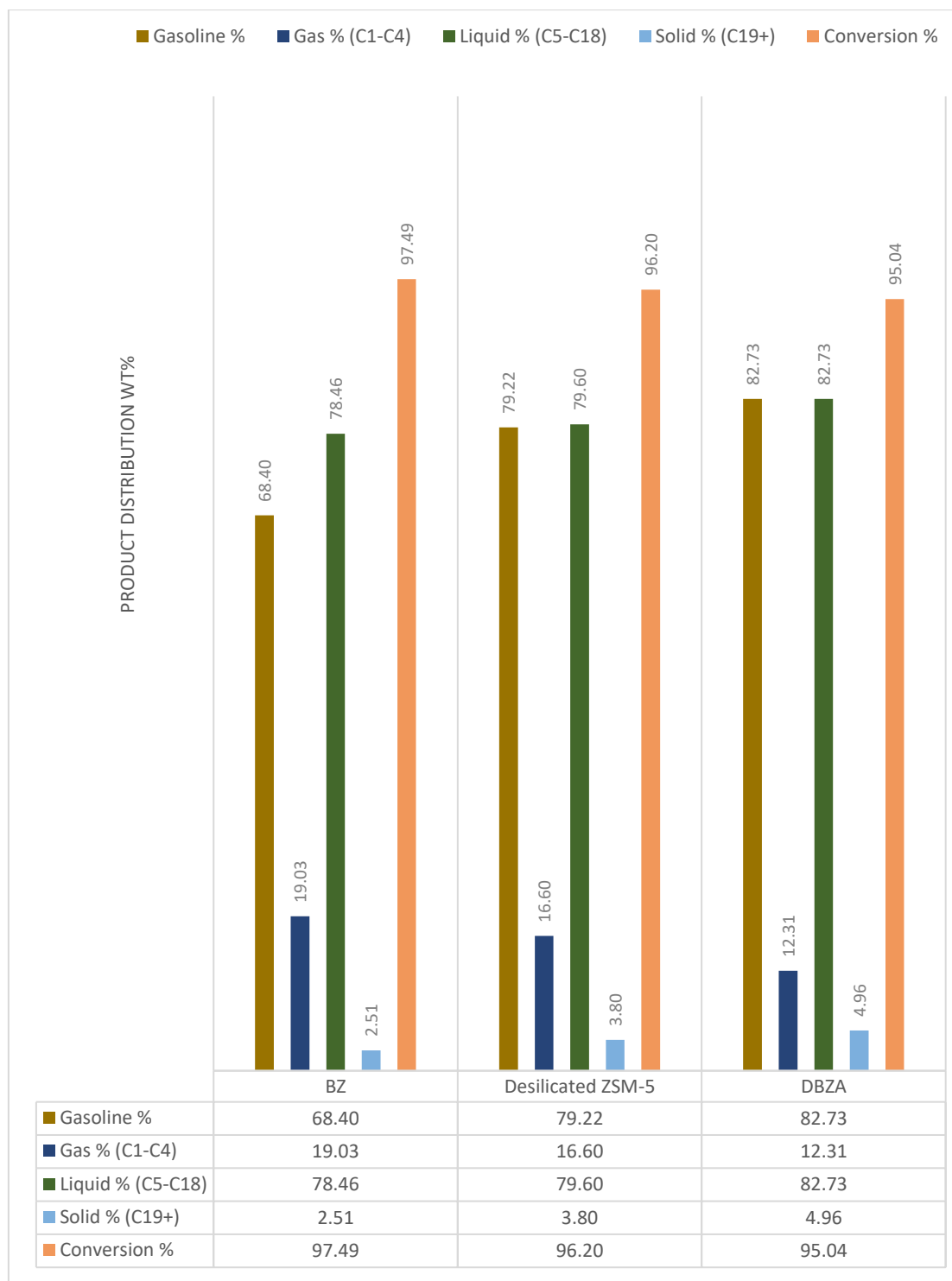


Fig. 40: Graphical and tabulated representation of preliminary experiments-2

4.2 Catalyst optimization results

Based on preliminary experiments, DBZA is found to be the best catalyst as it gives better liquid yield and the obtained liquid yield is in the range of useful fuel (gasoline). This liquid yield can be improved more by optimizing the catalyst preparation parameters. Hence all the catalyst samples are desilicated first based on the parameters chosen in section 4.1.2 Table (15), after which design of experiment is carried out varying alumina impregnation parameters to find the setting which gives the optimum liquid yield.

According to CCD for 5 levels and 2 factors, the 5 level settings are depicted in Table (17) with chosen range of factors and Table (18) shows the parameters with coded and uncoded values along with the experiments.

Table (17): Coded levels of each factor with actual values using CCD for catalyst optimization

Levels	Factors	
	Amt. Alumina Nitrate Impregnated (g)	Synthesis Temperature (°C)
-1.414	0.5 (4.56 wt% Al ₂ O ₃ loading)	50
-1	1 (8.74 wt% Al ₂ O ₃ loading)	60
0	2 (16.07 wt% Al ₂ O ₃ loading)	70
1	3 (22.30 wt% Al ₂ O ₃ loading)	80
1.414	5 (32.38 wt% Al ₂ O ₃ loading)	90

Table (18): DOE Table for 2 factor CCD design for catalyst optimization with results

Exp. No.	Amt. $\text{Al}(\text{NO}_3)_3$ impreg. (coded)	Synthesis Temp. (coded)	Amt. $\text{Al}(\text{NO}_3)_3$ impreg. (uncoded) (g)	Synthesis Temp. (uncoded) ($^{\circ}\text{C}$)	Response: Liquid Yield (g)
1	0	-1.414	2	50	2.1
2	-1	-1	1	60	1.1
3	1	-1	3	60	3.4
4	-1.414	0	0.5	70	3.3
5	0	0	2	70	5.7
6	1.414	0	5	70	7.5
7	-1	1	1	80	1.1
8	1	1	3	80	9.4
9	0	1.414	2	90	5.9
10	0	0	2	70	5.2
11	1.414	1.414	5	90	2.3
12	0	0	2	70	5.6
13	0	0	2	70	5.9
OPT	1	1.414	3	90	9.9

All experiments are carried out as per Table (12), based on which the liquid yield was weighed and reported (which is the response factor in this DOE). The obtained response values were then used in MINITAB (version 18.0) software for optimizing of liquid yield, determining coefficients for

the equation along with all regression and graphical analysis. The aim of this exercise is to maximize the liquid yield of the catalyst at a particular process parametric setting. The evaluation of the experimental data, liquid yield that has been weighed is given much more significance than the GCMS data's categorized 'liquid'. Hence, although GCMS has been carried out for all the experiments, maximizing is done based on the 'liquid weight' which is the response factor in DOE.

Following the experimental observation, DOE was carried out to study the optimum. The following Fig. (41) to (46) summarises the design of experiments data derived from MINITAB software, where the analysis were carried out, where A stands for amount of alumina impregnated in grams and B stands for temperature of the synthesis in degree celcius. Fig. (41) pareto chart indicates that the involved variables have significant interaction with each other as they extend beyond the red vertical reference line. Even the 2-way interaction indicate significance except A*A. However, among them aluminum loading factor is more significant than rest of the factors. Fig. (42) exhibits normal distribution. The residuals versus fits graph appear to be randomly scattered both above and below 0, that indicates constant variance. The histogram shows that the data is normally distributed, while the normal probability graph verifying the normal distribution which shows reasonable scattering of the data around the model values. Fig. (43) main effects plots assess the effect of selected variables on response. It is well known fact that different levels of the factor, affect differently on the response. In main effect of plots, slope of the line determines the magnitude of the main effect i.e. steeper the slope of line, higher will be the value of the main effect. If slope of the line is horizontal, it indicates that the factor does not have any effect on the response. It can be seen from the temperature factor in main effect plot that

at low level the response is also low. Response increases with the increase of levels and shows a maximum value at its high level, then slightly decrease when it comes to the extreme level. This can be attributed to the catalyst crystallinity which is low at low temperature and becomes high with the increase of temperature. Slight decrease in liquid yield after reaching maximum at higher temperature may be due to agglomeration of the catalyst particles which results in decrease of surface area so the liquid yield (Irfan et al. 2008). Aluminum impregnation also shows increasing trend i.e. at low level the response is also low but with increase of levels the response also increases. This can be explained that more loading of aluminum makes the catalyst more acidic. Hence, increase of aluminum loading, increase the acidity, and so increase the response (liquid yield). Fig. (44) i.e. 2D contour plot shows the placement of optimization value, for the given range of experiments, optimum value is reached at the maximum coded values of $A=+1.414$, $B=+1.414$ i.e. maximum synthesis temperature and alumina load. However, temperatures above 90°C cannot be explored as the temperatures easily escalats to boiling point of the solution and alumina impregnation at 5g was attempted that didnt give significant liquid product yield as only 3.4g was acheived. This could be due to over loading of the catalyst which ends up blocking the pores of the catalyst resulting in early deactivation of the catalayst and consequently lower liquid yield. Fig. (45) indicates the 3D surface plot where the peak indicates the maximum liquid product acheived. It is tideous to see optimum configuration from 3D surface and 2D contour plots, hence plot optimizor plot is used. Fig. (46) is the optimizor plot which suggest on (+1, +1.414) at 3g aluminium nitrate impregnation (22.3 wt% alumina per zeolite) and at 90°C ; liquid of 8.8g can be acheived. However, on carrying out this experiment liquid of 9.8g was acheived.

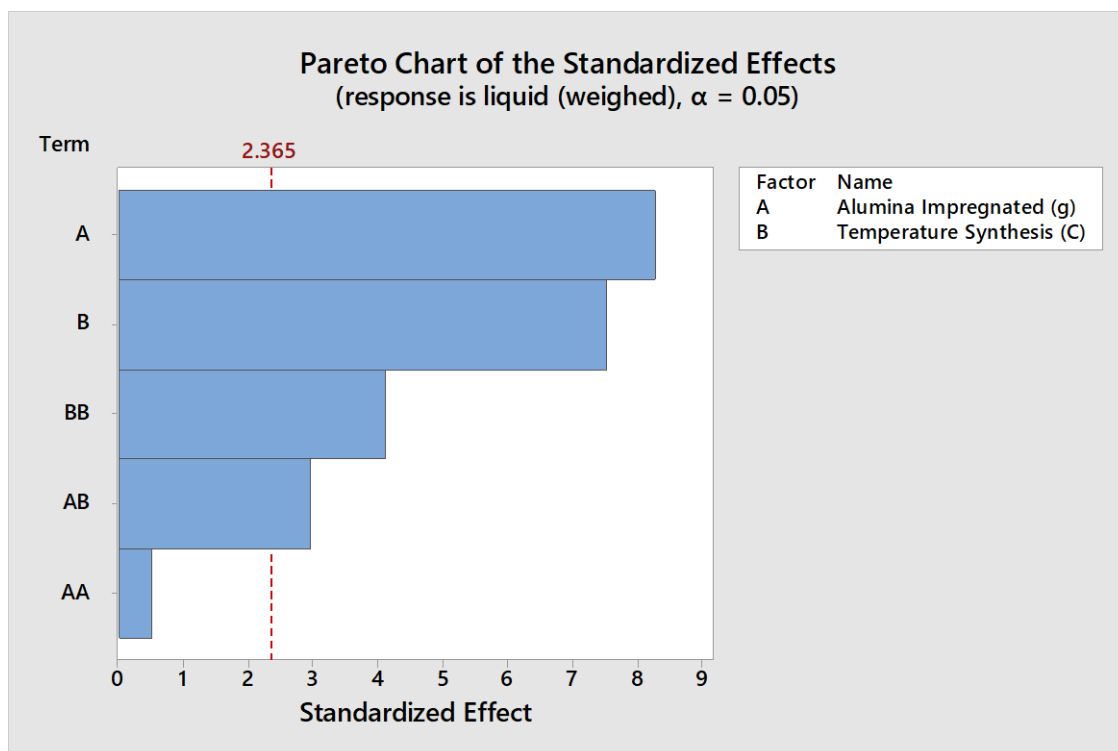


Fig. 41: Pareto chart of optimization of the catalyst

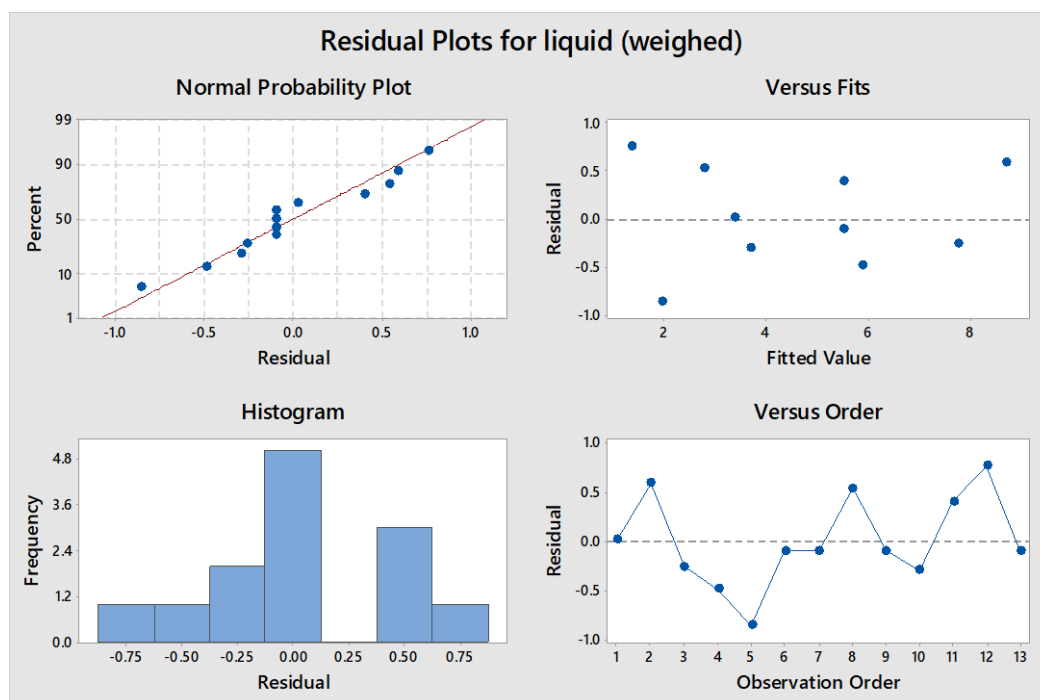


Fig. 42: Residual plots of optimization of the catalyst

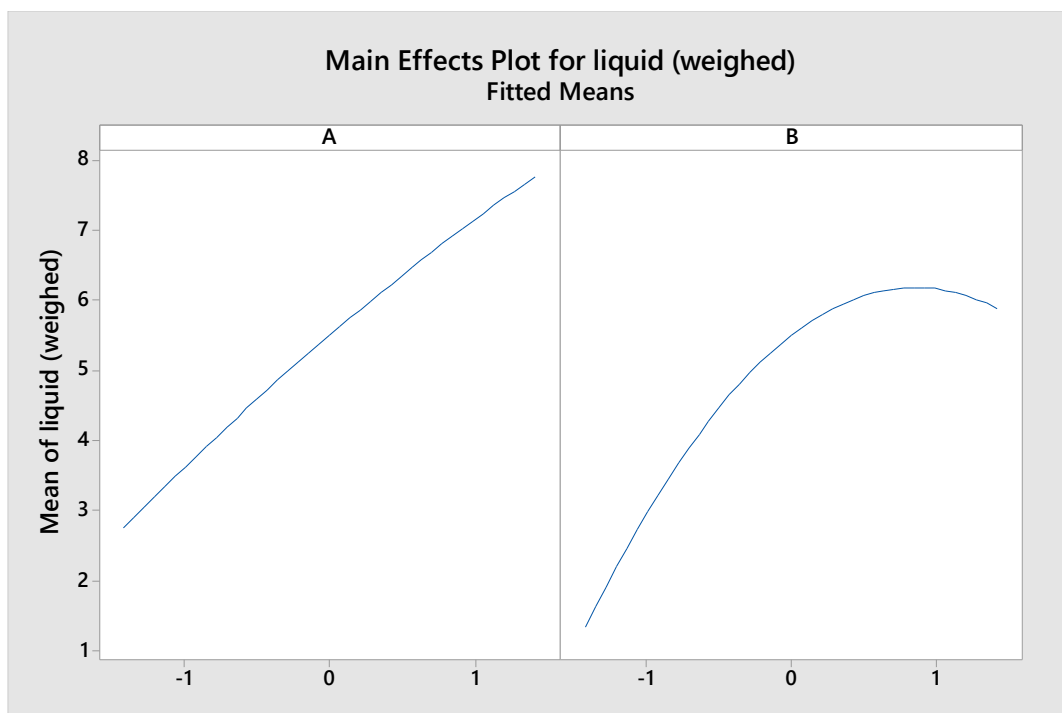


Fig. 43: Main effects plot for the optimization of the catalyst

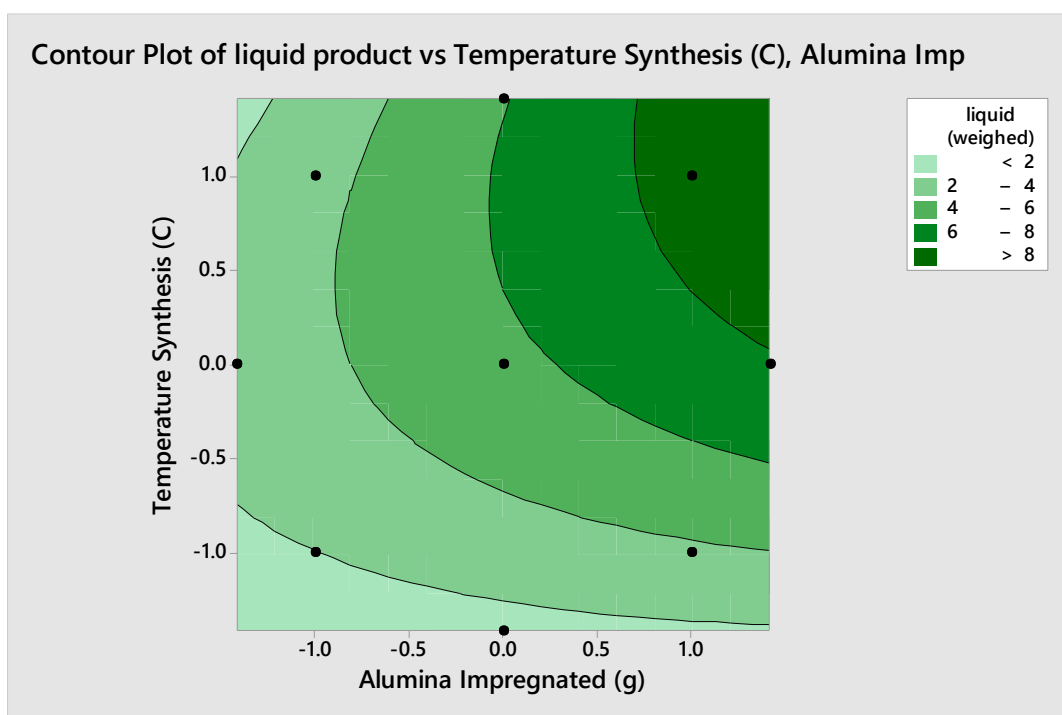


Fig. 44: 2D contour plot for the effect of aluminum loading and synthesis temperature on maximum liquid yield (g)

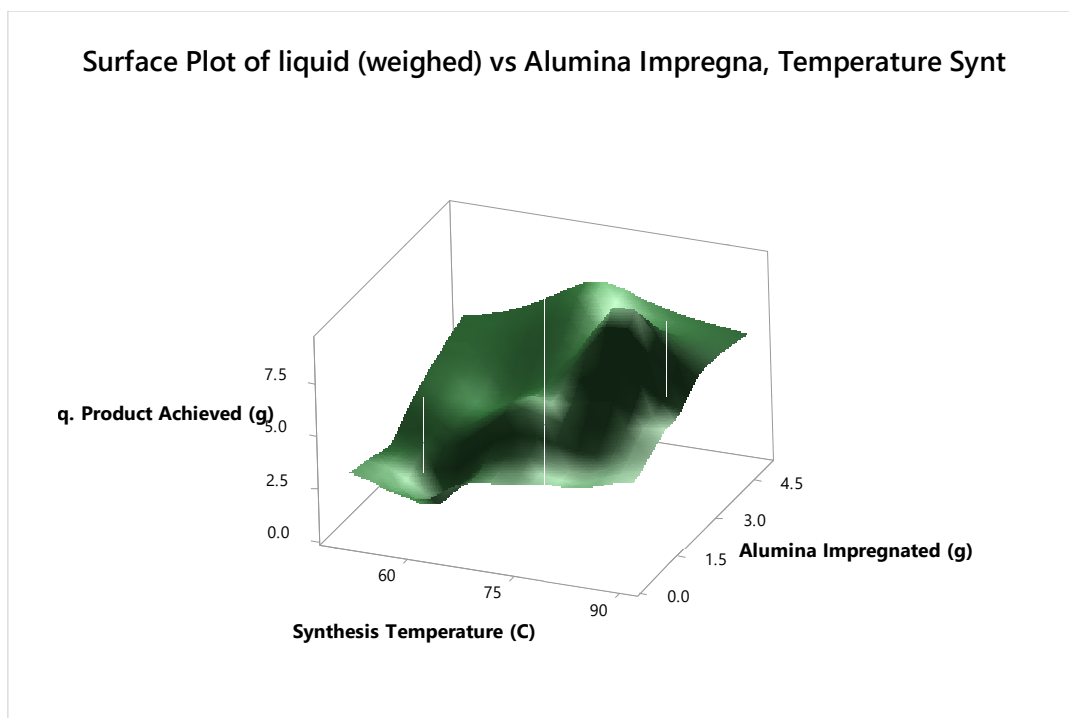


Fig.45: 3D surface plot for the of effect of aluminum loading and synthesis temperature on maximum liquid yield (g)

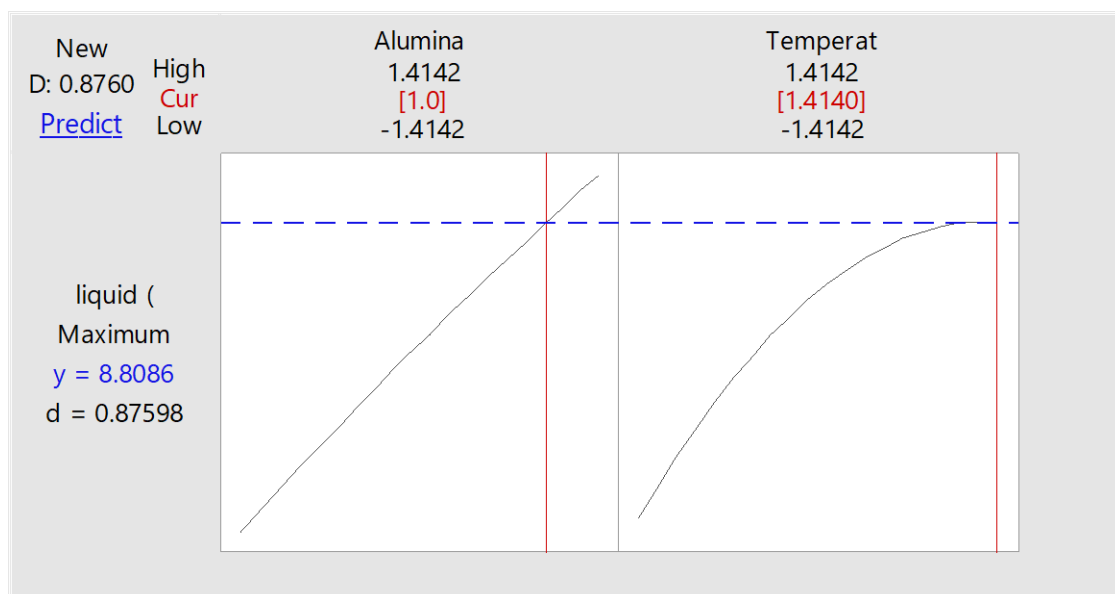


Fig. 46: Response optimizer plot for liquid yield for the catalyst optimziation

For catalyst optimization, RSM with CCD was implemented. The experimental data (liquid yield) obtained were utilized for the formulation of the following quadratic regression equation (4.2.1) using coded

variables to predict liquid yield from the plastic waste mixture. It must be noted that coded variables were used for all statistical analysis in order to maintain DOE as orthogonal. Since orthogonal design provides options to estimate model terms (each main effect and interaction) independently (i.e. bias less) and thereby makes the analysis straightforward. Equation (4.2.1) represents the general model equation which includes all significant and non-significant factors. On plotting the model equation to predict the liquid yield, Fig. (47) shows the regression between experimental and predicted data with respect to each run. The value of R^2 was found to be 95.6% which is quite good that shows the regression model fitted well with the experimental data. Fig. (47) also shows the adjusted coefficient of determination ($\text{adj. } R^2 = 0.952$) for the liquid yield, suggesting that model can clarify 95.2% of the variability and only 4.8% of the total variations are not interpreted by the model, which is acceptable. Experimental vs. predicted values along with errors are also summarized in Table (20), the average error percentage turns out to be 23.9%. Besides this, the model seems to be a good fit to the data.

Model equation (in Uncoded Units): $Liquid\ (weighed) = 5.500 + 1.767 A + 1.608 B - 0.119 A * A - 0.944 B * B + 0.900 A * B$ _____ (4.2.1)

In ANOVA Table (19), it is deduced that all one-way interaction parameters are significant since their p-values are lower than alpha of 0.05. Furthermore, all 2-way interactions have p-values lower than 0.05 except $A*A$ which can be removed from the model as its contribution to the response factor does not make a difference to the outcome of the model. The following model equation (4.2.2) in uncoded values represents the truncated equation where insignificant factors are truncated. The p-values of the truncated model and both factors (A and B) in the truncated

regression model are found to be the same ($p=0.000$) as that of previous model i.e. equation (4.2.1). However, p -values of linear ($p=0.003$) and cross ($p=0.014$) interactions are decreased slightly. The truncated model was also fitted to the data and it was fitted well to the results with almost the same value of R^2 (95.4%).

Truncated model equation based on significance (in Uncoded Units):

$$\text{Liquid (weighed)} = 5.417 + 1.767 A + 1.608 B - 0.928 B * B + 0.900 A * B \quad (4.2.2)$$

To validate the model, the experiments were carried out twice to get the data as 9.8g and 9.9g (the weighing machine at which these data were recorded only displayed upto one decimal point). At optimum set of conditions i.e. synthesis temperature of 90°C and aluminum loading of 3g, keeping other factors pressure (1 atm), reaction temperature (400°C), catalyst to plastic ratio (1:20) and H_2/N_2 flow rate (0.01 L/min) same and obtained maximum average liquid yield 9.85g (for two runs). The percent error was calculated to be about 10%. It can be said that there is a good agreement between experimental results and model prediction and the model can adequately describe the maximizing of liquid yield from waste plastic mixture.

**Table (19): Analysis of Variance(ANOVA)
with remarks**

Model	5	55.1221	11.0244	30.26	0.000	R²-95.6%
Linear	2	45.6860	22.8430	62.70	0.000	
A	1	24.9914	24.9914	68.60	0.000	Significant
B	1	20.6947	20.6947	56.80	0.000	Significant
Square	2	6.1961	3.0980	8.50	0.013	
A*A	1	0.0981	0.0981	0.27	0.620	Not Signi.

B*B	1	6.1959	6.1959	17.01	0.004	Significant
2-Way Interaction	1	3.2400	3.2400	8.89	0.020	
A*B	1	3.2400	3.2400	8.89	0.020	Significant
Error	7	2.5502	0.3643			
Lack-of-Fit	3	2.3502	0.7834	15.67	0.011	
Pure Error	4	0.2000	0.0500			
Total	12	57.6723				

Table (20): Experimental vs predicted using model equation of optimziation of catalyst

1	0.00	-1.41	2.10	1.34	36.29
2	-1.00	-1.00	1.10	1.96	78.36
3	1.00	-1.00	3.40	3.70	8.71
4	-1.41	0.00	3.30	2.76	16.27
5	0.00	0.00	5.70	5.00	12.28
6	1.41	0.00	7.50	7.76	3.48
7	-1.00	1.00	1.10	1.88	70.73
8	1.00	1.00	9.40	8.71	7.32
9	0.00	1.41	5.90	5.89	0.24
10	0.00	0.00	5.20	5.50	5.77
11	1.41	1.41	3.40	5.95	74.89
12	0.00	0.00	5.60	6.00	3.45
13	0.00	0.00	5.90	5.50	6.78
OPT	1.00	1.41	9.90	8.80	10.03
Average					23.90

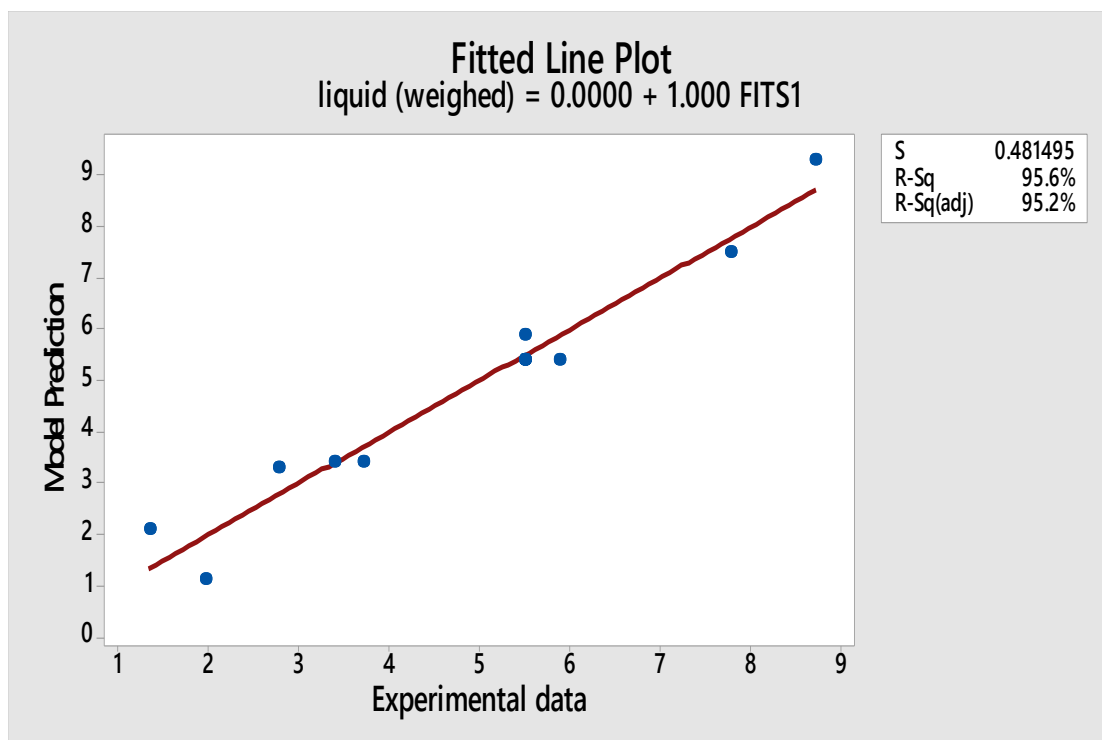


Fig. 47: Model predictions vs. experimental data for liquid yield (g) from waste plastic mixture (for all factors and interactions)

Fig. (48) summaries the GCMS data along with various other data, that is compared to the unmodified BZ as well as the optimum DBZA. For details of Fig. (48), please refer to Appendix-X. Again, these values are derived from the GCMS analysis of the liquid yield achieved according to which they are categorized as ‘aromatics, olefins, saturated aliphatic’ which make up 100%. Gas, liquid and solid also make 100% and they are categorized based on the ranges of carbon atoms i.e. C_1 - C_4 , C_5 - C_{18} and C_{19} plus, respectively. Amongst which gasoline is separately categorized based on range of carbon atoms falling from C_5 to C_{12} (Munir et al. 2017). Aromatics (like benzene, toluene), Isoparaffins (that are well branched like octadecene, dodecane) and olefins (alkenes and alkynes) have much higher antiknock value as compared to isoparaffins with less branching. Straight chained hydrocarbons or paraffins (like n-hexane) display lowest antiknock values. As a rule of thumb, the knock resistance rises as number of bonds increases making stable radicals that allow smoother and slower

reactions. Antiknock value is known by its octane rating. Usually, 87-90 octane rating is what recent cars are designed to use. The antiknock value is the fuel's friction to spontaneous combustion under compression. The larger the antiknock value, the more compression it takes to make the fuel spontaneously ignite (Horne and Lee, 2006). The alkanes, alkenes and aromatic component are the content of fuel in which the percentage of these components have significant influence on the octane number as well burning efficiency. The aromatic yield increases with the increase in doping load, this is a result of the combination of metal function and strong acid function of zeolite. The more aromatic yield produced lead to high solid yield; because the aromatics components being heavy hydrocarbons have high tendency to coke formation, which causes catalyst deactivation and hence increase the solid yield. Aromatics are crucial in gasoline blending as they are the source of valued octane rating. Since few aromatics like benzene are toxic to humans and has other various environmental concerns, hence it is undesired (Kwon et al. 2019; Garba and Galadima, 2018).

On comparing the amount of gasoline in the liquid yield from GCMS data it is deduced that optimum run has 87.39% gasoline as compared to unmodified BZ which stands at 68.4%. As per the defined set of experiments that were carried out, the maximum liquid yield of 9.4g was achieved in experiment no.8. Based on the optimum configuration, (derived from DOE results from Minitab) the optimum experiment carried out at coded value of +1,+1.414 (i.e. 3g Aluminum nitrate impregnated (22.30 wt.% alumina/zeolite) at synthesis temperature of 90°C) maximum liquid yield of 9.9g is achieved as seen in Fig. (49). Two validation experiments were also carried out for the optimum configuration for which 9.8g and 9.9g were achieved. Fig. (50) summarizes the liquid yield

achieved based on the list of experiments in Table (18). Parent BZ gives a liquid product of 3.3g whereas optimum modified BZ gives a liquid product of 9.9g. For details of Fig. (50), please refer to Appendix-V. Catalyst modification does not necessarily give better results unless the parameters have been optimized, studied and looked at. There are modifications carried out at various different parameters that do not give satisfying liquid product for instance experiment 1, 2 and 7 all give liquid product lesser than the parent BZ. On the other hand, experiment no. 8 gave about three times higher value of a liquid product of 9.4g as compared to parent BZ. Furthermore, as depicted in Fig. (50), the optimum catalyst gives 9.9g of product liquid that has 87.3% in the gasoline range as compared to the parent BZ which gives 3.3g product liquid yield and mere 68.4% in the gasoline range.

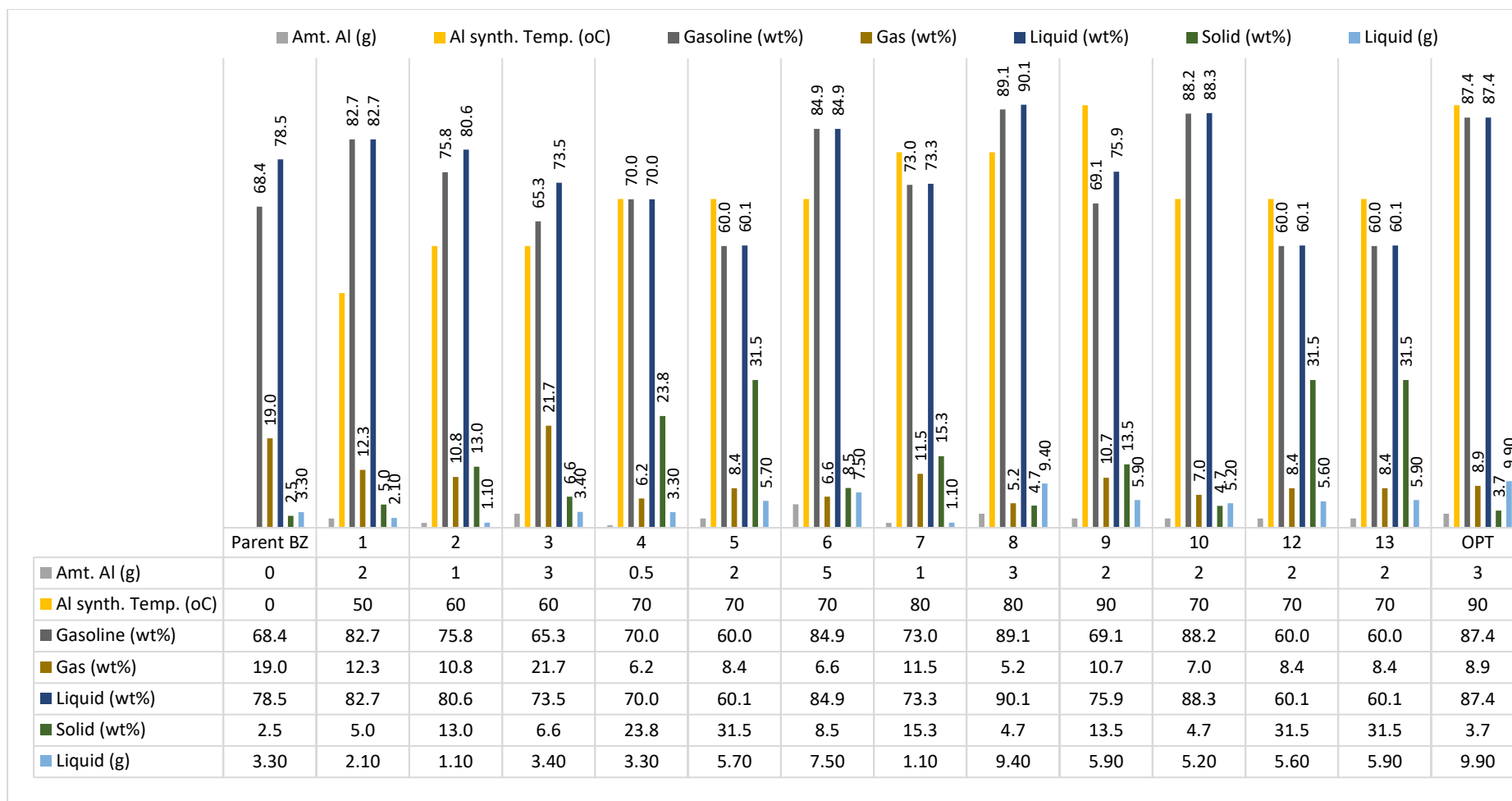


Fig. 48: Graphical and tabulated representation of catalyst optimization experiments with GCMS data

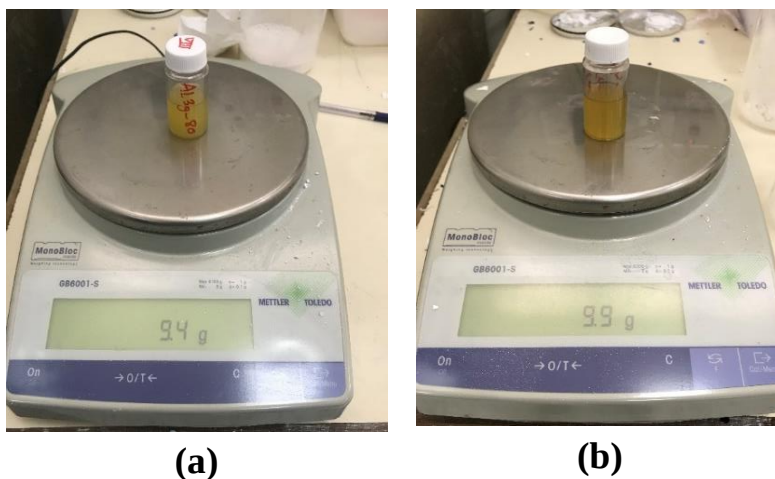


Fig. 49: (a) Exp. 8 liquid product weighted (b) optimum experiment's liquid yield weighted

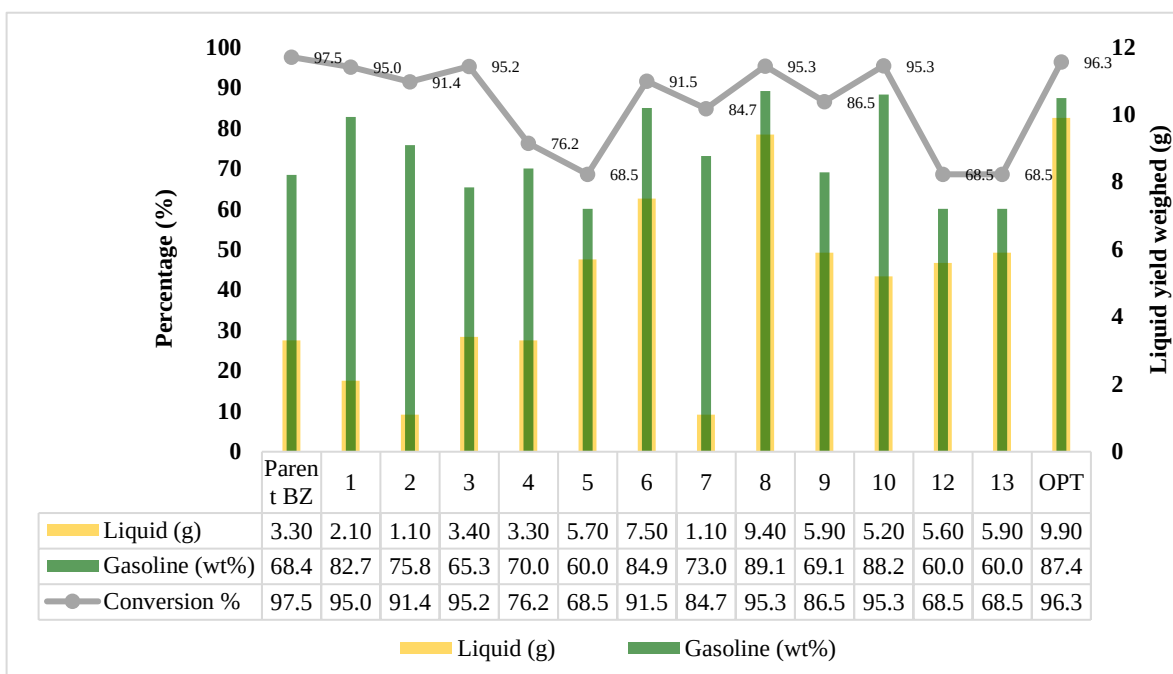


Fig. 50: Liquid product in gasoline range and conversion of plastic

Amongst the prepared desilicated-alumina impregnated samples, EDS and SEM were carried out for 8 experiment's samples out of all; namely experiment no. 1, 2, 6, 7, 8, 9, 10 and optimum; these were chosen based on different temperatures and alumina impregnation; which depicts the catalyst samples collected to dispatch for analysis based on liquid yield achieved.

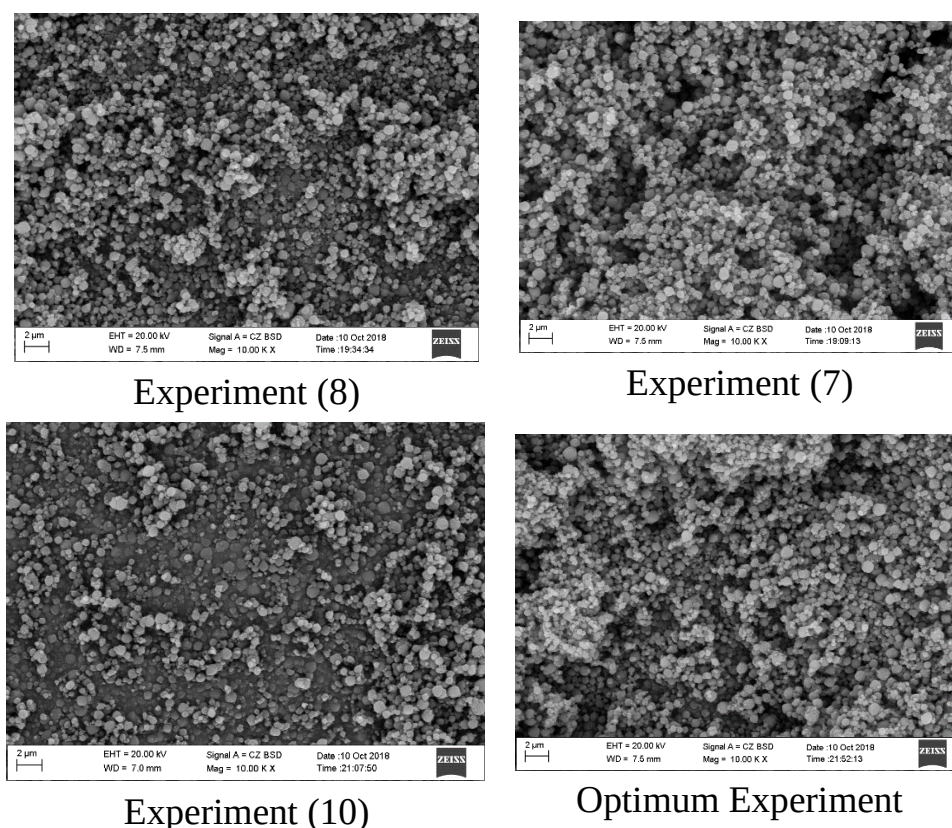


Fig. 51: SEM images of some DBZA catalyst samples

Table (21): Ratio of Si/Al from EDS data for DBZA samples

Exp. No.	1	2	6	7	8	9	10	Opt.
Si/Al Ratio	0.06	5.92	0.22	0.23	14.8	0.36	0.61	14.2

Fig. (51) depicts the SEM images of the DBZA samples based on different temperatures and impregnation. These rounded shaped particles have grown in high density and agglomerated due to electrostatic force of attraction. Each sphere has diameter in the range of 0.25-5 micrometer. Due to impregnation, morphology of the formed zeolite slightly changed in comparison to unmodified BZ. There are numerous particles scattered over the zeolite structure in the SEM images which can be alumina that

was loaded during alumina impregnation within the zeolite structure and some may have dispersed over the surface (Moliner and Corma, 2018). Note that the BZ were desilicated first, after which they were impregnated with alumina with varying load and varying synthesis temperature based on the design of experiment's table. After desilication of the BZ, it is noted that it has a Si/Al ratio of 32.47. On alumina impregnation, the ratio is expected to decrease in all samples, which it does as seen in Table (21). The optimum catalyst has a Si/Al ratio of 14.15. The catalyst that gave the highest liquid yield of 9.4g is sample no.8. Another sample was prepared based on optimum parameters suggested derived from the DOE and optimum liquid yield of 9.9g was achieved.

The aforementioned results show that the purpose of the optimization of catalyst modification is successfully achieved as the DBZA gives high amount of liquid yield with better quality (excellent percentage in the gasoline range) at the optimum conditions. The DBZA catalyst at optimum experimental conditions gives liquid yield of 9.9g and gasoline contents (wt%) of 87.4% in comparison to parent BZ that has a liquid yield of 3.3g and gasoline contents (wt%) of 68.4%. Hence the optimum catalyst is desilicated at 0.1M sodium hydroxide at 75°C and alumina impregnated with 3g alumina nitrate at synthesis temperature of 90°C gives the maximum liquid product and is prepared in bulk to be used in the optimization of process parameters.

4.3 Process parameters optimization results

On the basis of catalyst optimization carried out in section 4.2, BZ is modified and prepared using hierarchical zeolite approach ‘desilication’ after which alumina is impregnated on BZ received from zeolyst international company that has a high Si/Al ratio of 300.

The catalyst is prepared to carry on the process parameters optimization. Hence all the catalyst samples are prepared as per Table (22). After which DOE is carried out at varying temperature, pressure and plastic to catalyst ratio to find the optimum setting which gives the maximum liquid product. The ranges of these factors have been chosen from literature, while the reaction time is fixed at 60 minutes.

Based on CCD for 3 factors (temperature, pressure and catalyst to plastic ratio), coded and uncoded values can be seen in Table (24). The 5 level settings are also tabulated in the Table (23) , which indicates the range of the opted factors. Table (24) enlists the no of experiments and the corresponding results i.e. oil yield(g) acheived.

It is important to note that the liquid product acheived here on refers to the oil acheived. The response in this DOE is the oil acheived as product (which is n-heptane soluble). The achieved liquid yield is mixed with n-heptane so it could dissolves lower hydrocarbons that are in the range of C₅-C₁₈ (useful fuel like eg: gasoline, diesel, kerosene etc). The soluble liquid in n-heptane is refered to as oil. The rest of the liquid which isn’t dissolved in n-heptane is then dissolved in THF, which is an excellent solvent to dissolve higher hydrocarbons (Munir et al. 2017; Wang et al. 2013).

Table (22): Parameters involved in bulk catalyst preparation of optimized DBZA for process parameters optimization

Sr. No.	Parameter	Desilication	Alumina Impregnation
1	Chemical Used	Sodium Hydroxide	Aluminum Nitrate
2	Dilution Ratio	1g per 30ml water	1g per 80ml water
3	Concentration/Molarity	0.1M	22.3 wt. % alumina loading per zeolite
4	Temperature Synthesized	75 °C	90 °C
5	Mixing Residence time	45 minutes	60 minutes
6	Mixing rate	500 rpm	500 rpm
7	Drying time	Overnight	Overnight

Table (23): 5-levels of the DOE Table for 3 factor CCD design for process optimization

Levels	Factors		
	Temperature (°C)	Pressure (Bar)	Catalyst to Plastic Ratio
-1.633	360	1	1:05
-1	380	10	1:10
0	400	20	1:20
1	420	30	1:30
1.633	440	40	1:40

Table (24): Tabulated results of experiments carried as per DOE (coded values are in brackets) with optimum

Experiments part of DOE	Experiment No.	Temp. (°C)	Press. (bar)	C-P Ratio	Oil produced (g)
	1	420 (1)	30 (1)	1:30 (1)	5.69
	2	420 (1)	30 (1)	1:10 (-1)	6.29
	3	420 (1)	10 (-1)	1:10 (-1)	6.70
	4	380 (-1)	30 (1)	1:30 (1)	1.18
	5	400 (0)	20 (0)	1:20 (0)	9.84
	6	400 (0)	20 (0)	1:20 (0)	9.84
	7	380 (-1)	10 (-1)	1:30 (1)	2.84
	8	380 (-1)	10 (-1)	1:10 (-1)	6.33
	9	420 (1)	10 (-1)	1:30 (1)	9.42
	10	400 (0)	20 (0)	1:20 (0)	9.84
	11	400 (0)	20 (0)	1:20 (0)	9.84
	12	380 (-1)	30 (1)	1:10 (-1)	5.49
	13	400 (0)	20 (0)	1:40 (1.633)	6.05
	14	400 (0)	20 (0)	1:05 (-1.633)	3.12
	15	400 (0)	20 (0)	1:20 (0)	9.84
	16	400 (0)	20 (0)	1:20 (0)	9.84
	17	440 (1.633)	20 (0)	1:20 (0)	5.13
	18	360 (-1.633)	20 (0)	1:20 (0)	1.20
	19	400 (0)	40 (1.633)	1:20 (0)	7.8
Additional Experiments	20	380 (-1)	30 (1)	No catalyst	2.63
	21 (OPT)	420 (1)	20 (0)	1:30 (1)	11.27
	22	400 (0)	20 (0)	1:30 (1)	6.4
	23	400 (0)	30 (1)	1:10 (-1)	7.29
	24	400 (0)	10 (-1)	1:10 (-1)	1.65
	25	400 (0)	10 (-1)	1:30 (1)	10.45

The following 10 figures (52) to (59) are derived from the minitab softwares that analyzes and summaries the DOE results, where 'Temp' represents Temperature of the reaction and 'Press' represents the start pressure of the reaction and 'C-P Ratio' is the catalyst to plastic ratio employed in the feed.

Fig. (52) pareto chart indicates that the involved variables have significant interaction with each other as they extend beyond the red vertical reference line. However, Pressure and C-P ratio show less significance as compared to temperature. Fig. (53) shows four graphs which exhibits normal distribution. The residuals versus fits graph appear to be randomly scattered both above and below 0, that indicates constant variance. The histogram shows that the data is normal distributed, while the normal probability graph verifying the normal distribution which shows reasonable scattering of the data around the model values. However, few variables having larger residuals. Fig. (54) main effects plot indicates the response and contribution of liquid product with changes in selected variables. It is observed that after a point raise in temperature does not add to the liquid yield, same goes with pressure and C-P ratio which shows a converse U curve. For instance, in case of temperature, at low level (-1.633) the response is also low. However, response increases with the increase of levels and shows a maximum value at its high level (+1), then slightly decrease when it comes to the extreme level (+1.633). This can be explained that at low temperature cracking is also low so less amount of liquid is produced. Upon increasing temperature, more cracking takes place which results more liquid yield. Decrease of liquid yield after reaching maximum at higher temperature may be due to cracking of liquid molecules into gas phase. Similarly, when C-P ratio is low, the cracking of plastic is also less and hence low oil yield is produced. Once the C-P ratio

is higher than the optimum value at medium level (0) then oil yield starts decreasing due to more cracking towards the gaseous phase than the liquid phase. Same explanation goes with the pressure for the response. Overall, the response of oil yield indicates that it is affected by all factors. However, reaction temperature factor is found to be the only statistically significant factor than pressure and C-P ratio. Fig. (55) shows the interaction of each factor with each other at different levels. It is observed that temperature vs. pressure as well as temperature vs. C-P ratio have significant interaction with each other. However, pressure and C-P ratio shows absolutely no interaction with each other. Fig. (56), (57) and (58) show the summarized 2D contour and 3D surface plots (all possible combinations), respectively, which show the data converges and points to an optimum value, which is expected as the selected range from the literature indicates that the optimum can be found within the selected range. Both response surface and contour plots were generated by selecting two parameters at a time while the other parameter(s) was kept constant at center level(s). Inner circles (dark green) in contour plots and concave surfaces (shining surfaces) in surface plots present the optimum (maximum) values of the response for each set of data. It shows the placement of optimum value for the given range values is reached. It is important to find exact optimum operating conditions (optimal point) where maximum oil yield is obtained. In order to find the exact optimal set a single optimal condition, response optimizer plot for oil yield was generated using MINITAB as depicted in Fig. (59). The optimum coded values (red in color) for reaction temperature, pressure and C-P ratio are +1, 0 and +1, respectively. For these coded values, the true values are calculated to be 420°C (temperature), 20 bar (pressure) and (1:30) (C-P ratio), which result the possible oil yield value of 10.49g.

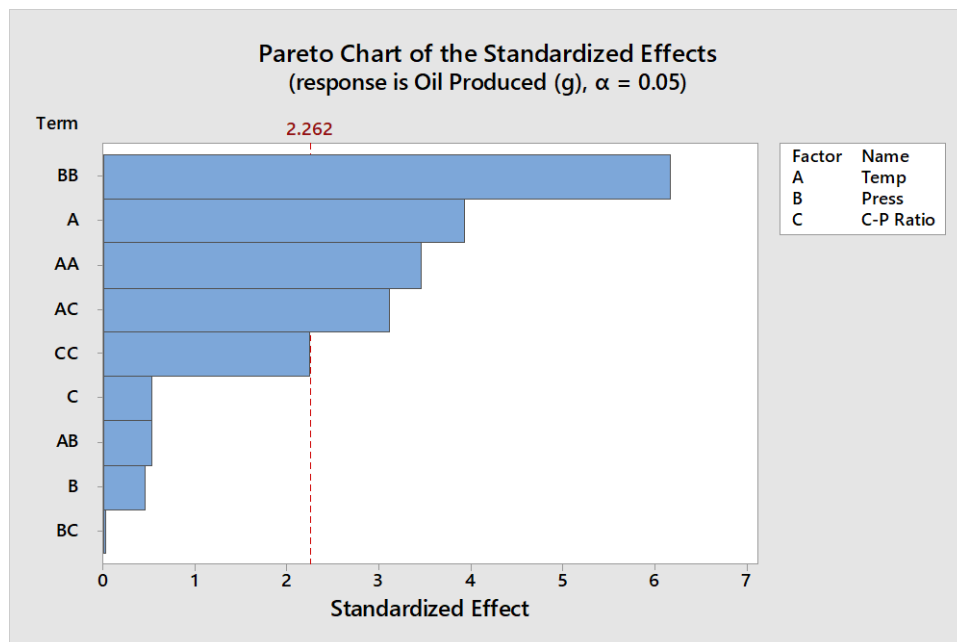


Fig. 52: Pareto chart for process optimization

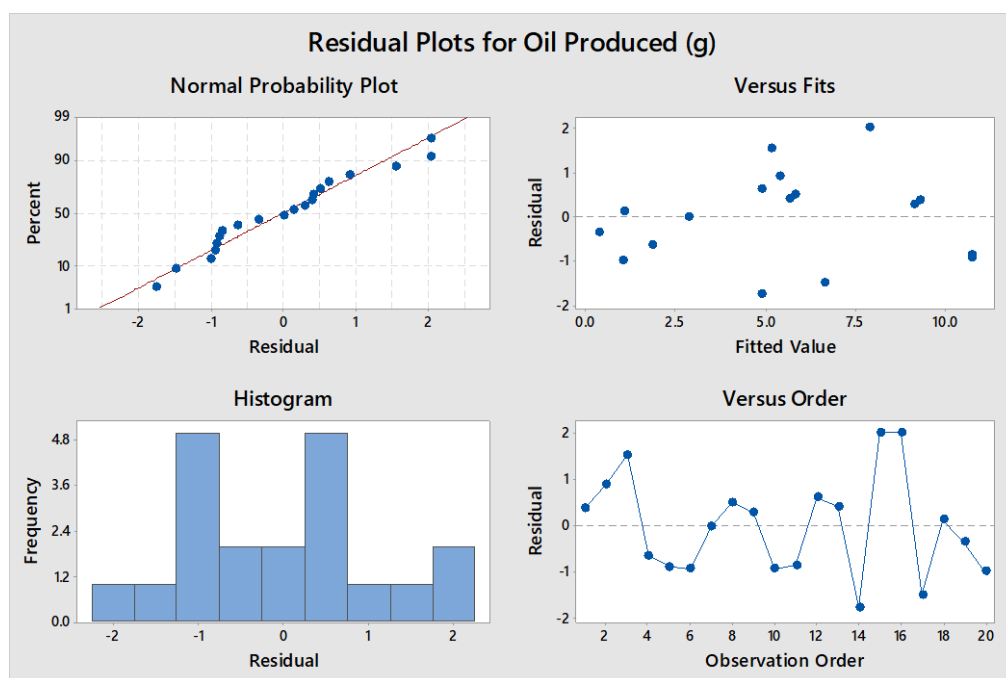


Fig. 53: Residual plots of process optimization

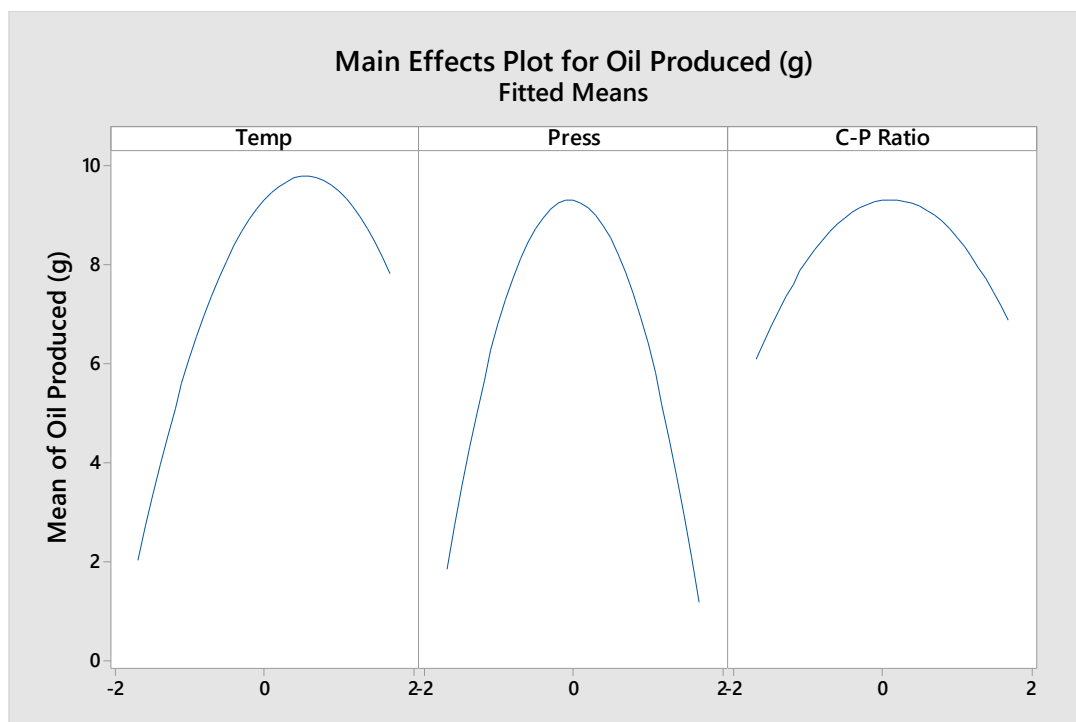


Fig. 54: Main effects plots of pressure, temperature and C-P ratio for response oil yield in process optimization

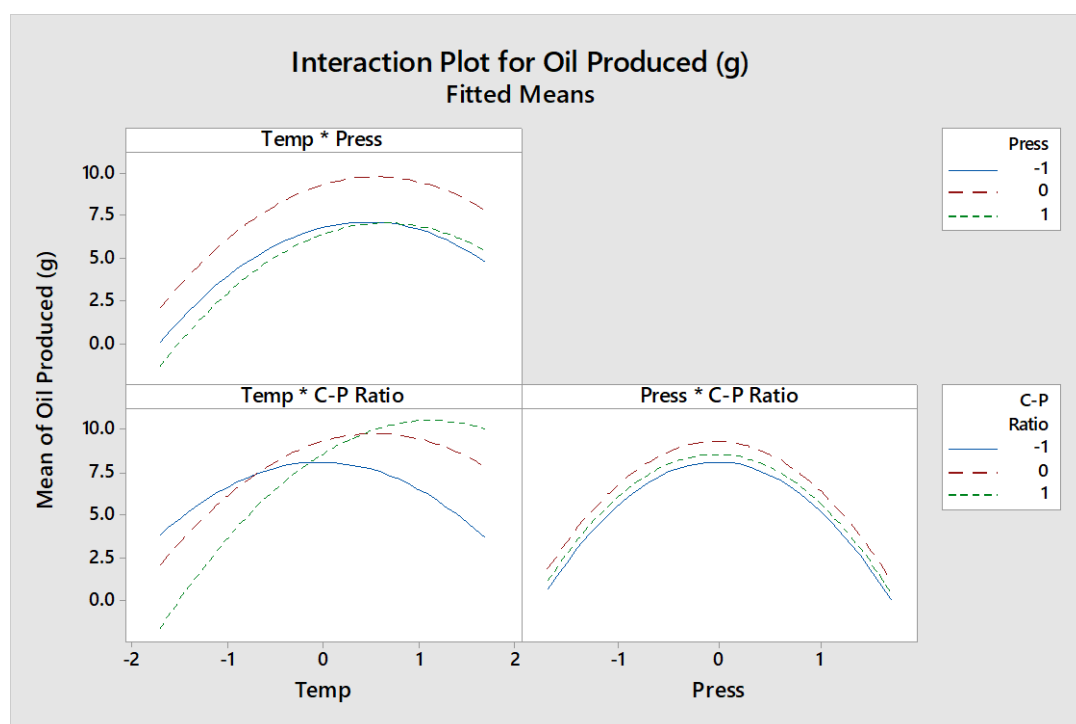


Fig. 55: Interaction plots of all factors for the process parameter optimization

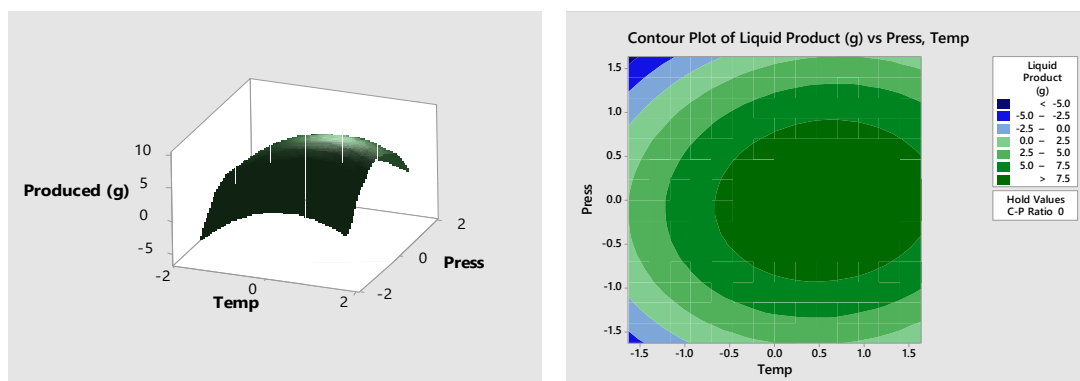


Fig. 56: Temp vs. Press 3D Surface and 2D contour plots for oil yield

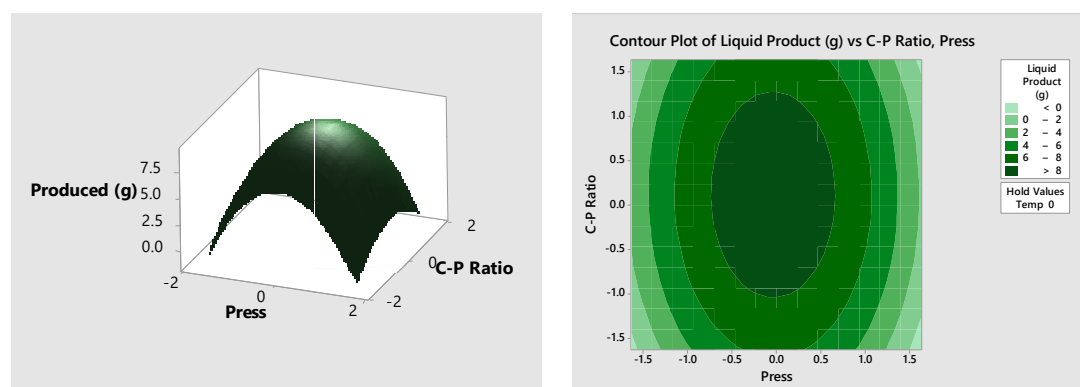


Fig. 57: Press vs. C-P ratio 3D Surface and 2D contour plots for oil yield

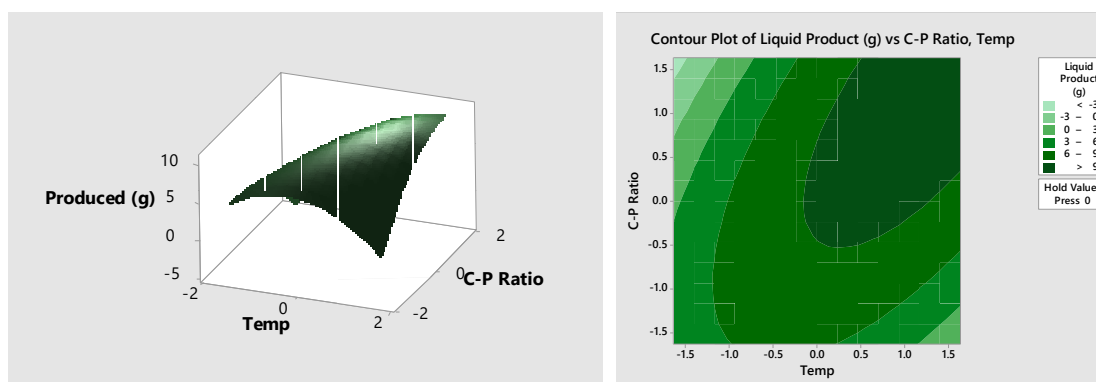


Fig. 58: Temp vs. C-P ratio 3D Surface and 2D contour plots for oil yield

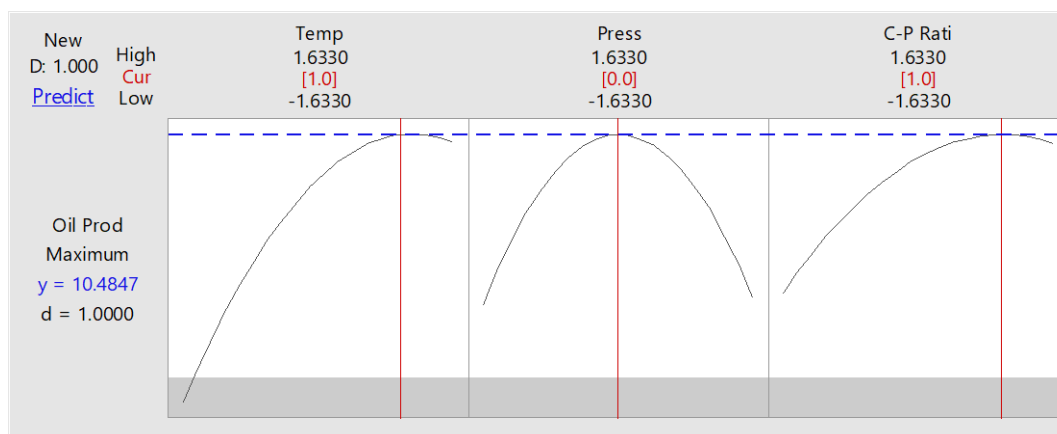


Fig. 59 Response optimizer plot for oil yield for process optimization

For process parameters optimization, RSM with CCD was again implemented. This time experimental data (oil yield) obtained were utilized for the formulation of the following quadratic regression equation (4.3.1) using coded variables to predict oil yield from the plastic waste mixture. Again coded variables were used for all statistical analysis to maintain DOE as orthogonal. Since orthogonal design provides options to estimate model terms (each main effect and interaction) independently (i.e. bias less) and thereby makes the analysis straightforward as discussed above.

Model regression equation in uncoded units

Liquid Oil Product (g) =

$$9.298 + 1.702 \text{ Temp} - 0.198 \text{ Press} + 0.232 \text{ C} - \\ P \text{ Ratio} - 1.511 \text{ Temp} * \text{Temp} - 2.696 \text{ Press} * \text{Press} - 0.977 \text{ C} - \\ P \text{ Ratio} * \text{C} - P \text{ Ratio} + 0.298 \text{ Temp} * \text{Press} + 1.742 \text{ Temp} * \text{C} - \\ P \text{ Ratio} - 0.016 \text{ Press} * \text{C} - P \text{ Ratio} \quad (4.3.1)$$

where, 'Temp', 'Press' and 'C-P Ratio' represent reaction temperature (°C), initial cold pressure (bar) (pressure attained at ambient temperature i.e. before start heating) and the catalyst to plastic ratio employed as a feed in the reactor. Fig. (60) shows the regression plot of experimental data with predicted data from model with respect to each run. The value of R^2 was found to be 91% which is quite good that shows the regression model fitted

well with the experimental data as can also be seen in Fig. (61). Fig. (60) also shows the adj. $R^2 = 0.905$ for the oil yield, suggesting that model can clarify 90.5% of the variability and only 9.5% of the total variations are not interpreted by the model, which is also acceptable as already discussed above. Experimental vs. predicted values along with percent errors for each run is also tabulated in Table (26), which indicates the average error to be 25.65%.

From ANOVA Table (25), it can be seen that amongst all the nine parameters, five are significant since their p-values are lower than 0.05 (alpha value). It can also be seen that all the squares of the factors have p-values lower than 0.05, so it can be concluded that these squares of the factors are significant and should not be removed from the model. Furthermore, 2-way interaction only Temperature and C-P Ratio shows significance, rest fail the p-test and can be truncated from the model.

Similar to catalyst optimization, a new truncated model equation (4.3.2) was developed using backward elimination method, based only on the significant factors (ignoring the insignificant factors), as given below:

Truncated model regression equation in uncoded units

$$\begin{aligned} \text{Oil yield}(g) = & 9.298 + 1.702 \text{ Temp} - 1.511 \text{ Temp} * \\ & \text{Temp} - 2.696 \text{ Press} * \text{Press} - 0.977 \text{ C} - \text{P Ratio} * \text{C} - \\ & \text{P Ratio} + 1.742 \text{ Temp} * \text{C} - \text{P Ratio} \end{aligned} \quad (4.3.2)$$

The p-values of the new truncated model (p-value=0.001) and linear interaction in pressure (p-value=0.000) in the new truncated regression model are found to be the same as compared to the previous model i.e. equation (4.3.1). However, p-values of temperature factor (p-value=0.011), linear interaction in temperature (p-value=0.022) and cross interaction between temperature and C-P ratio (p-value=0.037) are increased slightly. Additionally, the linear interaction in C-P ratio becomes statistically

insignificant in new model. The new truncated model was also fitted to the data and the value of R^2 is found to be 74.68%. This decrease in R^2 value may be due to the less number of factors in the model. It is well known fact that if the number of factors are less in a model then deleting insignificant terms is not recommended as this makes the model non-hierarchical (Irfan et al. 2020). To make the model hierarchical, at least individual factors (pressure and C-P ratio) are needed.

Table (25): ANOVA Table for process optimization

Source	DF	Adj SS	Adj MS	F-Value	P-Value	Remarks
Model	10	229.69	22.96	9.14	0.001	
Blocks	1	39.31	39.31	15.63	0.00	
Linear	3	39.85	13.28	5.28	0.02	
Temp	1	38.61	38.61	15.36	0.00	Significant
Press	1	0.52	0.52	0.21	0.66	Not Signi.
C-P Ratio	1	0.72	0.72	0.29	0.61	Not Signi.
Square	3	125.57	41.86	16.65	0.00	
Temp*Temp	1	30.15	30.15	11.99	0.01	Significant
Press*Press	1	96.02	96.02	38.19	0.00	Significant
C-P Ratio*C-P Ratio	1	12.62	12.61	5.02	0.05	Significant
2-Way Interaction	3	24.98	8.32	3.31	0.07	
Temp*Press	1	0.71	0.71	0.28	0.61	Not Signi.
Temp*C-P Ratio	1	24.26	24.26	9.65	0.01	Significant
Press*C-P Ratio	1	0.00	0.00	0.00	0.98	Not Signi.
Error	9	22.63	2.51			
Lack-of-Fit	5	22.62	4.52	3572.9	0.00	
Pure Error	4	0.01	0.00			
Total	19	252.33				

**Table (26): Experimental vs predicted liquid yield
from the model**

Exp. No.	Actual oil yield(g)	Predicted oil yield(g)	Error (%)
1	5.6978	5.8740	3.09
2	6.2942	6.9580	10.55
3	6.7016	5.7260	14.56
4	1.1764	0.9900	15.84
5	9.8374	9.2980	5.48
6	9.8374	9.2980	5.48
7	2.8386	1.9140	32.57
8	6.3370	4.4020	30.53
9	9.4174	7.7060	18.17
10	9.8374	9.2980	5.48
11	9.8374	9.2980	5.48
12	5.4910	4.4420	19.10
13	6.0514	7.0715	16.86
14	3.1174	3.3138	6.30
15	9.8374	9.2980	5.48
16	9.8374	9.2980	5.48
17	5.1272	8.0480	56.97
18	1.1954	1.4893	24.58
19	7.8000	6.7853	13.01
20	2.6260	2.4319	7.39
21	11.2740	10.5750	6.20
22	6.4630	8.5530	32.34
23	7.2920	5.2110	28.54
24	1.6484	2.4860	50.81
25	10.4514	6.0710	41.91
Average			25.65

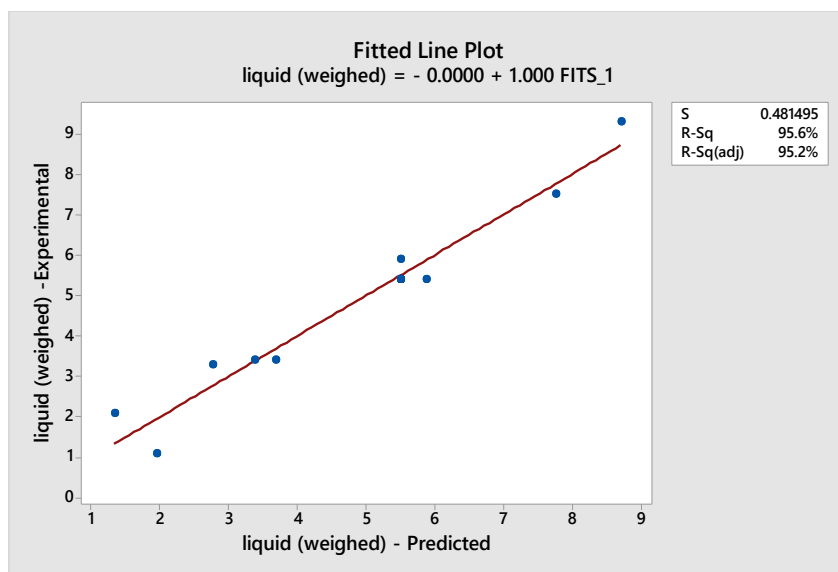


Fig. 60: Fitted line plot

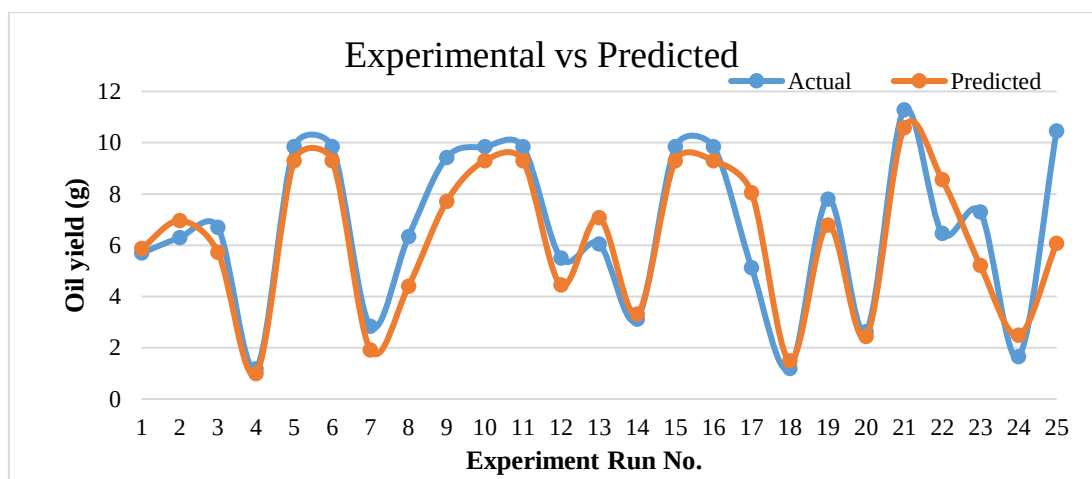


Fig. 61: Experimental vs predicted oil yield from the model

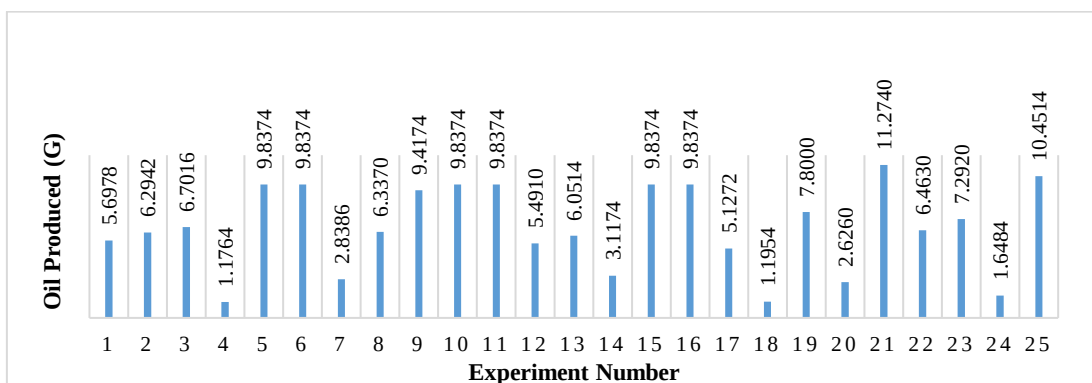


Fig. 62: Summary of product oil yield (g) based on experiments carried out

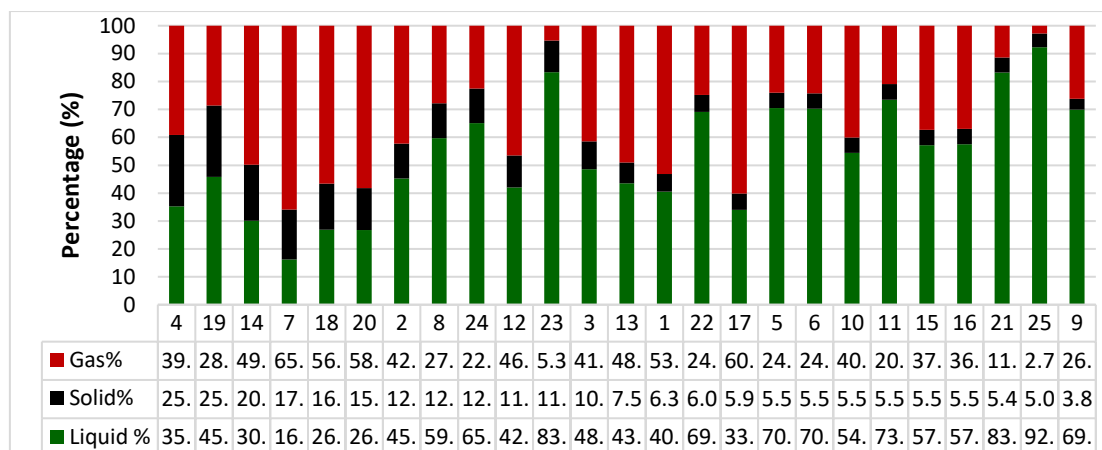


Fig. 63: Solid, liquid and gas yield distribution of the product yield

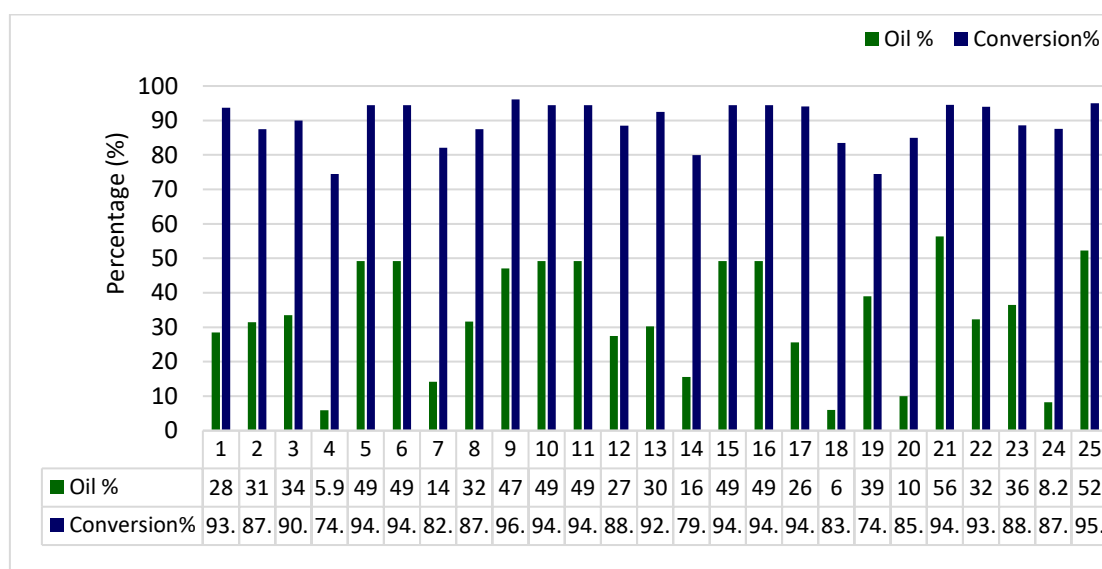


Fig. 64: Amount of oil percentage achieved in liquid yield and conversion of all experiments carried

Based on the optimizer plot, it suggests that at [1,0,1] configuration, i.e. temperature (420°C), pressure (20bar) and C-P ratio (1:30), the model predicted liquid product should be 10.487g. On carrying out this experiment no. 21, a product yield of 11.27g is achieved. To validate the model outcome, two experiments were carried out in which 11.14g and 11.28g were achieved. It is indeed the optimum at the suggested configuration, however with a tolerance in predicted value. Purely judging and going by the amount of oil achieved it is concluded that the optimum

condition is temperature 420°C, pressure 20 bar and C-P ratio of 1:30. However, if energy factors are to be taken as constraints at this point, the best is experiment no. 25 that is carried out at configuration [0,-1,1] i.e. temperature (400°C), pressure (10bar) and C-P ratio (1:30) that gives a oil weight of about 10.45g. At pressure and temperature lower than the optimum, if energy factors is to be considered, this would be the best configuration, as it has a difference to the optimum of only 0.82g. Furthermore, experiment no. 25 gives a higher liquid yield percentage of 92% as compared to that of , experiment 21 which gives 83%. Experiment no. 25 also gives the highest conversion acheived which is 95%.

Observing Fig. (62), (63) and (64), the product distribution varies extensively and difficult to predict, which indicates the complexities in polymer process and the need for process optimization of the process of cracking of plastics to fuel. It can be concluded that considering energy factors as constraints, liquid yield (%), conversion (%) and oil acheived (g), the experiment no. 25 is the optimum, which gives 95% conversion, 92% liquid yield amongst which 52% is in the useful fuel range, 5% solids and 3% gas.

Discussing the catalytic degradation of plastics in the recent past 5 years: Kumar and Singh (2014) also carried out optimization for HDPE at C-P ratio of 1:4 and they obtained maximum liquid yield of 78.7% at 450°C. Hong et al. (2017) used desilicated ZSM-5 on PP to achieve a conversion of about 90%. Shehata et al. (2017) used PP, PET, PVC and PE over natural zeolite where maximum liquid yield of 50% was acheived at 550°C. In another recent study done by Akubo et al. (2019), HDPE has been pyrolysed in a fixed bed two stage pyrolysis-catalysis reactor at a catalyst temperature of 600°C. Abdulkareem et. al (2019) studied waste PP in catalytic process where the waste polymer was degraded in an organic

solvent (Toluene) by a bi-metallic catalyst (CoMo/Al₂O₃) into solid residue, liquid fuel oil and flammable gaseous hydrocarbon products after 1.25 hr of the catalytic reaction at temperature range of 260 – 325°C and they achieved 72% of conversion and 36% of liquid yield. Another study done by Erawati et al. (2019) where PP was employed in pyrolysis-catalysis reactor at varied temperatures of 400-430°C achieved highest liquid yields and the highest gas yield of 55.74% and 49.10%, respectively, which had no residue solid. Further comparison of present research work to some recent literature is illustrated in Table (27) (a lot more of it is cited in Appendix-1, but these are most relevant).

The closest comparable research work in terms of process and feed conditions is a study done by Munir et al. (2017), where hydrocracking of waste plastic mixture using micro-mesoporous composite zeolite (i.e: Al-SBA-15, MZ-15, Al-SBA-16 and MZ-16) are used at 425°C, cold hydrogen pressure of 20 bar, reaction time of 60 min and feed to catalyst ratio equal to 20:1, achieving a maximum conversion of 90%, maximum liquid yield of 70% and oil yield of 65%. Another more recent work by Miandad et al. (2019) can be compared to our work as it roughly has the same plastic feed (ie: PP+PE+PS) and about the same reaction temperature. On using natural zeolite they have achieved a maximum liquid yield of 44% whereas our work used modified BZ and achieved a liquid yield of 92% at optimization conditions. This research work has reported the best liquid yield, conversion and oil yield at the process conditions in comparison to the literature found to the best of our knowledge.

**Table (27): Comparison of present study with
the past five years**

Researcher	Plastic type used	Temp. (°C)	Catalyst	Liquid Yield (%)
Our research	PS, PP, LDPE, HDPE	380-440	Hierarchical BZ	26-92
Miandad et al. (2019)	PS PP PE PS+PP PS+PE PP+PE PS+PE+PP PS+PE+PP+PET	450	Hierarchical natural zeolite	70 40 40 54 44 44 44 30
Supatra et al. (2019)	PS, PP, LDPE, HDPE	500	Bentonite clay	86-90
Anene et al. (2018)	PP, LDPE, PP + LDPE	460	CAT-2 zeolite	51-68
Munir et al. (2017)	PS, PP, LDPE, HDPE	425	Al-SBA-15, MZ-15, Al-SBA-16 and MZ-16	70
Miandad et al. (2017)	PS, PP, PE, PS + PP, PS + PE, PP + PE, PS + PE + PP, PS + PE + PP + PET	450	Hierarchical natural zeolite	14-60
Lerici et al. (2015)	PS, PP, LDPE, HDPE	500	H–Y zeolite	42-71

4.4 Kinetic study

The plastic mixture used for this study using different differential and integral approaches is 24.76% LDPE, 29.85% HDPE, 10.57% PP and 34.82% PS. The activation energy value is obtained using isoconversional approach based on differential methods like Friedman, Freeman and Carroll (FC) and Ozawa and integral methods such as Flynn Walle Ozawa (FWO), Kissinger Akahirae Sunose (KAS), Coats Redfern (CR), Modified Coats Redfern (MCR), Doyle's approximation and Distributed Activation Energy Model (DAEM). The activation energy value is obtained by plotting their respective equations using the data from TGA and obtaining apparent activation energy and pre-exponential factor from the slope and intercept of the graph. TGA was carried out at a selected heating rate of 10°C/min, where the samples were first crushed into powdered form of which 10mg was used for TGA. The TG-conversion curves for the degradation of waste plastics show a single stage gradual degradation with single peak as seen in Fig. (65). This graph shows the degradation of mixed plastics on using BZ, ZSM-5 and optimum DBZA catalysts. Due to limited resources, TGA couldn't be carried out without catalyst. Furthermore, these TGA analyses were carried out in an inert atmosphere (N₂), it would have supported the research work strongly if it had been carried out in the presence of hydrogen.

The plastic wastes show degradation behavior with rapid loss of weight of hydrocarbons within narrow range of temperatures, as normally observed in literature too. The main reaction process starts at 550K (277°C) approximately and ends at 780K (427°C). The single step decomposition corresponds to the presence of a carbon-carbon bond that promotes the random scission mechanism with the increase in temperature (Kim et al. 2006). The curves shown in Fig. (65) have one main inflection point during

reaction. The onset of decomposition is moved to higher temperatures so the curve shifts to the right, as seen below in Fig. (65). This indicates that higher temperatures are required to achieve the same conversion level. Although the aim of the present study is not the analysis of the reaction mechanism of degradation, it should be mentioned that the presence of the hierarchical catalyst influences not only the rate of degradation, but also the course of the reaction, clearly seen in the shape of TG curve in Fig. (65). Although different heating rates have not been carried out here, it has been reported by numerous researchers that when the heating rates increases, shorter time is required for the sample to reach a given temperature at a faster heating rates. The shifting of the curves has also been observed by other authors using TGA to investigate pyrolysis of HDPE, LDPE and PP, in co-pyrolysis of oil shale with PE (Miteva et al. 2016). The TG curves of mixed plastic waste demonstrated a similar behavior but at different thermal decomposition temperatures. The curves shown in Fig. (65) are in agreement with typical decomposition trends as published by Supattra et al. (2019).

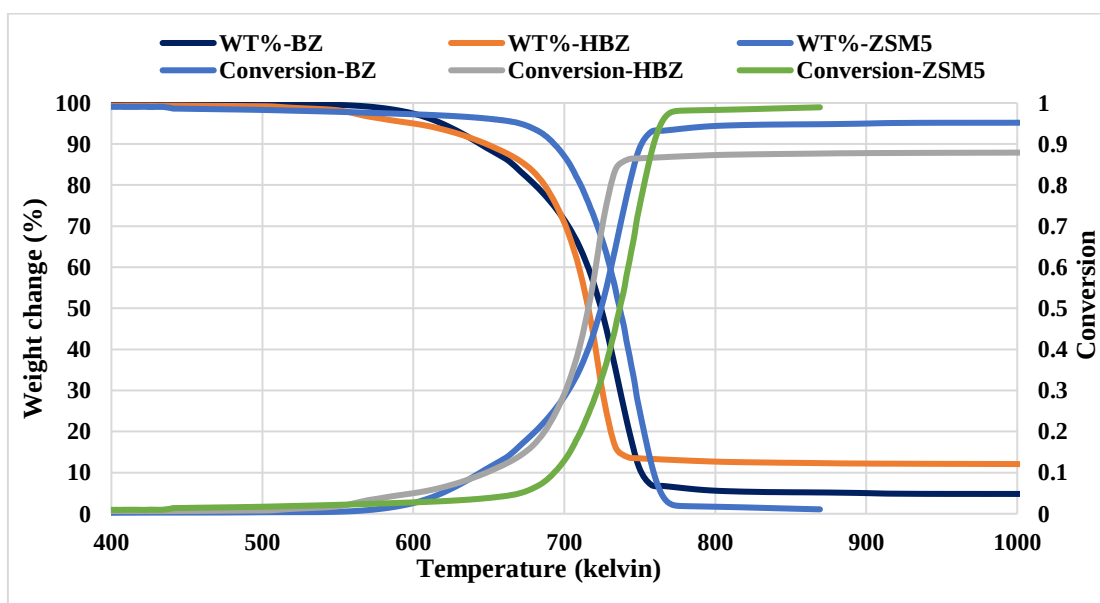


Fig. 65: TG-Conversion plot for mixed plastics at 10°C/min heating rate for ZSM-5, BZ and Hierarchical BZ (HBZ)

**Table (28): Activation energy calculated from
TGA data using various methods**

Approach		Ea ZSM-5 catalyst (kJ/mol)	R ²	Ea HBZ catalyst (kJ/mol)	R ²	Ea BZ catalyst (kJ/mol)	R ²
Differential	Friedman	133.80	0.95	44.74	0.96	60.80	0.96
	Ozawa	156.40	0.91	55.66	0.85	59.20	0.87
	FC	91.68	0.99	49.40	0.99	51.10	0.99
Integral	Doyle	170.80	0.99	67.02	0.95	86.80	0.98
	FWO	148.70	0.91	52.91	0.85	56.30	0.87
	KAS	156.10	0.94	54.71	0.85	57.50	0.87
	CR	167.80	0.99	56.54	0.94	74.70	0.97
	DAEM	156.10	0.94	54.71	0.85	57.50	0.87

**Table (29):Pre-exponential factor calculated from
TGA data using various methods**

Approach		A ZSM-5 catalyst (min ⁻¹)	A HBZ catalyst (min ⁻¹)	A BZ catalyst (min ⁻¹)
Differential	Friedman	7.70E+04	1.66E+02	2.31E+03
Integral	Doyle	3.87E+14	2.10E+07	5.25E+08
	Coats Redfern	2.07E+09	1.03E+01	2.80E+01
	DEAM	3.45E+01	1.21E+01	1.27E+01
	FWO	2.66E+01	7.48E+01	7.03E+01
	KAS	1.04E+04	1.04E+04	1.18E+04
	MCR	1.04E+04	1.04E+04	1.18E+04

Table (28) and Table (29) present the activation energy and pre-exponential factor values for BZ, DBZA and ZSM-5 calculated by using various different integral and differential approaches. Please refer to Appendix-IX for all the graphs from which the kinetic parameters has been derived. Methods such as FWO, KAS and MCR generate similar activation energy results as they are based on the same equation with very minor difference. Based on different mathematical methods, the range of activation energy values are found to be 91.68-170.80 kJ/mol, 51.10-86.80 kJ/mol and 44.74-67.40kJ/ mol for ZSM-5, BZ and DBZA, respectively. It is evident that on using DBZA, the process requires lowest activation energy in comparison to unmodified BZ and ZSM-5. Please refer to Appendix-VII for graphs generated by respective methods by which the E and A are calculated.

On employing the mathematical methods mentioned in section 3.2 on the TGA data, the order of the reaction (n) is found to be 0.5, 1.5 and 1.3 for DBZA, BZ and ZSM-5 catalysts, respectively.

**Table (30): Order of reaction comparison
with literature**

MPW	Order of Reaction (n)			
	Diaz et. al. (2016)	Wu et. al (2015)	Saha et. al (2005)	This research
HDPE	1.7	0.74	-	1.5 using BZ 1.3 using ZSM-5 0.5 using HBZ
LDPE	0.95	0.63	-	
PP	0.75	0.9	-	
PS	0.9	0.5	-	
PET	2.8	-	1-1.82	-

**Table (31): Activation Energy comparison
with literature**

MPW	Activation Energy (kJ/mol)				
	Encinar & González (2008)	Díaz et. al (2016)	Zing & Zhang (2019)	Miteva et. al (2016) [using FWO method]	This research [using FWO method]
PP	153-265	261	64.69	267.4 174.9 using ZSM-5	56.3 using BZ 148.7 using ZSM-5 52.9 using HBZ
HDPE	-	202			
LDPE	220-259	267		-	
PS	104-251	192		-	

Table (30) & Table (31) respectively reflects order of reaction and activation energy comparison to literature. In literature, it is reported that all polymers follow the same pattern: single step decomposition shifted to higher temperatures (in the following order: PS < PET < PP < LDPE < HDPE). It is also widely accepted in literature that substituted/branched polymers (PET or PP) degrade at lower temperatures than linear polymers (HDPE and LDPE). Plastic waste thermal decomposition ranges are as follows: HDPE: 425-565°C, LDPE: 443-535°C, PP: 415-540°C, PET: 395-520°C, and PS: 372-452°C (Silvarrey and Phan, 2016).

Encinar and González, (2008) reported the values of activation energy in isothermal and dynamic regimen which are as follows: natural polystyrene: 136, and 168 to 286 kJ/mol, recycled plastic: 250, and 150 to 290 kJ/mol, LDPE: 285, and 220 to 259 kJ/mol, acrylonitrile butadiene styrene: 118, and 104 to 251 kJ/mol, polyenterophthalate of ethylene: 161,

and 117 to 255 kJ/mol, PP: 169, and 153 to 265 kJ/mol. A lot has been reported in literature on independent plastic's activation energy. Miteva et al. (2016) reported that “on analysis of non-isothermal data using FWO and KAS methods, values of 267.34 and 269.07 kJ/mol for E were obtained, respectively. They also claimed that apparent activation energy for the degradation of polyolefin mixture decreases considerably with addition of catalyst (174.97 and 171.80 kJ/mol determined by FWO and KAS methods, respectively)”. It is important to note that the individual degradation of various plastic types having higher activation energy than mixed plastics; which is observed by various researchers like Murichan and Cherntongchai, (2014). This was also reported way earlier by Miranda et al. (2001) in their study that for the PP/PE mixture, PP caused a reduction of the activation energy. They explained that free radicals were initially formed from the less stable polymer, which was PP in this case, due to a transfer of hydrogen. Then, these free radicals destabilized the more stable polymer (LDPE), resulting in the lower activation energy of the polyolefin mixture. The same explanation was also addressed by Chowlu et al. (2009). There are no kinetic parameters for the degradation of waste plastic mixture using BZ catalyst in literature to the best of our knowledge.

Recently, TGA data was used to study the combustion characteristics of waste plastics and semi coke mixture at different heating rates with temperature ranging from room temperature to 1173 K, the E value was found to be 64.69 kJ/mol (Zing and Zhang, 2019). The most recent work with plastic feed mixture (i.e. PP+PS+PE) and reaction temperature (same as our study) is reported by Miandad et al. (2019). The decomposition mechanism pattern of Fig. (65) is completely in line and agreement with TGA reported and discussed by Miandad et al. (2019) as well.

It is imperative to note that the activation energy values do not signify in any sort of direction regarding the mechanism of the reaction that

happens during the reaction process. However, these values only quantify the overall reaction rate and energy requirements for the catalytic process. Although the aim of the present study is not the analysis of the reaction mechanism of degradation, it should be mentioned that the presence of the catalyst influences not only the rate of degradation, but also the course of the reaction as clearly seen from the TG curves. It can be concluded that one of the main issues of pyrolysis of plastic waste is that the thermal decomposition reaction largely varies depending on the nature of the feedstock.

4.5 Conclusion

Preliminary experiments were carried out to establish the best approach and screen the best catalyst for the application of degradation of waste plastic mixture after which optimization of the catalyst preparation parameters were carried out to understand the synthesis of catalyst preparation at a specific process parameter that gave the best liquid yield, which were supported by catalyst characterization data i.e. EDS, XRD and SEM. It is important here to note that, the analyses carried out were not enough and hence further analyses such as sorption analysis (to confirm the mesoporosity) and acidity measurement (for cracking activity) are highly recommended. However due to unavailability of these, they were not carried out. A pressure setup (autoclave vessel) was used to evaluate pressure parameter. In order to examine the maximum liquid yield that can be achieved, catalyst optimization is carried out first using the optimum conditions of the catalyst preparation approach. Catalyst was prepared and then used for the process parameters optimization to understand the influence of various factors on the liquid yield. TGA was also carried out to find out the kinetic parameters like activation energy and compared with various prominent models.

From first set of preliminary experiments carried out with ZSM-5 catalyst, desilicated ZSM-5 shows better results (liquid yield and gasoline) in comparison to dealuminated ZSM-5 and unmodified ZSM-5. Desilicated ZSM-5 gave a liquid yield of 79.6% amongst which 83.51% falls in gasoline range and conversion of 96.2% in comparison to unmodified ZSM-5 which gave a liquid yield of 45.05% amongst which 54.39% falls in gasoline range and conversion of 48.28%. Desilicated ZSM-5 gives highest liquid yield as well as highest percentage of gasoline.

From second set of preliminary experiments carried out with BZ catalyst. Alumina is impregnated on BZ as it has a Si/Al ratio of 300 and has barely any alumina in it. So, it is desilicated first then alumina is impregnated. Given the Si/Al ratio, dealumination is not carried out as there is barely any alumina to be removed. Catalyst preparation is carried out such that the structure does not collapse or dissolve upon desilication, which is prepared by 0.1M NaOH solution (using 1/30 dilution ratio) at 75°C which is stirred for about 45 minutes. DBZA catalyst leads to best liquid yield of 82.73% which is in the gasoline range as compared to mere 68% and 79.6% on employing unmodified BZ and desilicated ZSM-5, respectively. The prepared catalysts were also characterized by different analytical techniques such as XRD, SEM/EDS etc. From XRD, diffraction patterns of catalysts show that the crystal structure of the zeolite is maintained even after desilication and dealumination treatments. However, peaks intensities are observed to be low after desilication (alkali treatment). SEM images deduce that the modified zeolites are mesoporous in nature having quasi spherical morphologies with large pore sizes. As DBZA is the best amongst all the zeolites, hence it is further used for catalyst optimization.

The catalyst optimization is an excellent addition, as it wasn't anticipated that catalyst fine tuning would be crucial for this application. For the DBZA optimization, DOE was carried out where 2 parameters are chosen i.e. synthesis temperature (50-90°C) and alumina loading (4.56-32.38wt% Al_2O_3 per zeolite). The response factor in optimization is the liquid yield (weighted). First BZ is desilicated after which alumina is impregnated in varying amounts and at different synthesis temperature. At optimum experimental conditions, DBZA gave a liquid yield of 9.9g and gasoline content of 87.4wt% in comparison to parent BZ that gave a liquid

yield of 3.3g and gasoline content of 68.4wt%. On analysis of the DOE in Minitab, all factors are proven as significant based on p-test. Synthesis temperature seems to be more significant than the amount of alumina loading factor. The contour plot shows convergence and the surface plots indicates the optimum. The model has an excellent fit with R^2 value of 95.58 %. Hence the catalyst that is desilicated at 0.1M sodium hydroxide at 75°C and alumina impregnated (22.3 wt.% alumina per zeolite) at synthesis temperature of 90°C gave the maximum liquid product and hence the catalyst is prepared in bulk and used in the optimization of process parameters.

For the process optimization, 3 factors were chosen namely temperature (360-440°C), pressure (1-40 bar) and C-P ratio (1:5 to 1:40). The response factor in optimization is the oil yield achieved (that is in the useful fuel range). From experiments the oil yield (g) achieved was ranging from 1.18g to 11.27g. Amongst five factors (amongst nine) are proven as significant based on p-test. Temperature factor shows stronger significance in comparison to pressure and C-P ratio. The contour plot shows convergence and the surface plots indicates the optimum. 11.27g is the oil yield obtained at the optimum conditions i.e. 420°C, 20bar and 1:30 C-P ratio. On analyzing the DOE in Minitab, R^2 value of 91% is achieved, indicating that the model is a good fit and matched well with the experimental results.

Various methods were deployed to analyze the TGA data to find the kinetic parameters. Range of activation energy values was found to be 91.68-170.80 kJ/mol, 51.10-86.80 kJ/mol and 44.74-67.40kJ/mol for ZSM-5, BZ, and MBZ, respectively. It is evident that on using MBZ, the process requires lowest activation energy in comparison to parent BZ or ZSM-5.

4.6 Future recommendations

There is still a lot that can be done as follows:

- Ideally differential scanning calorimetry (DSC) is to be carried for the identification and quantification of polymers for samples and to study the influence of heat on the polymers
- Refining the liquid product fuel's quality that can be studied further by treating it further by chemical treatment or by blending it with diesel or other fuels. Basically, studying how the product is on blending or any further treatment
- Studying on what approaches can be adopted to remove impurities which in turn would improve products quality.
- Life cycle assessment (LCA) of the feed stocks, products and processes to understand the environmental, technical as well as economic aspects. Only one research study is found in this regard by Wang et al. (2015).
- Exergy analysis to understand further on the thermodynamic of the process. There is barely anything written about it in literature.
- Employing different types of zeolite catalyst in this application.
- Attempting different approaches of preparing hierarchical zeolites like templating, recrystallization, zeolitization, surfactant templating, ADOR etc.
- Since this research work explored areas of desilication, trying different desilication agents like TPAOH/TBrAOH or combination and comparing them would be a study, although this has been limitedly explored, however not under the influence of significant pressure range.

- Attempting different synthesizing agents like HCl, H₃PO₄ etc. for dealumination, which again hasn't been explored under the influence of significant pressure range.
- Exploring possibilities of reactivating the spent catalyst, and the number of cycles it can be used before considered inactive or underivable.
- Studying the coking process and how can it be reduced for respective catalyst and a comparative study of this with diverse hierarchical zeolite preparation methods. No coking study was done in this research due to inaccessibility to the residues, given the tubular structure of the reactor.
- In this study X-Ray diffraction (XRD) and Scanning electron microscope (SEM) are done. There are numerous other ways catalyst's characterizations can be done i.e. X-ray fluorescence spectroscopy (XRF), Thermogravimetric analysis and differential thermal analysis (TG-DTA), Sorptometric studies, MAS NMR (Magic angle spinning Nuclear Magnetic Resonance) spectroscopy etc. to understand the catalyst performance better.
- Gas chromatography and mass spectroscopy (GC/MS) is done in this research study. Analyzing the liquid product oil by Fourier Transformation Infrared Spectroscopy (FTIR), detailed hydrocarbon analyzer (DHA) etc.
- Surface adsorption was not studied in this research due to unavailability of resources. It can be done by nitrogen adsorption/desorption isotherms i.e. Brunauer, Emmett and Teller (BET) method.
- The plastics that are employed in this study are of waste origin, so it is adamant to carry out tests like FTIR-ATR spectra to understand

which waste it represents. Ideally differential scanning calorimetry (DSC) is to be carried as well for the identification and quantification of polymers for samples and to study the influence of heat on the polymers.

- It is important to note that this study doesn't explore PET and PVC in its composition due to complexities and undesirability it brings along with it. There has been numerous studies on in the past where mixed plastic waste is studied but with many giving PVC and PET a skip, however a setup that can be proposed which takes care of PVC and PET's undesirability would be an interesting study which can be coupled with addition of hierarchical zeolites and explore a range of pressure parameter which also hasn't been explored in literature.

The approach of adopting hierarchical zeolite in application of degradation of mixed plastic to fuels is just one novel approach. Certainly, there are numerous other ways this application can be approached that awaits a researcher to ponder upon it and explore infinite possibilities in ultimate goal to reduce plastic waste and convert them to something more useful like fuel of decent quality that can be scaled-up to commercial setup to be adopted.

4.7 Economic prospects of plastic (chemical) recycling

It is estimated that approximately 6300 Mt of plastic waste had been generated globally, as of 2015, out of which about 12% was incinerated, 9% was recycled, and 79% was accumulated in landfills or the natural environment. If current production and waste management trends continue, roughly 12,000 Mt of plastic waste will be in landfills or in the natural environment by 2050. Regarding global recycling, as of 2014, the highest recycling rates i.e. 30%, 25%, 9% and 9% were reported in Europe, China, the US and Canada, respectively. Bahrain is generating approximately 4000 tons/day of MSW out of which about 15-25% i.e. 1050 tons/day is plastic waste. Only little quantity is collected, segregated and sent for recycling, rest is disposed of at Asker landfill site.

As Bahrain is a small island with limited area to spare and most of the plastic materials are landfilled hence it is adamant to come up with alternatives by which certain revenue is generated instead of just adding burden to the landfilling practice. This aforementioned burden gives loss to the economy as no plastic is recovered or recycled from land filled areas. Scale back the amount of plastic currently produced and design better products that fit into a circular economy are also possible alternatives. Scaling back seems not practical due to high demand of plastics for daily use. Recycling could be a better option and more practical as it not only helps in reducing the energy usage and consumption of virgin plastics, but it has also great impact on the environment in terms of reduction in water pollution (reducing the need for conventional waste disposal) and air pollution (mitigation of greenhouse gases emissions) from the landfilling. Recycling is also the part of the new bold plastic economy plan (i.e. reuse, reduce and recycle) to combat the plastic pollution. To overcome this economic loss, recycling needs to be increased enormously (at least

quadruple) from its present level that significantly needs to be scaled up taking into account at readiness levels. In addition, there is need to benefit from the energy obtained from waste plastics that are not only easily cracked but also need to develop such techniques that can deal with the remaining volumes and hard-to-recycle plastics. Recycling (chemical recycling) also holds promise in not only curbing such pervasive pollution but also providing a significant economic benefit to humanity. The American Chemistry Council estimates chemical recycling (plastic to fuel) facilities in the US alone would create nearly 39,000 jobs and almost \$9 billion in economic output, making the global market potential of such an industry huge. Additionally, fuels derived from plastics are also capable of producing a cleaner burning fuel than traditional sources due to low sulphur contents. The beauty of this chemical recycling process is that it's not very picky i.e. it can degrade all sorts of waste. There is a big room for the chemical recycling (hydrocracking) of waste plastic but presently it is not so economical mainly due to the employment of catalysts, which are expensive to make and hence make this recycling process unfeasible. So, there is need to develop more effective and cheap catalysts (from cheap and natural raw materials) that can reinforce chemical recycling technology. The collection and segregation of plastics from the municipal solid waste can be another factor to be considered in the design of the recycling process. Over the years, there have been various solutions proposed to overcome plastic pollution (burning etc.). However, nothing to date has proven to be truly effective or environmentally responsible solution to the burgeoning global landfill problem. It's only now, with the chemical recycling technology, that there is a solution that is not only economically viable, but that is remarkably simple and green as well.

Reference

- Abdulkareem, S. A., Taofiqat Omotayo, A. B. U., and Eleburuike, N. A. (2019). Thermal and Catalytic Pyrolysis of Low-Density Polyethylene (LDPE) Wastes into Useful Fuel Oils: Comparative Studies. *ABUAD Journal of Engineering Research and Development (AJERD)* ISSN: 2645-2685, Volume 2, Issue 1, 36-41
- Abdullah, N. A., Novianti, A., Hakim, I. I., Putra, N., and Koestoer, R. A. (2018, January). Influence of temperature on conversion of plastics waste (polystyrene) to liquid oil using pyrolysis process. In *IOP Conference Series: Earth and Environmental Science* (Vol. 105, No. 1, p. 012033). IOP Publishing.
- Abello, S., Bonilla, A., and Perez-Ramirez, J. (2009). Mesoporous ZSM-5 zeolite catalysts prepared by desilication with organic hydroxides and comparison with NaOH leaching. *Applied Catalysis A: General*, 364(1-2), 191-198. Doi: 10.1016/j.apcata.2009.05.055
- Aboulkas, A., and El Bouadili, A. (2010). Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. *Energy Conversion and Management*, 51(7), 1363-1369.
- Aguado, J., and Serrano, D. P. (2007). *Feedstock recycling of plastic wastes*. Royal society of chemistry.
- Akah, A., Hernandez-Martinez, J., and Garforth, A. (2013). Enhanced Feedstock Recycling–NovaCrack TM. Retrieved from https://www.researchgate.net/profile/Arthur_Garforth/publication/291312110_Enhanced_Feedstock_Recycling_-

[NovaCrack/links/569f67a708aee4d26ad1ea3c/Enhanced-Feedstock-Recycling-NovaCrack.pdf](#)

Akaha, A., Hernandez-Martinez, J., Rallan, C., and Garforth, A. A. (2015). Enhanced feedstock recycling of post-consumer plastic waste. *Chemical Engineering*, 43. Retrieved from https://www.researchgate.net/profile/Chandni_Rallan/publication/276920134_Enhanced_Feedstock_Recycling_of_Post-Consumer_Plastic_Waste/links/555e061308ae8c0cab2c5dd3/Enhanced-Feedstock-Recycling-of-Post-Consumer-Plastic-Waste.pdf

Akahira, T. (1971). Trans. Joint convention of four electrical institutes. *Res. Rep. Chiba Inst. Technol.*, 16, 22-31.

Akubo, K., Nahil, M. A., and Williams, P. T. (2017). Aromatic fuel oils produced from the pyrolysis-catalysis of polyethylene plastic with metal-impregnated zeolite catalysts. *Journal of the Energy Institute*.

Albano, C., and de Freitas, E. (1998). Thermogravimetric evaluation of the kinetics of decomposition of polyolefin blends. *Polymer degradation and stability*, 61(2), 289-295. Doi: 10.1016/S0141-3910(97)00211-5

Ali, M. F., Nahid, M., and Redhwi, S. S. H. H. (2004). Study on the conversion of waste plastics/petroleum resid mixtures to transportation fuels. *Journal of Material Cycles and Waste Management*, 6(1), 27-34. Doi: 10.1007/s10163-003-0102-x

Al-Salem, S. M., Antelava, A., Constantinou, A., Manos, G., and Dutta, A. (2017). A review on thermal and catalytic pyrolysis of plastic solid waste (PSW). *Journal of Environmental Management*, 197, 177-198. Doi: 10.1016/j.jenvman.2017.03.084

- Anene, A., Fredriksen, S., Sætre, K., and Tokheim, L. A. (2018). Experimental study of thermal and catalytic pyrolysis of plastic waste components. *Sustainability*, 10(11), 3979.
- Arkhangel'skii, I. V., Dunaev, A. V., Makarenko, I. V., Tikhonov, N. A., Belyaev, S. S., and Tarasov, A. (2013). Non-Isothermal Kinetic Methods.
- Auerbach, S. M., Carrado, K. A., and Dutta, P. K. (2003). *Handbook of zeolite science and technology*. CRC press.
- Australia, E. (1999). Incineration and dioxins: review of formation processes. *Environmental and safety services for environment Australia. Canberra, Australia*. Retrieved from <https://www.environment.gov.au/system/files/resources/fec3b9ff-4a26-4b17-9bcb-1ba3c066ca8b/files/incineration-review.pdf>
- Aznar, M. P., Caballero, M. A., Sancho, J. A., and Francés, E. (2006). Plastic waste elimination by co-gasification with coal and biomass in fluidized bed with air in pilot plant. *Fuel Processing Technology*, 87(5), 409-420. Retrieved from <http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.471.196a&ndrep=rep1&ndtype=pdf>
- Ballice, L., and Reimert, R. (2002). Classification of volatile products from the temperature-programmed pyrolysis of polypropylene (PP), atactic-polypropylene (APP) and thermogravimetrically derived kinetics of pyrolysis. *Chemical Engineering and Processing: Process Intensification*, 41(4), 289-296. Doi: 10.1016/S0255-2701(01)00144-1

- Bate, D. M., and Lehrle, R. S. (1998). The effect of blending on polymer stability: kinetics and mechanisms. *Polymer Degradation and stability*, 62(1), 57-66. Doi: 10.1016/S0141-3910(97)00261-9
- Bhaskar, T., Uddin, M. A., Murai, K., Kaneko, J., Hamano, K., Kusaba, T., ... and Sakata, Y. (2003). Comparison of thermal degradation products from real municipal waste plastic and model mixed plastics. *Journal of Analytical and Applied Pyrolysis*, 70(2), 579-587. Doi: 10.1016/S0165-2370(03)00027-5
- Bioplastics and biodegradable plastics - How do they work? (2018, June 05). Retrieved from <http://www.explainthatstuff.com/bioplastics.html>
- Blazso, M. (1999). Thermal decomposition of polymers modified by catalytic effects of copper and iron chlorides. *Journal of Analytical and Applied Pyrolysis*, 51(1-2), 73-88. Doi: 10.1016/S0165-2370(99)00009-1
- Bockhorn, H., Hornung, A., and Hornung, U. (1998). Stepwise pyrolysis for raw material recovery from plastic waste. *Journal of Analytical and Applied Pyrolysis*, 46(1), 1-13. Doi: 10.1016/S0165-2370(98)00066-7
- Bockhorn, H., Hornung, A., Hornung, U., Jakobströer, P., and Kraus, M. (1999). Dehydrochlorination of plastic mixtures. *Journal of analytical and applied pyrolysis*, 49(1-2), 97-106. Doi: 10.1016/S0165-2370(98)00124-7
- Bonilla, A., Baudouin, D., and Pérez-Ramírez, J. (2009). Desilication of ferrierite zeolite for porosity generation and improved effectiveness

- in polyethylene pyrolysis. *Journal of Catalysis*, 265(2), 170-180.
Doi: 10.1016/j.jcat.2009.04.022
- Braun, R. L., and Burnham, A. K. (1987). Analysis of chemical reaction kinetics using a distribution of activation energies and simpler models. *Energy and Fuels*, 1(2), 153-161.
- Bronsted and Lewis Acid Sites. (n.d.). Retrieved March 25, 2018, from <https://www.e-education.psu.edu/fsc432/content/bronsted-and-lewis-acid-sites>
- Buekens, A. G., and Huang, H. (1998). Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes. *Resources, Conservation and Recycling*, 23(3), 163-181.
Doi: 10.1016/S0921-3449(98)00025-1
- Busca, G. (2017). Acidity and basicity of zeolites: A fundamental approach. *Microporous and Mesoporous Materials*, 254, 3-16. Doi: 10.1016/j.micromeso.2017.04.007
- Calemma, V., Peratello, S., and Perego, C. (2000). Hydroisomerization and hydrocracking of long chain n-alkanes on Pt/amorphous SiO₂–Al₂O₃ catalyst. *Applied Catalysis A: General*, 190(1-2), 207-218.
Doi: 10.1016/S0926-860X(99)00292-6
- Cejka, J., and van Bekkum, H. (Eds.). (2005). *Zeolites and ordered mesoporous materials: progress and prospects: the 1st FEZA School on Zeolites, Prague, Czech Republic, August 20-21, 2005* (Vol. 157). Gulf Professional Publishing.
- Chattopadhyay, J., Pathak, T. S., Srivastava, R., and Singh, A. C. (2016). Catalytic co-pyrolysis of paper biomass and plastic mixtures (HDPE

- (high density polyethylene), PP (polypropylene) and PET (polyethylene terephthalate)) and product analysis. *Energy*, 103, 513-521. Doi: 10.1016/j.energy.2016.03.015
- Chen, D., Yin, L., Wang, H., and He, P. (2015). Reprint of: pyrolysis technologies for municipal solid waste: a review. *Waste management*, 37, 116-136. Doi: 10.1016/j.wasman.2015.01.022
- Chen, J. P., Kim, S. L., and Ting, Y. P. (2003). Optimization of membrane physical and chemical cleaning by a statistically designed approach. *Journal of membrane Science*, 219(1-2), 27-45. [doi:10.1016/S0376-7388\(03\)00174-1](https://doi.org/10.1016/S0376-7388(03)00174-1)
- Chiellini, E., Chiellini, F., Cinelli, P., and Scott, G. (2002). Degradable polymers: Principles and application, Chapman and Hall, eds
- Chowlu, A. C. K., Reddy, P. K., and Ghoshal, A. K. (2009). Pyrolytic decomposition and model-free kinetics analysis of mixture of polypropylene (PP) and low-density polyethylene (LDPE). *Thermochimica acta*, 485(1-2), 20-25.
- Ciliz, N. K., Ekinici, E., and Snape, C. E. (2004). Pyrolysis of virgin and waste polypropylene and its mixtures with waste polyethylene and polystyrene. *Waste management*, 24(2), 173-181. Doi: 10.1016/j.wasman.2003.06.002
- Cleetus, C., Thomas, S., and Varghese, S. (2013). Synthesis of petroleum-based fuel from waste plastics and performance analysis in a CI engine. *Journal of Energy*, 2013. Doi: 10.1155/2013/608797
- Coelho, A., Fonseca, I. M., Matos, I., Marques, M. M., do Rego, A. M. B., Lemos, M. A. N. D. A., and Lemos, F. (2010). Catalytic degradation

- of low and high density polyethylenes using ethylene polymerization catalysts: Kinetic studies using simultaneous TG/DSC analysis. *Applied Catalysis A: General*, 374(1-2), 170-179. Doi: 10.1016/j.apcata.2009.12.001
- Cui, Q., Zhou, Y., Wei, Q., Tao, X., Yu, G., Wang, Y., and Yang, J. (2012). Role of the zeolite crystallite size on hydrocracking of vacuum gas oil over NiW/Y-ASA catalysts. *Energy and Fuels*, 26(8), 4664-4670.
- Davis, M. E. (2015). *Mesoporous zeolites: preparation, characterization and applications*. John Wiley and Sons.
- DeCoursey, W. (2003). *Statistics and probability for engineering applications*. Elsevier.
- Montgomery, D. C., Custer, L., and McCarville, D. R. (2009). Design and analysis of experiments. New York: Wiley
- Demirbas, A. (2004). Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons. *Journal of Analytical and Applied Pyrolysis*, 72(1), 97-102. Doi: 10.1016/j.jaap.2004.03.001
- Difference between thermal cracking and catalytic cracking | Definition, Mechanism, Examples. (2017, September 27). Retrieved from <http://pediaa.com/difference-between-thermal-cracking-and-catalytic-cracking>
- Ding, W., Liang, J., and Anderson, L. L. (1997). Hydrocracking and hydroisomerization of high-density polyethylene and waste plastic over zeolite and silica– alumina-supported Ni and Ni– Mo sulfides. *Energy and Fuels*, 11(6), 1219-1224. Doi: 10.1021/ef970051q

- Ding, W., Liang, J., and Anderson, L. L. (1997). Thermal and catalytic degradation of high density polyethylene and commingled post-consumer plastic waste. *Fuel Processing Technology*, 51(1-2), 47-62. Doi: [10.1016/S0378-3820\(96\)01080-6](https://doi.org/10.1016/S0378-3820(96)01080-6)
- Doğan, O., Çelik, M. B., and Özdalyan, B. (2012). The effect of tire derived fuel/diesel fuel blends utilization on diesel engine performance and emissions. *Fuel*, 95, 340-346. Doi: [10.1016/j.fuel.2011.12.033](https://doi.org/10.1016/j.fuel.2011.12.033)
- Doyle, C. D. (1961). Kinetic analysis of thermogravimetric data. *Journal of applied polymer science*, 5(15), 285-292.
- Eastern Research Group (1998), Preferred and alternative methods for estimated air emission methods from plastic products manufacturing, Volume 2, Chapter 11. Retrieved from <https://dep.wv.gov/daq/planning/inventory/Documents/EIIP%20V02%20Ch11%20Plastic%20Products%20Manufacturing.pdf>
- Encinar, J. M., and González, J. F. (2008). Pyrolysis of synthetic polymers and plastic wastes. Kinetic study. *Fuel Processing Technology*, 89(7), 678-686.
- Erawati, E., Hamid, and Permatasari, R. D. (2019, June). Pyrolysis of polypropylene waste with natural zeolite as catalyst. In *AIP Conference Proceedings* (Vol. 2114, No. 1, p. 050019). AIP Publishing.
- Est. (2015, October 23). Plastic Building Materials. Retrieved from <https://www.slideshare.net/E185/bld62003-mak-plastics>

- Esser S. (2018, December 16). FSC 432: Petroleum Processing course notes, PennState, College of Earth and Mineral Science, John A. Dutton e-education institute.
<https://www.e-education.psu.edu/fsc432/content/bronsted-and-lewis-acid-sites>
- Farneth, W. E., and Gorte, R. J. (1995). Methods for characterizing zeolite acidity. *Chemical reviews*, 95(3), 615-635. Doi: 10.1021/cr00035a007
- Feliczak-Guzik, A. (2018). Hierarchical zeolites: synthesis and catalytic properties. *Microporous and Mesoporous Materials*, 259, 33-45. Doi: [10.1016/j.micromeso.2017.09.030](https://doi.org/10.1016/j.micromeso.2017.09.030)
- Feng, R., Yan, X., Hu, X., Wang, Y., Li, Z., Hou, K., and Lin, J. (2018). Hierarchical ZSM-5 zeolite designed by combining desilication and dealumination with related study of n-heptane cracking performance. *Journal of Porous Materials*, 1-14. Doi: 10.1007/s10934-018-0587-2
- Feng, Z., Zhao, J., Rockwell, J., Bailey, D., and Huffman, G. (1996). Direct liquefaction of waste plastics and coliquefaction of coal-plastic mixtures. *Fuel processing technology*, 49(1-3), 17-30. Doi: [10.1016/S0378-3820\(96\)01036-3](https://doi.org/10.1016/S0378-3820(96)01036-3)
- Fischer, P. E., Jou, C. S., and Gokalgandhi, S. S. (1987). Obtaining the kinetic parameters from thermogravimetry using a modified Coats and Redfern technique. *Industrial and engineering chemistry research*, 26(5), 1037-1040.
- Flynn, J. (1983). The isoconversional method for determination of energy of activation at constant heating rates: corrections for the Doyle

approximation. *Journal of Thermal Analysis and Calorimetry*, 27(1), 95-102.

Flynn, J. H., and Wall, L. A. (1966). General treatment of the thermogravimetry of polymers. *J Res Nat Bur Stand*, 70(6), 487-523.

Freeman, E. S., and Carroll, B. (1958). The application of thermoanalytical techniques to reaction kinetics: the thermogravimetric evaluation of the kinetics of the decomposition of calcium oxalate monohydrate. *The Journal of Physical Chemistry*, 62(4), 394-397. doi:10.1021/j150562a003

Friedman, H. L. (1964). Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. In *Journal of Polymer Science Part C: Polymer Symposia* (Vol. 6, No. 1, pp. 183-195). New York: Wiley Subscription Services, Inc., A Wiley Company.

Fuentes-Ordóñez, E. G., Salbidegoitia, J. A., González-Marcos, M. P., Ayastuy, J. L., Gutiérrez-Ortiz, M. A., and González-Velasco, J. R. (2015). Pt/ITQ-6 zeolite as a bifunctional catalyst for hydrocracking of waste plastics containing polystyrene. *Journal of Material Cycles and Waste Management*, 17(3), 465-475. Doi: 10.1007/s10163-014-0322-2

Gao, N., Xie, S., Liu, S., An, J., Zhu, X., Hu, L. and Xu, L. (2014). Catalytic degradation of LDPE and PP over MCM-49 based micro-mesoporous composites. *Catalysis Letters*, 144(7), 1296-1304. Doi: [10.1007/s10562-014-1205-9](https://doi.org/10.1007/s10562-014-1205-9)

Gao, N., Xie, S., Liu, S., An, J., Zhu, X., Hu, L. and Xu, L. (2014). Catalytic degradation of LDPE and PP over MCM-49 based micro-

mesoporous composites. *Catalysis Letters*, 144(7), 1296-1304. Doi: 10.1007/s10562-014-1205-9

Garba, M. D., and Galadima, A. (2018). Catalytic Hydrogenation of Hydrocarbons for Gasoline Production. *Journal of Physical Science*, 29(2), 153-176.

Gonzalez, G., Sagarzazu, A., and Zoltan, T. (2013). Influence of microstructure in drug release behavior of silica nanocapsules. *Journal of Drug Delivery*, 2013, 1-8.

Gosh, S., and Rao, C. R. (1996). Handbook of Statistics. v. 13: Design and analysis of experiments.

Gregory, M. R., and Andrady, A. L. (2003). Plastics in the marine environment. *Plastics and the Environment*, 379, 389-390.

Groen, J. C., Jansen, J. C., Moulijn, J. A., and Pérez-Ramírez, J. (2004). Optimal aluminum-assisted mesoporosity development in MFI zeolites by desilication. *The Journal of Physical Chemistry B*, 108(35), 13062-13065. Doi: 10.1021/jp047194f

Groen, J. C., Jansen, J. C., Moulijn, J. A., and Pérez-Ramírez, J. (2004). Optimal aluminum-assisted mesoporosity development in MFI zeolites by desilication. *The Journal of Physical Chemistry B*, 108(35), 13062-13065. Doi: 10.1021/jp047194f

Haag, W. O., Lago, R. M., and Weisz, P. B. (1984). The active site of acidic aluminosilicate catalysts. *Nature*, 309(5969), 589. Doi: 10.1038/309589a0

Haggam, R. A., El-Sayed, H. A., Said, S. A., Ahmed, M. H. M., Moustafa, A. H., and Abd-El-Noor, R. E. (2017). O-Glycosylation/Alkylation

and Antimicrobial Activity of 4, 6-Diaryl-2-Oxonicotinonitrile Derivatives. *Journal of Heterocyclic Chemistry*, 54(1), 375-383. Doi: [10.1002/jhet.2593](https://doi.org/10.1002/jhet.2593)

Hartmann, M., Machoke, A. G., and Schwieger, W. (2016). Catalytic test reactions for the evaluation of hierarchical zeolites. *Chemical Society Reviews*, 45(12), 3313-3330. Doi: [10.1039/C5CS00935A](https://doi.org/10.1039/C5CS00935A)

Hesse, N. D., and White, R. L. (2004). Polyethylene catalytic hydrocracking by PtHZSM-5, PtHY, and PtHMCM-41. *Journal of applied polymer science*, 92(2), 1293-1301. Doi: [10.1002/app.20083](https://doi.org/10.1002/app.20083)

Hoff, T. C., Gardner, D. W., Thilakaratne, R., Proano-Aviles, J., Brown, R. C., and Tessonnier, J. P. (2017). Elucidating the effect of desilication on aluminum-rich ZSM-5 zeolite and its consequences on biomass catalytic fast pyrolysis. *Applied Catalysis A: General*, 529, 68-78. Doi: [10.1016/j.apcata.2016.10.009](https://doi.org/10.1016/j.apcata.2016.10.009). https://www.researchgate.net/publication/326526189_different_approches_to_kinetics_degradation_of_polyester_resin_from_renewable_resources/

Hong, Y., Lee, Y., Rezaei, P. S., Kim, B. S., Jeon, J. K., Jae, J., ... and Park, Y. K. (2017). In-situ catalytic copyrolysis of cellulose and polypropylene over desilicated ZSM-5. *Catalysis Today*, 293, 151-158.

Horne, G., and Lee, S. (2006). Fuels Analysis, Regulatory Specifications for. *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*, 1-79.

Huffman, G. P., Rockwell, J., Shah, N., Anderson, L. L., and Ding, W. (1997). Catalytic liquefaction of waste plastic. *Proceedings of the*

1997 Coal Liquefaction and Solid Fuels Contractors Review Conference, DOE/FETC/PGH-97-0001.

Ibáñez, M., Epelde, E., Aguayo, A. T., Gayubo, A. G., Bilbao, J., and Castaño, P. (2017). Selective dealumination of HZSM-5 zeolite boosts propylene by modifying 1-butene cracking pathway. *Applied Catalysis A: General*, 543, 1-9. Doi: 10.1016/j.apcata.2017.06.008

Ibrahim, M. M., Hopkins, E., and Seehra, M. S. (1996). Thermal and catalytic degradation of commingled plastics. *Fuel processing technology*, 49(1-3), 65-73. Doi: 10.1016/S0378-3820(96)01023-5

Ivanova, I. I., Kasyanov, I. A., Maerle, A. A., and Zaikovskii, V. I. (2014). Mechanistic study of zeolites recrystallization into micro-mesoporous materials. *Microporous and Mesoporous Materials*, 189, 163-172. Doi: [10.1016/j.micromeso.2013.11.001](https://doi.org/10.1016/j.micromeso.2013.11.001)

Irfan, M. F., Goo, J.H., and Kim, S.D. (2008). Co₃O₄ based catalysts for NO oxidation and NO_x reduction in fast SCR process. *Applied Catalysis B: Environmental*, 78, 267–274.

Irfan, M. F., Hossain, S.M. Z. Tariq, I., Khan, N.A., Tawfeeqi, A., Goeva, A., Wael, M. (2020). Modeling and Optimization of Aqueous Mineral Carbonation for Cement Kiln Dust using Response Surface Methodology Integrated with Box-Behnken and Central Composite Design Approaches. *Mining, Metallurgy Exploration*, 37, 1367–1383.

Jacobsen, C. J., Madsen, C., Houzvicka, J., Schmidt, I., and Carlsson, A. (2000). Mesoporous zeolite single crystals. *Journal of the American Chemical Society*, 122(29), 7116-7117. Doi: 10.1021/ja000744c

- Jha, B., and Singh, D. N. (2016). Fly Ash Zeolites. *Advanced Structured Materials*, 78, 978-981.
- Jha, B., and Singh, D. N. (2016). *Fly ash zeolites: innovations, applications, and directions* (Vol. 78). Springer.
- Ji, Y., Yang, H., and Yan, W. (2017). Strategies to enhance the catalytic performance of ZSM-5 zeolite in hydrocarbon cracking: A review. *Catalysts*, 7(12), 367.
- Jin, S., Cui, K., Guan, H., Yang, M., Liu, L., and Lan, C. (2012). Preparation of mesoporous MCM-41 from natural sepiolite and its catalytic activity of cracking waste polystyrene plastics. *Applied Clay Science*, 56, 1-6. Doi: 10.1016/j.clay.2011.11.012
- Kaminsky, W., and Kim, J. S. (1999). Pyrolysis of mixed plastics into aromatics. *Journal of Analytical and Applied Pyrolysis*, 51(1-2), 127-134. Doi: 10.1016/S0165-2370(99)00012-1
- Kaminsky, W., and Zorriquetta, I. N. (2007). Catalytical and thermal pyrolysis of polyolefins. *Journal of Analytical and Applied Pyrolysis*, 79(1-2), 368-374. Doi: 10.1016/j.jaap.2006.11.005
- Kaminsky, W., Schlesselmann, B., and Simon, C. (1995). Olefins from polyolefins and mixed plastics by pyrolysis. *Journal of Analytical and Applied Pyrolysis*, 32, 19-27. Doi: 10.1016/0165-2370(94)00830-T
- Kaminsky, W., Schlesselmann, B., and Simon, C. M. (1996). Thermal degradation of mixed plastic waste to aromatics and gas. *Polymer Degradation and Stability*, 53(2), 189-197. Doi: 10.1016/0141-3910(96)00087-0

- Karagöz, S., Yanik, J., Uçar, S., and Song, C. (2002). Catalytic coprocessing of low-density polyethylene with VGO using metal supported on activated carbon. *Energy and fuels*, 16(5), 1301-1308. Doi: 10.1021/ef020064q
- Kawai, Y. (2009). Operation report of pyrolysis gas melting system. *Takuma Tech. Rev*, 17, 1-20.
- Kerrod, R. (1994). *Energie en grondstoffen in de toekomst*. Artis-Historia.
- Khedri, S., and Elyasi, S. (2016). Kinetic analysis for thermal cracking of HDPE: A new isoconversional approach. *Polymer Degradation and Stability*, 129, 306-318.
- Kim, J. R., Yoon, J. H., and Park, D. W. (2002). Catalytic recycling of the mixture of polypropylene and polystyrene. *Polymer degradation and stability*, 76(1), 61-67. Doi: 10.1016/S0141-3910(01)00266-X
- Kim, J. S., Kaminsky, W., and Schlesselmann, B. (1997). Pyrolysis of a fraction of mixed plastic wastes depleted in PVC. *Journal of analytical and applied pyrolysis*, 40, 365-372. Doi: 10.1016/S0165-2370(97)00042-9
- Kim, S. W., Koo, B. S., Ryu, J. W., Lee, J. S., Kim, C. J., Lee, D. H., ... and Choi, S. (2013). Bio-oil from the pyrolysis of palm and Jatropha wastes in a fluidized bed. *Fuel Processing Technology*, 108, 118-124. Doi: 10.1016/j.fuproc.2012.05.002
- Kiran, N., Ekinici, E., and Snape, C. E. (2000). Recycling of plastic wastes via pyrolysis. *Resources, Conservation and Recycling*, 29(4), 273-283. Doi: 10.1016/S0921-3449(00)00052-5

- Kissinger, H. E. (1957). Reaction kinetics in differential thermal analysis. *Analytical chemistry*, 29(11), 1702-1706.
- Koohsaryan, E., and Anbia, M. (2016). Nanosized and hierarchical zeolites: A short review. *Chinese Journal of Catalysis*, 37(4), 447-467. Doi: [10.1016/S1872-2067\(15\)61038-5](https://doi.org/10.1016/S1872-2067(15)61038-5)
- Kpere-Daibo, T. S. (2009). *Plastic catalytic degradation study of the role of external catalytic surface, catalytic reusability and temperature effects* (Doctoral dissertation, UCL (University College London)). Retrieved from <http://discovery.ucl.ac.uk/18914/>
- Kumar, S., and Singh, R. K. (2014). Optimization of process parameters by response surface methodology (RSM) for catalytic pyrolysis of waste high-density polyethylene to liquid fuel. *Journal of Environmental Chemical Engineering*, 2(1), 115-122.
- Kumar, S., Panda, A. K., and Singh, R. K. (2011). A review on tertiary recycling of high-density polyethylene to fuel. *Resources, Conservation and Recycling*, 55(11), 893-910. Doi: [10.1016/j.resconrec.2011.05.005](https://doi.org/10.1016/j.resconrec.2011.05.005)
- Kunwar, B., Moser, B. R., Chandrasekaran, S. R., Rajagopalan, N., and Sharma, B. K. (2016). Catalytic and thermal depolymerization of low value post-consumer high density polyethylene plastic. *Energy*, 111, 884-892.
- Kwon, H., Jain, A., McEnally, C. S., Pfefferle, L. D., and Xuan, Y. (2019). Numerical investigation of the pressure-dependence of yield sooting indices for n-alkane and aromatic species. *Fuel*, 254, 115574.

- Lee, Hyung Won, Suek Joo Choi, Sung Hoon Park, Jong-Ki Jeon, Sang-Chul Jung, Sang Chai Kim, and Young-Kwon Park. "Pyrolysis and co-pyrolysis of *Laminaria japonica* and polypropylene over mesoporous Al-SBA-15 catalyst." *Nanoscale research letters* 9, no. 1 (2014): 376. Doi: 10.1186/1556-276X-9-376
- Lei, X. G., Jockusch, S., Ottaviani, M. F., and Turro, N. J. (2003). In situ EPR investigation of the addition of persistent benzyl radicals to acrylates on ZSM-5 zeolites. Direct spectroscopic detection of the initial steps in a supramolecular photopolymerization. *Photochemical and Photobiological Sciences*, 2(11), 1095-1100. Doi: 10.1039/B307735G
- Lerici, L. C., Renzini, M. S., and Pierella, L. B. (2015). Chemical catalyzed recycling of polymers: catalytic conversion of PE, PP and PS into fuels and chemicals ov
- Li, J., Liu, M., Guo, X., Xu, S., Wei, Y., Liu, Z., & Song, C. (2017). Interconnected hierarchical ZSM-5 with tunable acidity prepared by a dealumination–realumination process: a superior MTP catalyst. *ACS Applied Materials & Interfaces*, 9(31), 26096-26106. er HY. *Procedia Materials Science*, 8, 297-303.
- Li, K., Lee, S., Yuan, G., Lei, J., Lin, S., Weerachanchai, P., ... and Wang, J. Y. (2016). Investigation into the catalytic activity of microporous and mesoporous catalysts in the pyrolysis of waste polyethylene and polypropylene mixture. *Energies*, 9(6), 431. Doi: 10.3390/en9060431
- Li, K., Valla, J., and Garcia-Martinez, J. (2014). Realizing the commercial potential of hierarchical zeolites: new opportunities in catalytic

cracking. *ChemCatChem*, 6(1), 46-66. Doi:
10.1002/cctc.201300345

Li, H., He, S., Ma, K., Wu, Q., Jiao, Q., & Sun, K. (2013). Micro-mesoporous composite molecular sieves H-ZSM-5/MCM-41 for methanol dehydration to dimethyl ether: Effect of SiO₂/Al₂O₃ ratio in H-ZSM-5. *Applied Catalysis A: General*, 450, 152-159.

Li, Y., White, R., Chen, D., Zhang, J., Li, B., Zhang, Y., ... and Edis, R. (2007). A spatially referenced water and nitrogen management model (WNMM) for (irrigated) intensive cropping systems in the North China Plain. *Ecological Modelling*, 203(3-4), 395-423. Doi: 10.1016/j.ecolmodel.2006.12.011

Lin, Y. H., and Yang, M. H. (2007). Catalytic pyrolysis of polyolefin waste into valuable hydrocarbons over reused catalyst from refinery FCC units. *Applied Catalysis A: General*, 328(2), 132-139. Doi: 10.1016/j.apcata.2007.05.039

Liu, K., and Meuzelaar, H. L. (1996). Catalytic reactions in waste plastics, HDPE and coal studied by high-pressure thermogravimetry with on-line GC/MS. *Fuel processing technology*, 49(1-3), 1-15. Doi: 10.1016/S0378-3820(97)86800-2

López, A., De Marco, I., Caballero, B. M., Laresgoiti, M. F., Adrados, A., and Aranzabal, A. (2011). Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud. *Applied Catalysis B: Environmental*, 104(3-4), 211-219. Doi: 10.1016/j.apcatb.2011.03.030

Lopez, G., Artetxe, M., Amutio, M., Bilbao, J., and Olazar, M. (2017). Thermochemical routes for the valorization of waste polyolefinic

- plastics to produce fuels and chemicals. A review. *Renewable and Sustainable Energy Reviews*, 73, 346-368. Doi: 10.1016/j.rser.2017.01.142
- Luo, M., and Curtis, C. W. (1996). Thermal and catalytic coprocessing of Illinois No. 6. coal with model and commingled waste plastics. *Fuel Processing Technology*, 49(1-3), 91-117. Doi: 10.1016/S0378-3820(96)01043-0
- Lysenko, N. D., Il'In, V. G., and Yaremov, P. S. (2011). Structural and sorption characteristics of the products from zeolitization of sba-15 in the presence of tetraalkylammonium hydroxides. *Theoretical and Experimental Chemistry*, 47(4), 257. Doi: 10.1007/s11237-011-9213-y
- M. K. Rocha, Vinicius and Ornaghi, Heitor and Amico, Sandro and Magalhães de Oliveira, Daniel and Benini, Kelly Cristina. (2018). Different Approches to Kinetics Degradation of Polyester Resin from Renewable Resources. 354-360. Doi: 10.21452/bccm4.2018.04.02.
- Ma, J., Weng, D., Wu, X., Si, Z., and Wu, Z. (2013). Highly dispersed iron species created on alkali-treated zeolite for ammonia SCR. *Progress in Natural Science: Materials International*, 23(5), 493-500. Doi: 10.1016/j.pnsc.2013.08.005
- Malkow, T. (2004). Novel and innovative pyrolysis and gasification technologies for energy efficient and environmentally sound MSW disposal. *Waste management*, 24(1), 53-79. Doi: 10.1016/S0956-053X(03)00038-2

- Marcilla, A., Beltrán, M. I., Hernández, F., and Navarro, R. (2004). HZSM5 and HUSY deactivation during the catalytic pyrolysis of polyethylene. *Applied Catalysis A: General*, 278(1), 37-43. Doi: 10.1016/j.apcata.2004.09.023
- Materials Engineering. (2018, November 13). Retrieved from http://www.substech.com/dokuwiki/doku.php?id=plastics_recycling
- Mayorga, M., Cadavid, J., Martinez, J., Rodriguez, L., Trujillo, C. A., Lopez, M., ... and Lopez, C. (2019). Evaluation of Zeolite-based Catalyst Supports for the Production of Biokerosene by Hydrotreating of Oils. *Chemical Engineering Transactions*, 74, 13-18.
- McSwiggen, P. (n.d.). WDS vs EDS. Retrieved November 26, 2018, from <http://www.mcswiggen.com/TechNotes/WDSvsEDS.htm>
- Messe Düsseldorf and Plastics Europe Deutschland e.V (2016), *Plastics-Facts 2016*, Retrieved from <https://www.plasticseurope.org/application/files/4315/1310/4805/plastic-the-fact-2016.pdf>
- Miandad, R., Barakat, M. A., Aburiazaiza, A. S., Rehan, M., Ismail, I. M. I., and Nizami, A. S. (2017). Effect of plastic waste types on pyrolysis liquid oil. *International biodeterioration and biodegradation*, 119, 239-252. Doi: 10.1016/j.ibiod.2016.09.017
- Miandad, R., Rehan, M., Barakat, M. A., Aburiazaiza, A. S., Khan, H., Ismail, I. M., and Nizami, A. S. (2019). Catalytic pyrolysis of plastic waste: Moving towards pyrolysis based biorefineries. *Frontiers in Energy Research*, 7(27).

- Miranda, R., Yang, J., Roy, C., and Vasile, C. (2001). Vacuum pyrolysis of commingled plastics containing PVC I. Kinetic study. *Polymer Degradation and stability*, 72(3), 469-491.
- Miteva, K., Aleksovski, S., and Bogoeva-Gaceva, G. (2016). Catalytic pyrolysis of waste plastic into liquid fuel. *Zaštita Materijala*, 57(4), 600-604.
- Miteva, K., Slavcho, A., and Bogoeva-Gaceva, G. (2016). Kinetic Analysis of Pyrolysis of Waste Polyolefin Mixture. *Arabian Journal for Science and Engineering*, 41(7), 2601-2609. Doi: 10.1007/s13369-016-2092-8
- Miura, K. (1995). A new and simple method to estimate $f(E)$ and $k_0(E)$ in the distributed activation energy model from three sets of experimental data. *Energy and Fuels*, 9(2), 302-307.
- Miura, K., and Maki, T. (1998). A simple method for estimating $f(E)$ and $k_0(E)$ in the distributed activation energy model. *Energy and Fuels*, 12(5), 864-869. Doi: <https://doi.org/10.1021/ef970212q>
- Moliner, M., and Corma, A. (2018). General Aspects on Structure and Reactivity of Framework and Extra-framework Metals in Zeolite Materials. In *Structure and Reactivity of Metals in Zeolite Materials* (pp. 53-90). Springer, Cham.
- Möller, K., and Bein, T. (2013). Mesoporosity—a new dimension for zeolites. *Chemical Society Reviews*, 42(9), 3689-3707. Doi: 10.1039/C3CS35488A

- Munir, D., Irfan, M. F., and Usman, M. R. (2018). Hydrocracking of virgin and waste plastics: A detailed review. *Renewable and Sustainable Energy Reviews*, 90, 490-515. Doi: 10.1016/j.rser.2018.03.034
- Munir, D., Piepenbreier, F., and Usman, M. R. (2017). Hydrocracking of a plastic mixture over various micro-mesoporous composite zeolites. *Powder Technology*, 316, 542-550. Doi: 10.1016/j.powtec.2017.01.037
- Murichan, N., and Cherntongchai, P. (2014). Kinetic analysis of thermal degradation of polyolefin mixtures. *International Journal of Chemical Engineering and Applications*, 5(2), 169.
- Murty, M. V. S., Rangarajan, P., Grulke, E. A., and Bhattacharyya, D. (1996). Thermal degradation/hydrogenation of commodity plastics and characterization of their liquefaction products. *Fuel processing technology*, 49(1-3), 75-90. Doi: 10.1016/S0378-3820(96)01040-5
- Na, K., and Somorjai, G. A. (2015). Hierarchically nanoporous zeolites and their heterogeneous catalysis: current status and future perspectives. *Catalysis Letters*, 145(1), 193-213. Doi: 10.1007/s10562-014-1411-5
- Newkirk, A. E. (1960). Thermogravimetric measurements. *Analytical Chemistry*, 32(12), 1558-1563.
- Ni, Y., Sun, A., Wu, X., Hai, G., Hu, J., Li, T., and Li, G., (2011). Preparation of hierarchical mesoporous Zn/HZSM-5 catalyst and its application in MTG reaction. *Journal of Natural Gas Chemistry*, 20, 237–242.

- Ochoa, R., Van Woert, H., Lee, W. H., Subramanian, R., Kugler, E., and Eklund, P. C. (1996). Catalytic degradation of medium density polyethylene over silica-alumina supports. *Fuel Processing Technology*, 49(1-3), 119-136. Doi: [10.1016/S0378-3820\(96\)01055-7](https://doi.org/10.1016/S0378-3820(96)01055-7)
- Ozawa, T. (1965). A new method of analyzing thermogravimetric data. *Bulletin of the chemical society of Japan*, 38(11), 1881-1886.
- Panda, A. K., and Singh, R. K. (2011). Catalytic performances of kaoline and silica alumina in the thermal degradation of polypropylene. *Journal of Fuel Chemistry and Technology*, 39(3), 198-202. Doi: [0.1016/S1872-5813\(11\)60017-0](https://doi.org/10.1016/S1872-5813(11)60017-0)
- Panda, A. K., Singh, R. K., and Mishra, D. K. (2010). Thermolysis of waste plastics to liquid fuel: A suitable method for plastic waste management and manufacture of value added products—A world prospective. *Renewable and Sustainable Energy Reviews*, 14(1), 233-248. Doi: [10.1016/j.rser.2009.07.005](https://doi.org/10.1016/j.rser.2009.07.005)
- Peng, H., Xu, L., Wu, H., Wang, Z., Liu, Y., Li, X., ... and Wu, P. (2012). Synthesis and formation mechanism of TS-1@ mesosilica core-shell materials templated by triblock copolymer surfactant. *Microporous and Mesoporous Materials*, 153, 8-17. Doi: [10.1016/j.micromeso.2011.11.055](https://doi.org/10.1016/j.micromeso.2011.11.055)
- Perera, K. U. C., and Narayana, M. (2018). Kissinger method: the sequential approach and DAEM for kinetic study of rubber and gliricidia wood. *Journal of the National Science Foundation of Sri Lanka*, 46(2).

- Pérez-Page, M., Makel, J., Guan, K., Zhang, S., Tringe, J., Castro, R. H., & Stroeve, P. (2016). Gas adsorption properties of ZSM-5 zeolites heated to extreme temperatures. *Ceramics International*, 42(14), 15423-15431.
- Perez-Ramirez, J., Christensen, C. H., Egeblad, K., Christensen, C. H., and Groen, J. C. (2008). Hierarchical zeolites: enhanced utilisation of microporous crystals in catalysis by advances in materials design. *Chemical Society Reviews*, 37(11), 2530-2542. Doi: 10.1039/B809030K
- Pérez-Ramírez, J., Verboekend, D., Bonilla, A., and Abelló, S. (2009). Zeolite Catalysts with Tunable Hierarchy Factor by Pore-Growth Moderators. *Advanced Functional Materials*, 19(24), 3972-3979. Doi: [10.1016/j.cattod.2011.03.045](https://doi.org/10.1016/j.cattod.2011.03.045)
- Pinto, F., Costa, P., Gulyurtlu, I., and Cabrita, I. (1999). Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield. *Journal of Analytical and Applied Pyrolysis*, 51(1-2), 39-55. Doi: 10.1016/S0165-2370(99)00007-8
- Pitt, G. J. (1962). The kinetic of the evolution of volatile products from coal. *Fuel*, 41, 267-274.
- Plastic. (2018, April 01). Retrieved from <https://en.wikipedia.org/wiki/Plastic>
- Plastics recycling information sheet (2018), Retrieved from <http://www.wasteonline.org.uk/resources/InformationSheets/Plastics.html>

- Poletto, M., Júnior, H. L. O. and Zattera, A. J. (2015). Thermal decomposition of natural fibers: kinetics and degradation mechanisms. *Reactions and Mechanisms in Thermal Analysis of Advanced Materials*, 515-545.
- Powell, D. A. (1957). An apparatus giving thermogravimetric and differential thermal curves simultaneously from one sample. *Journal of Scientific Instruments*, 34(6), 225.
- Qin, Z., Shen, B., Gao, X., Lin, F., Wang, B., and Xu, C. (2011). Mesoporous Y zeolite with homogeneous aluminum distribution obtained by sequential desilication–dealumination and its performance in the catalytic cracking of cumene and 1, 3, 5-triisopropylbenzene. *Journal of Catalysis*, 278(2), 266-275. Doi: 10.1016/j.jcat.2010.12.013
- Ragaert, K., Delva, L., and Van Geem, K. (2017). Mechanical and chemical recycling of solid plastic waste. *Waste Management*, 69, 24-58. Doi: 10.1016/j.wasman.2017.07.044
- Ramdoss, P. K., and Tarrer, A. R. (1998). High-temperature liquefaction of waste plastics. *Fuel*, 77(4), 293-299. Doi: 10.1016/S0016-2361(97)00193-2
- Ramesh, S. (2017, July 18). Plastic industry statistics. Retrieved from http://www.cipet.gov.in/plastics_statics.html
- Ratnasari, D. K., Nahil, M. A., and Williams, P. T. (2017). Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils. *Journal of Analytical and Applied Pyrolysis*, 124, 631-637. Doi: 10.1016/j.jaap.2016.12.027

- Ratnasari, D. K., Nahil, M. A., and Williams, P. T. (2017). Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils. *Journal of analytical and applied pyrolysis*, 124, 631-637. Doi: 10.1016/j.jaap.2016.12.027
- Renzini, M. S., Lerici, L. C., Sedran, U., and Pierella, L. B. (2011). Stability of ZSM-11 and BETA zeolites during the catalytic cracking of low-density polyethylene. *Journal of analytical and Applied Pyrolysis*, 92(2), 450-455. Doi: 10.1016/j.jaap.2011.08.008
- Reule, A. A., Sawada, J. A., and Semagina, N. (2017). Effect of selective 4-membered ring dealumination on mordenite-catalyzed dimethyl ether carbonylation. *Journal of Catalysis*, 349, 98-109. Doi: 10.1016/j.jcat.2017.03.010
- Rohayati, Krisnandi, Y. K., & Sihombing, R. (2017, July). Synthesis of ZSM- 5 zeolite using Bayat natural zeolite as silica and alumina source. In *AIP Conference Proceedings* (Vol. 1862, No. 1, p. 030094). AIP Publishing LLC.
- Rostamizadeh, M., and Yaripour, F. (2017). Dealumination of high silica H-ZSM-5 as long-lived nanocatalyst for methanol to olefin conversion. *Journal of the Taiwan Institute of Chemical Engineers*, 71, 454-463. Doi: 10.1016/j.jtice.2016.12.003
- Rutkowska, M., Pacia, I., Basąg, S., Kowalczyk, A., Piwowska, Z., Duda, M., ... and Chmielarz, L. (2017). Catalytic performance of commercial Cu-ZSM-5 zeolite modified by desilication in NH₃-SCR and NH₃-SCO processes. *Microporous and Mesoporous Materials*, 246, 193-206. Doi: 10.1016/j.micromeso.2017.03.017

- Rybicki, M., and Sauer, J. (2019). Acid strength of zeolitic Brønsted sites—Dependence on dielectric properties. *Catalysis Today*, 323, 86-93. Doi: [10.1016/j.cattod.2018.04.031](https://doi.org/10.1016/j.cattod.2018.04.031)
- Sadowska, K., Góra-Marek, K., and Datka, J. (2013). Accessibility of acid sites in hierarchical zeolites: quantitative IR studies of pivalonitrile adsorption. *The Journal of Physical Chemistry C*, 117(18), 9237-9244. Doi: [10.1021/jp400400t](https://doi.org/10.1021/jp400400t)
- Sadowska, K., Góra-Marek, K., Drozdek, M., Kuśtrowski, P., Datka, J., Triguero, J. M., and Rey, F. (2013). Desilication of highly siliceous zeolite ZSM-5 with NaOH and NaOH/tetrabutylamine hydroxide. *Microporous and Mesoporous Materials*, 168, 195-205. Doi: [10.1016/j.micromeso.2012.03.045](https://doi.org/10.1016/j.micromeso.2012.03.045)
- Sadowska, K., Wach, A., Olejniczak, Z., Kuśtrowski, P., and Datka, J. (2013). Hierarchic zeolites: Zeolite ZSM-5 desilicated with NaOH and NaOH/tetrabutylamine hydroxide. *Microporous and Mesoporous Materials*, 167, 82-88. Doi: [10.1016/j.micromeso.2012.03.045](https://doi.org/10.1016/j.micromeso.2012.03.045)
- Sahooli, M., Rahimpour, M., and Khorram, M. (2017). Fine-Tuning Synthesis and Characterization of Mono-Sized H-Beta Zeolite-Supported Palladium-Iridium Nanoparticles and Application in the Selective Hydrogenation of Acetylene. *Catalysts*, 7(11), 343.
- Sakaki, S. A., Roozbehani, B., Shishesaz, M., and Abdollahkhani, N. (2014). Catalytic degradation of the mixed polyethylene and polypropylene into middle distillate products. *Clean Technologies and Environmental Policy*, 16(5), 901-910. Doi: [10.1007/s10098-013-0688-1](https://doi.org/10.1007/s10098-013-0688-1)

- Sakata, Y., Uddin, A., Muto, A., Koizumi, K., Narazaki, M., Murata, K., and Kaji, M. (1996). Thermal and catalytic degradation of municipal waste plastics into fuel oil. *Polymer Recycling*, 2(4), 309-315. Retrieved from <https://okayama.pure.elsevier.com/en/publications/thermal-and-catalytic-degradation-of-municipal-waste-plastics-int>
- Sakata, Y., Uddin, M. A., Koizumi, K., and Murata, K. (1996). Thermal degradation of polyethylene mixed with poly (vinyl chloride) and poly (ethyleneterephthalate). *Polymer Degradation and Stability*, 53(1), 111-117. Doi: 10.1016/0141-3910(96)00077-8
- Sarker, M., Rashid, M. M., Molla, M., and Rahman, M. S. (2012). A new technology proposed to recycle waste plastics into hydrocarbon fuel in USA. *International Journal of Energy and Environment*, 3(5), 749-760. Retrieved from http://www.ijee.ieefoundation.org/vol3/issue5/IJEE_09_v3n5.pdf
- Schwieger, W., Machoke, A. G., Weissenberger, T., Inayat, A., Selvam, T., Klumpp, M., and Inayat, A. (2016). Hierarchy concepts: classification and preparation strategies for zeolite containing materials with hierarchical porosity. *Chemical society reviews*, 45(12), 3353-3376. Doi: 10.1039/C5CS00599J
- Scott G (1997). Abiotic control of polymer biodegradation. *Trends in Polymer Science*; 5(11), 361–368. Retrieved from <https://www.infona.pl/resource/bwmata1.element.elsevier-dacdd126-ce07-372a-a3f8-2c99214712ec/tab/summary>
- Scott, G. (1997). *Antioxidants in science, technology, medicine and nutrition*. Elsevier.

- Scott, G. (1999). *Polymers and the Environment*. Royal Society of Chemistry. Retrieved from <https://pubs.rsc.org/en/content/ebook/978-0-85404-578-5>
- Scott, G. G. (2000). "polymers. *Polymer Degradation and Stability*, 68, 1-7. Retrieved from [https://www.scirp.org/\(S\(351jmbntvnsjt1aadkposzje\)\)/reference/ReferencesPapers.aspx?ReferenceID=1702481](https://www.scirp.org/(S(351jmbntvnsjt1aadkposzje))/reference/ReferencesPapers.aspx?ReferenceID=1702481)
- Scott, G., and Wiles, D. M. (2001). Programmed-life plastics from polyolefins: a new look at sustainability. *Biomacromolecules*, 2(3), 615-622. Doi: 10.1021/bm010099h
- Sebestyén, Z., Barta-Rajnai, E., Bozi, J., Blazsó, M., Jakab, E., Miskolczi, N., and Czégény, Z. (2017). Catalytic pyrolysis of biomass and plastic mixtures using HZSM-5 zeolite. *Energy Procedia*, 105, 718-723. Doi: 10.1016/j.egypro.2017.03.381
- Seo, Y. H., and Shin, D. H. (2002). Determination of paraffin and aromatic hydrocarbon type chemicals in liquid distillates produced from the pyrolysis process of waste plastics by isotope-dilution mass spectrometry. *Fuel*, 81(16), 2103-2112. Doi: 10.1016/S0016-2361(02)00197-7
- Serrano, D. P., and Pizarro, P. (2013). Synthesis strategies in the search for hierarchical zeolites. *Chemical Society Reviews*, 42(9), 4004-4035. Doi: 10.1039/C2CS35330J
- Serrano, D. P., Aguado, J., Morales, G., Rodriguez, J. M., Peral, A., Thommes, M., ... and Chmelka, B. F. (2009). Molecular and meso- and macroscopic properties of hierarchical nanocrystalline ZSM-5

- zeolite prepared by seed silanization. *Chemistry of Materials*, 21(4), 641-654. Doi: 10.1021/cm801951a
- Serrano, D. P., Arroyo, M., and Alba, A. (2014). Conversion of LDPE into transportation fuels by a two-stage process using Ni/Al-SBA-15 as catalyst. *Journal of Material Cycles and Waste Management*, 16(3), 435-441. Doi: 10.1007/s10163-014-0249-7
- Shah, N., Rockwell, J., and Huffman, G. P. (1999). Conversion of waste plastic to oil: direct liquefaction versus pyrolysis and hydroprocessing. *Energy and fuels*, 13(4), 832-838. Doi: 10.1021/ef9802431
- Sharuddin, S. D. A., Abnisa, F., Daud, W. M. A. W., and Aroua, M. K. (2016). A review on pyrolysis of plastic wastes. *Energy conversion and management*, 115, 308-326. Doi: 10.1016/j.enconman.2016.02.037
- Shehata, N., Mohamed, H. S., Emam, H. M., and Ahmed, S. Fuel produced from catalytic pyrolysis of waste plastic. *Emirates Journal for Engineering Research*, 22 (4), 1-6 (2017)
- Silvarrey, L. D., and Phan, A. N. (2016). Kinetic study of municipal plastic waste. *International Journal of Hydrogen Energy*, 41(37), 16352-16364.
- Šimon, P. (2004). Isoconversional methods. *Journal of Thermal Analysis and Calorimetry*, 76(1), 123.
- Singh, M. V., Kumar, S., and Sarker, M. (2018). Waste HD-PE plastic, deformation into liquid hydrocarbon fuel using pyrolysis-catalytic

cracking with a CuCO_3 catalyst. *Sustainable Energy and Fuels*, 2(5), 1057-1068.

Smail, H. A., Rehan, M., Shareef, K. M., Ramli, Z., Nizami, A. S., and Gardy, J. (2019). Synthesis of Uniform Mesoporous Zeolite ZSM-5 Catalyst for Friedel-Crafts Acylation. *ChemEngineering*, 3(2), 35.

Somidi, A. K., Das, U., and Dalai, A. K. (2016). One-pot synthesis of canola oil based biolubricants catalyzed by $\text{MoO}_3/\text{Al}_2\text{O}_3$ and process optimization study. *Chemical Engineering Journal*, 293, 259-272.
Doi: 10.1016/j.cej.2016.02.076

Sonawane, Y. B., Shindikar, M., and Khaladkar, M. (2015). Use of catalyst in pyrolysis of polypropylene waste into liquid fuel. *Int Res J Environ Sci*, 4(7), 24-28. Retrieved from
https://www.researchgate.net/profile/Y_Sonawane/publication/317429097_Use_of_Catalyst_in_Pyrolysis_of_Polypropylene_Waste_into_Liquid_Fuel/links/593a9642aca27233340ba639/Use-of-Catalyst-in-Pyrolysis-of-Polypropylene-Waste-into-Liquid-Fuel.pdf

Song, G., Chen, W., Dang, P., Wang, Y., and Li, F. (2018). Synthesis of an excellent MTP catalyst: hierarchical ZSM-5 zeolites with great mesoporosity. *Royal Society open science*, 5(12), 181691.

Sriningsih, W., Saerodji, M. G., Trisunaryanti, W., Armunanto, R., and Falah, I. I. (2014). Fuel production from LDPE plastic waste over natural zeolite supported Ni, Ni-Mo, Co and Co-Mo metals. *Procedia Environmental Sciences*, 20, 215-224.
Doi: 10.1016/j.proenv.2014.03.028

- Stephan J.(2018, March 18), Investigation of hydrocarbon transport on surface modified zeolites. Retrieved from <https://www.elitenetzwerk.bayern.de/elitenetzwerk-home/forschungsarbeiten/naturwissenschaften/2009/reitmeier-zeolites/>
- Supatra, B., Hunt, A. J., and Ngernyen, Y. (2019). Catalytic pyrolysis of plastic waste for the production of liquid fuels for engines. *RSC advances*, 9(10), 5844-5857.
- Szekely, T., Varhegyi, G., Till, F., Szabo, P., and Jakab, E. (1987). The effects of heat and mass transport on the results of thermal decomposition studies: part 2. Polystyrene, polytetrafluoroethylene and polypropylene. *Journal of Analytical and Applied Pyrolysis*, 11, 83-92. Doi: [10.1016/0165-2370\(87\)85021-0](https://doi.org/10.1016/0165-2370(87)85021-0)
- TU Chemical Engineering. (n.d.). Retrieved November 24, 2018, from <http://personal.utulsa.edu/~geoffrey-price/zeolite/index.html>
- Usman, M. A., Alaje, T. O., Ekwueme, V. I., and Adekoya, T. E. (2012). Catalytic degradation of water sachet waste (LPDE) using mesoporous silica KIT-6 modified with 12-tungstophosphoric acid. *Petroleum and Coal*, 54(2). Retrieved from [https://www.researchgate.net/publication/281468554 Catalytic degradation of water sachet waste LPDE using mesoporous silica KIT-6 modified with 12-tungstophosphoric acid](https://www.researchgate.net/publication/281468554_Catalytic_degradation_of_water_sachet_waste_LPDE_using_mesoporous_silica_KIT-6_modified_with_12-tungstophosphoric_acid)
- Valtchev, V., Balanzat, E., Mavrodinova, V., Diaz, I., El Fallah, J., and Goupil, J. M. (2011). High energy ion irradiation-induced ordered macropores in zeolite crystals. *Journal of the American Chemical Society*, 133(46), 18950-18956. Doi: 10.1021/ja208140f

- Van Laak, A. N., Sagala, S. L., Zečević, J., Friedrich, H., de Jongh, P. E., and de Jong, K. P. (2010). Mesoporous mordenites obtained by sequential acid and alkaline treatments—Catalysts for cumene production with enhanced accessibility. *Journal of Catalysis*, 276(1), 170-180. [Doi: 10.1016/j.jcat.2010.09.011](https://doi.org/10.1016/j.jcat.2010.09.011)
- Van Oers, C. J., Stevens, W. J., Bruijn, E., Mertens, M., Lebedev, O. I., Van Tendeloo, G., ... and Cool, P. (2009). Formation of a combined micro-and mesoporous material using zeolite Beta nanoparticles. *Microporous and Mesoporous Materials*, 120(1-2), 29-34. [Doi: 10.1016/j.micromeso.2008.08.056](https://doi.org/10.1016/j.micromeso.2008.08.056)
- Vasile, C., Pakdel, H., Mihai, B., Onu, P., Darie, H., and Ciocâlțu, S. (2001). Thermal and catalytic decomposition of mixed plastics. *Journal of analytical and Applied Pyrolysis*, 57(2), 287-303. [Doi: 10.1016/S0165-2370\(00\)00151-0](https://doi.org/10.1016/S0165-2370(00)00151-0)
- Venkatesh, K. R., Hu, J., Tierney, J. W., and Wender, I. (1995). Hydrocracking of polyolefins to liquid fuels over strong solid acid catalysts. *Preprints of Papers-American Chemical Society Division Fuel Chemistry*, 40, 788-788. [Doi: 10.1021/ie9015842](https://doi.org/10.1021/ie9015842)
- Vennestrøm, P. N., Grill, M., Kustova, M., Egeblad, K., Lundegaard, L. F., Joensen, F., ... and Beato, P. (2011). Hierarchical ZSM-5 prepared by guanidinium base treatment: Understanding microstructural characteristics and impact on MTG and NH₃-SCR catalytic reactions. *Catalysis today*, 168(1), 71-79. [Doi: 10.1016/j.cattod.2011.03.045](https://doi.org/10.1016/j.cattod.2011.03.045)
- Verboekend, D., Caicedo-Realpe, R., Bonilla, A., Santiago, M., and Pérez-Ramírez, J. (2010). Properties and functions of hierarchical ferrierite

- zeolites obtained by sequential post-synthesis treatments. *Chemistry of Materials*, 22(16), 4679-4689. Doi: 10.1021/cm100886y
- Verboekend, D., Chabaneix, A. M., Thomas, K., Gilson, J. P., and Pérez-Ramírez, J. (2011). Mesoporous ZSM-22 zeolite obtained by desilication: peculiarities associated with crystal morphology and aluminium distribution. *CrystEngComm*, 13(10), 3408-3416. Doi: 10.1039/C0CE00966K
- Verboekend, D., Vilé, G., and Pérez-Ramírez, J. (2012). Hierarchical Y and USY zeolites designed by post-synthetic strategies. *Advanced Functional Materials*, 22(5), 916-928. Doi: org/10.1002/adfm.201102411
- Verboekend, D., Vilé, G., and Pérez-Ramírez, J. (2012). Mesopore formation in USY and beta zeolites by base leaching: selection criteria and optimization of pore-directing agents. *Crystal Growth and Design*, 12(6), 3123-3132. Doi: 10.1021/cg3003228
- Walendziewski, J., and Steininger, M. (2001). Thermal and catalytic conversion of waste polyolefines. *Catalysis Today*, 65(2-4), 323-330. Doi: 10.1016/S0920-5861(00)00568-X
- Wang, H., Wang, L., and Shahbazi, A. (2015). Life cycle assessment of fast pyrolysis of municipal solid waste in North Carolina of USA. *Journal of Cleaner Production*, 87, 511-519. Doi: 10.1016/j.jclepro.2014.09.011
- Wang, J., and Wang, L. (2011). Catalytic Pyrolysis of Municipal Plastic Waste to Fuel with Nickel-loaded Silica-alumina Catalysts. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 33(21), 1940-1948. Doi: 10.1080/15567030903436814

- Wang, S., Jiang, X., Han, X., and Tong, J. (2013). Effect of residence time on products yield and characteristics of shale oil and gases produced by low-temperature retorting of dachengzi oil shale. *Oil Shale*, 30(4).
- Waters, D. N., and Paddy, J. L. (1988). Equations for isothermal differential scanning calorimetric curves. *Analytical chemistry*, 60(1), 53-57.
- Yan, G., Jing, X., Wen, H., and Xiang, S. (2015). Thermal cracking of virgin and waste plastics of PP and LDPE in a semibatch reactor under atmospheric pressure. *Energy and Fuels*, 29(4), 2289-2298.
- Weitkamp, J. (2000). Zeolites and catalysis. *Solid State Ionics*, 131(1-2), 175-188. Doi: [10.1016/S0167-2738\(00\)00632-9](https://doi.org/10.1016/S0167-2738(00)00632-9)
- Williams, E. A., and Williams, P. T. (1997). Analysis of products derived from the fast pyrolysis of plastic waste. *Journal of analytical and applied pyrolysis*, 40, 347-363. Doi: [10.1016/S0165-2370\(97\)00048-X](https://doi.org/10.1016/S0165-2370(97)00048-X)
- Williams, P. T., and Williams, E. A. (1998). Recycling plastic waste by pyrolysis. *Journal of the Institute of Energy*, 71(487), 81-93. Retrieved from <https://www.cheric.org/research/tech/periodicals/view.php?seq=1115192>.
- Wu, C. H., Chang, C. Y., Lin, J. P., and Liang, Y. (1998). Effects of hydrogen chloride on the pyrolysis of polyethylene: pyrolysis kinetics. *Journal of hazardous materials*, 58(1-3), 195-205. Doi: [10.1016/S0304-3894\(97\)00131-3](https://doi.org/10.1016/S0304-3894(97)00131-3)

- Xing, X., Wang, S., and Zhang, Q. (2019). Thermogravimetric Analysis and Kinetics of Mixed Combustion of Waste Plastics and Semicoke. *Journal of Chemistry*, 2019.
- Xue, T., Liu, H., Zhang, Y., Wu, H., Wu, P., and He, M. (2017). Synthesis of ZSM-5 with hierarchical porosity: In-situ conversion of the mesoporous silica-alumina species to hierarchical zeolite. *Microporous and Mesoporous Materials*, 242, 190-199. Doi: 10.1016/j.micromeso.2017.01.021
- Yang, K., Basem, S., and El-Haik, B. (2003). *Design for six sigma* (pp. 184-186). New York: McGraw-Hill.
- Yao, X., Yu, Q., Xie, H., Duan, W., Han, Z., Liu, S., and Qin, Q. (2017). Syngas production through biomass/CO₂ gasification using granulated blast furnace slag as heat carrier. *Journal of Renewable and Sustainable Energy*, 9(5), 053101. Doi: 10.1063/1.4993259
- Yue, M. B., Sun, L. B., Zhuang, T. T., Dong, X., Chun, Y., and Zhu, J. H. (2008). Directly transforming as-synthesized MCM-41 to mesoporous MFI zeolite. *Journal of Materials Chemistry*, 18(17), 2044-2050. Doi: 10.1039/B717634A
- Zafar, S. (2017, July 18). Solid Waste Management in Bahrain. Retrieved from <https://www.ecomena.org/solid-waste-bahrain/>
- Zahara, Z., Krisnandi, Y. K., Wibowo, W., Nurani, D. A., Rahayu, D. U. C., and Haerudin, H. (2018, October). Synthesis and characterization of hierarchical ZSM-5 zeolite using various templates as cracking catalysts. In AIP Conference Proceedings (Vol. 2023, No. 1, p. 020088). AIP Publishing.

- Zenonos, C., Sankar, G., García-Martínez, J., Aliev, A., and Beale, A. M. (2003). Direct hydrothermal conversion of high-silica faujausite and zeolite β to Zsm-5 and its catalytic performance. *Catalysis letters*, 86(4), 279-283. Doi: 10.1023/A:10226886
- Zeolyst. (n.d.). Retrieved October 9, 2018, from <https://www.zeolyst.com/our-products/standard-zeolite-powders/>
- Zhang, H., Shao, S., Luo, M., and Xiao, R. (2017). The comparison of chemical liquid deposition and acid dealumination modified ZSM-5 for catalytic pyrolysis of pinewood using pyrolysis-gas chromatography/mass spectrometry. *Bioresource Technology*, 244, 726-732. Doi: 10.1016/j.biortech.2017.08.036
- Zhang, K., and Ostraat, M. L. (2016). Innovations in hierarchical zeolite synthesis. *Catalysis today*, 264, 3-15. Doi: 10.1016/j.cattod.2015.08.012
- Zhang, Z., Wang, Q., Chen, H., and Zhang, X. (2017). Hydroconversion of waste cooking oil into green biofuel over hierarchical USY-supported NiMo catalyst: a comparative study of desilication and dealumination. *Catalysts*, 7(10), 281.
- Zhou, J., Hua, Z., Liu, Z., Wu, W., Zhu, Y., and Shi, J. (2011). Direct synthetic strategy of mesoporous ZSM-5 zeolites by using conventional block copolymer templates and the improved catalytic properties. *Acs Catalysis*, 1(4), 287-291. Doi: 10.1021/cs1000976
- Zhou, X., Chen, H., Zhu, Y., Song, Y., Chen, Y., Wang, Y., ... and Zhao, J. (2013). Dual-Mesoporous ZSM-5 Zeolite with Highly b-Axis-Oriented Large Mesopore Channels for the Production of Benzoin

Ethyl Ether. *Chemistry–A European Journal*, 19(30), 10017-10023.

Doi: [10.1002/chem.201300245](https://doi.org/10.1002/chem.201300245)

Zia, K. M., Bhatti, H. N., and Bhatti, I. A. (2007). Methods for polyurethane and polyurethane composites, recycling and recovery: A review. *Reactive and functional polymers*, 67(8), 675-692. Doi: [10.1016/j.reactfunctpolym.2007.05.004](https://doi.org/10.1016/j.reactfunctpolym.2007.05.004)

Publication list

- Mumtaz, F., Irfan, M. F. and Usman, M.R. Recent advances in hierarchical zeolites; a brief review [Under process]
- Mumtaz, F. and Irfan, M. F. Optimization of oil yield form waste plastic mixture by hydrocracking using hierarchical zeolite [Under process]

Appendices

Table of Contents

Appendix No.	Subject
I	Tabulated Literature Review
II(A)	MSDS of Catalyst used, ZSM-5 and BZ
II(B)	Characterization (BET) of BZ and ZSM-5
II(C)	List of chemicals used
III	GCMS data for preliminary experiment-1
IV	GCMS data for preliminary experiment-2
V	GCMS data for catalyst synthesis optimization
VI	Observations on desilication of BZ
VII	Kinetic analysis graphs
VIII	Catalyst & liquid products characterization techniques
IX	Various other methods of Hierarchical zeolites preparation

Appendix-I

Tabulated Literature Review

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N ₂ /H ₂ flowrate or ratio	Yield	Products
1	Maria et al.	2011	Pyrolysis	Stability of ZSM-11 and BETA zeolites during the catalytic cracking of low-density polyethylene	25-500C	-	Low density polyethylene	ZSM-11 (MEL, H-Z, Si/Al = 17) and BETA zeolites (BEA, H-B, Si/Al = 17)	Polymer to Catalyst mass ratio 2/1	Fixed bed batch reactor	25 L/min	Upto 80 wt%	mainly C3 - C9
2	J.F Mastral et al.	2006	Pyrolysis	Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite	350-550C	ambient pressure	High density polyethylene	nanocrystalline HZSM-5 zeolite (by Sud Chemie Corporation & the physical properties are: MFI structure (5.3 5.6/5.1 5.5 Å° pore size), Si:Al ratio ¼ 35, crystal size ¼ 100 nm, BET surface ¼ 397 m2/g)	Polymer to Catalyst ratio (HDPE/Cat):0.93, 1.41, 9.20 and Infinity (Thermal)	Fluidized bed reactor	-	Upto 80 wt%	C1-C7
3	Yusaku.S et al.	1997	Pyrolysis	Catalytic degradation of polyethylene into fuel oil over mesoporous silica (KFS-16) catalyst	430C	-	High density polyethylene	mesoporous silica (KFS-16: Kanemitederived folded silica) catalyst (prepared using colloidal silica having a composition of 30.5 wt% SiO2 and 0.4 wt% Na2O and 69 wt% H2O)	10g of HDPE to 1g of catalyst	Semi-Batch reactor	-	-	C2-C25
4	Karmina et al.	2016	Pyrolysis	Catalytic pyrolysis of waste plastic into liquid fuel	400-550C	ambient pressure	Waste Polyolefin mixture	Al2O3 & SiO2 catalyst (The purchsed pelletized catalyst (5mm) of Al2O3 has specific surface 400 m2/g. The specific surface area of SiO2 (assigned as S) is 39.3 m2/g.)	Ratio varied	Semi-Batch reactor	-	77-88 wt%	C5-C16
5	Niraj.N et al.	2016	Pyrolysis	Catalytic conversion of plastic waste to fuel	50-550C	1 atm	Low density polyethylene	Calcium Bantonite and Zeolite	-	Batch Reactor	-	60-74 wt%	-
6	Devy K. et al.	2017	Pyrolysis	Catalytic pyrolysis of waste plastics using staged catalysis for production of gasoline range hydrocarbon oils	500C	-	High density polyethylene	MCM-41,ZSM-5	Plastic:catalysts:1:2	2-staged fixed bed reactor	-	Upto 97 wt%	C2-C4
7	A.Lopez et al.	2011	Pyrolysis	Catalytic pyrolysis of plastic wastes with two different types of catalysts- ZSM-5 zeolite and Red Mud	440C,500C	ambient pressure	Mixture of plastic resembles municiple waste	ZSM-5 zeolite & Red mud (ZSM-5 zeolite, in NH4+ cation form and with a SiO2/Al2O3 ratio of 50, was provided by Zeolist International. Red Mud was obtained from a German alumina production company)	10g of catalyst/100g of plastics	Semi-Batch reactor	-	Upto 80 wt%	C2-C20
8	Y.H Lin, M.H Yang	2007	Pyrolysis	Catalytic pyrolysis of polyolefin waste into valuable hydrocarbons over reused catalyst from refinery FCC units	330-450C	ambient pressure	Polyolefin waste (PE/PP polymer)	Reused catalyst form FCC: Rcatc1, USY, ZSM-5, SAHA & silicalite (Si/Al: 2.1,17.5,13.6,3.6,1000 respectively.)	Polymer to catalyst ration-0.1:1 to 0.6:1	Fluidized bed reactor	300-900 ml/min	Upto 85 wt%	C2 -C9
9	Sonawane YB et al.	2015	Pyrolysis	Use of Catalyst in Pyrolysis of Polypropylene Waste into Liquid Fuel	Upto 450C	-	Polypropylene waste	Natural Zeolite (NZ)	10% of natural zeolite	Semi-Batch reactor	-	Upto 85 wt%	C5-C22
10	Kaixin li et al.	2016	Pyrolysis	Investigation into the Catalytic Activity of microporous and mesoporous catlaysts in the pyrolysis of waste polyethylene mixture	300-500C	-	Polyethylene Polypropylene mixture	microporous catalysts : conventional Zeolite Socony Mobil-5 (C-ZSM-5), highly uniform nanocrystalline ZSM-5 (HUN-ZSM-5) and β-zeolite, Mesoporous catalysts: highly hydrothermally stable Al-MCM-41 with accessible void defects (Al-MCM-41(his), Kanemite-derived folded silica (KFS-16B) and well-ordered Al-SBA-15 (Al-SBA-15(wo))	-	Batch Reactor	200 ml/min	Upto 90 wt%	C1-C40
11	Kaixin li et al.	2016	Pyrolysis	Fe-, Ti-, Zr- and Al-pillared clays for efficient catalytic pyrolysis of mixed plastics	473-624K	-	Mixed plastic including HDPE,PS,PP & PET	Fe-,Ti-,Zr-Al-pillared clays	-	Tube Reactor	-	Upto 80 wt%	C6-C40
12	Bahrooz et al.	2015	Pyrolysis	Taguchi method approach on catalytic degradation of polyethylene and polypropylene into gasoline	410-450C	ambient pressure	Polyolefin waste (PE/PP polymer)	Supplied by Abadan Petro Frayande Polymer Ltd, made up of five separate main components like, Zeolite (molecular sieve), Platinum, Active matrix component, Inactive matrix component, and Binder	Catalyst 10-50 wt%	Semi-Batch reactor	-	-	C2 -C11+

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N2/H2 flowrate or ratio	Yield	Products
13	J.Aguado et al.	2006	Pyrolysis	Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins	250-550C	-	LDPE,HDPE	Three Zeolitic materials: Standard ZSM-5, Nanocrystalline n-ZSM-5, Beta-ZSM-5 Three Mesostructured solids: sol–gel Al-SBA-15,hydrothermal Al-MCM-41 (hy) and sol–gel Al-CM-41 (sg). Amorphous silica (SiO2), a non-acid porous solid	Catalyst 10 wt%	TA Instruments SDT 2960 simultaneous TGA-DSC thermogravimetric analyser	100 ml/min	-	-
14	D.P.Serano et al.	2007	Pyrolysis	Catalytic cracking of polyethylene over nanocrystalline HZSM-5- Catalyst deactivation and regeneration study	340C	-	Polyethylene	nanocrystalline HZSM-5	-	Batch Reactor	-	Upto 70 wt%	C1-C5
15	A.Garforth et al.	1997	Pyrolysis	Catalytic degradation of high density polyethylene-An evaluation of mesoporous and microporous catalysts using thermal analysis	450C	-	High density polyethylene	Silica-Alumina (SAHA or Syndyst 25) HY (H-Y zeolite), HUSY (H-Ultrastabilised Y zeolite), HZSM-5 zeolite, HASM-5 zeolite, MCM-41(Al), MCM-41(Si)	-	Batch Reactor	-	-	-
16	A.Coelho et al.	2010	Pyrolysis	Catalytic degradation of low and high density polyethylenes using ethylene polymerization catalysts-Kinetic studies using simultaneous TG/DTG analysis	100-550C	-	Polyethylene	NaY zeolite (LZ-Y52, with a Si/Al ratio of 2.5 as indicated by the manufacturer) was supplied by Union Carbide	-	Batch Reactor	80 ml/min	-	C1 -C9
17	Nnamso S. et al.	2005	Pyrolysis	Catalytic degradation of plastic waste to liquid fuel over commercial cracking catalysts- Effect of polymer to catalyst ratio/acidity content	100-600C	-	Polyethylene	commercial cracking catalysts, named cracking catalyst 1 and cracking catalyst 2, containing 20% and 40% US-Y, respectively(average particle size, 100 m) kindly provided by AKZO-NOBEL	Ratio assessed	Semi-Batch reactor	-	upto 90 wt%	-
18	Isabel C.N et al.	2007	Pyrolysis	Catalytic degradation of polyethylene- An evaluation of the effect of dealuminated Y zeolites using thermal analysis	300-800K	-	High density polyethylene	Y zeolites USY (CBV 500), HY(4) (CBV 400), HY(12) (CBV 712) and HY(20) (CBV 720), were obtained from ZEOLYST with the specific surface area of 730–780 m ² g ⁻¹ , were used in powder form	Ratio- 9:1	-	20 ml/min	-	-
19	G.J.T fernandes et al.	2004	Pyrolysis	Catalytic degradation of polyethylene over SAPO-37 molecular sieve	380-520C	ambient pressure	High density polyethylene	silicoaluminophosphate (SAPO-37) catalyst	25%SAPO-37/HDPE	Batch Reactor	-	upto 90 wt%	C2-C25
20	Ali .D et al	2005	Pyrolysis	Thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites	400-1100K	ambient pressure	polypropylene	different type of zeolite catalysts BEA, ZSM-5 and MOR with different surface areas, pore structures, acidities and Si/Al molar ratios	varies	Shimadzu TGA-50, Thermogravimetric Analyzer	50 ml/min	-	-
21	Pengru C. et al.	2017	Pyrolysis	Catalytic depolymerization of the hydrolyzed lignin over mesoporous catalysts	260-320C	10 bar	depolymerization of the hydrolyzed lignin	Mesoporous catalysts Ni/Al-SBA-15 and Ni/MCM-41 with 20 wt.% of Ni	-	Batch Reactor	-	upto 80 wt%	-
22	Jose´ Geraldo A. Pacheco Filho et al.	2005	Pyrolysis	Thermo gravimetric kinetics of polypropylene degradation on ZSM-12 and ZSM-5 catalysts	30-900C	-	polypropylene	ZSM-12 and ZSM-5 catalysts	ratio of 10, 30 and 50 wt%	Mettler-TGA/SDTA851.TG	25 ml/min	upto 95 wt%	-
23	Ayhan D.	2004	Pyrolysis	Pyrolysis of municipal plastic wastes for recovery of gasoline-range hydrocarbons	298-1025K	-	Polystyrene (PS), polyethylene (PE) and polypropylene (PP)	Thermal pyrolysis (no catalysts)	-	Batch Reactor	-	Upto 70 wt%	C1-C20
24	Shenming J. Et al.	2012	Pyrolysis	Preparation of mesoporous MCM-41 from natural sepiolite and its catalytic activity of cracking waste polystyrene plastics	683K	-	polystyrene	mesoporous MCM-41	Ratio varied	Batch Reactor	-	Upto 85 wt%	C5-C12
25	S.Ali et al.	2002	Pyrolysis	Polymer waste recycling over “used” catalysts	360,450C	ambient pressure	High density polyethylene	ZSM-5, US-Y, ASA, fresh FCC (fluid catalytic cracking) commercial catalyst (Cat-A) and equilibrium FCC catalysts with different levels of metal poisoning	polymer feed ratio of 2:1 & 6:1	Fluidized bed reactor	50 ml/min	-	C2-C8
26	Mochamad,S et al.	2013	Pyrolysis	Fuel Oil Production from Municipal Plastic Wastes in Sequential Pyrolysis and Catalytic Reforming Reactors	450C	-	Municipal plastic waste	zeolite (CBV 780 CY) was obtained from Zeolyst International. It has SiO2/Al2O3 mole ratio of 80, the unit cell size of 24.24 Å and the surface area of 780 m ² /g in the powder form	-	Batch Reactor	-	Upto 60 wt%	C5-C20

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N ₂ /H ₂ flowrate or ratio	Yield	Products
27	M.S.Khan et al.	2016	Pyrolysis	Conversion of Mixed Low-Density Polyethylene Wastes into Liquid Fuel by Novel CaO-SiO ₂ Catalyst	40-1000C	-	Mixed low density polyethylene	Equal molar mixture of analytical grade reagents Calcium oxide (Merck) and Silicon dioxide (Scharlau) was used as a catalyst	-	PerkinElmer Diamond Thermogravimetric/Differential Thermal Analysis (TG/DTA) system	-	Upto 70 wt%	-
28	Nadia C. et al.	2016	Pyrolysis	Coprocessing of Waste Plastic and Hydrocarbons over MFI (HZSM-5	40-600C	-	high- and low-density polyethylene (HDPE and LDPE, respectively) and waste plastic film (polyethylene-based plastic wastes)	The catalyst used was MFI (HZSM-5) commercially supplied by Zeolyst, with a molar Si/Al ratio of 15.	-	TA Instruments SDT 2960 simultaneous DSC/TGA apparatus.	80 ml/min	-	C1-C8+
29	Antonio et al.	2017	Pyrolysis	Development of HZSM-12 zeolite for catalytic degradation of high-density polyethylene	100-600C	autogenous pressure	High density polyethylene	HZSM-12 zeolites with different Si/Al ratio	-	termobalance Metler model TGA/SDTA	25 ml/min	-	C1-C22
30	Moinudding et al.	2012	Pyrolysis	Polystyrene (PS) waste plastic conversion into aviationkerosene category of fuel by using fractional column distillation process	100-400C	ambient pressure	Polystyrene	No Catalyst, thermal degradation	-	fractional distillation column tower	-	77 wt%	C6-C16
31	D.P. Serrano et al.	2004	Pyrolysis	Influence of nanocrystalline HZSM-5 external surface on the catalytic cracking of polyolefins	50-250C	autogenous pressure	high and low density polyethylene	nanocrystalline HZSM-5	mixture of 10 g of plastic and 0.1 g of catalyst (plastic/catalyst mass ratio = 100)	stirred batch reactor	35 ml/min	-	C2-C5
32	Christine et al.	2013	Pyrolysis	Synthesis of Petroleum-Based Fuel from Waste Plastics and Performance Analysis in a CI Engine	400-550C	-	Polyethylene	silica, alumina, Y zeolite, barium carbonate, zeolite, and their combinations	polymner to catalyst ratio of 10 : 1	ceramic electric heater (Batch reactor)	10 ml/min	Upto 65 wt%	C9-C19
33	I.C. Neves et al	2007	Pyrolysis	Feedstock recycling of polyethylene over AITUD-1 mesoporous catalyst	300-800K	-	High density polyethylene	Two mesoporous catalysts AITUD-1 (AITUD-1A and Al-TUD-1B) with different Si/Al atomic ratios, surface areas and porosities	polymer/catalyst ratio of 9:1.	Batch Reactor	20 ml/min	Upto 80 wt%	-
34	J. Aguado et al.	1999	Pyrolysis	Catalytic conversion of polyolefins into fuels over zeolite beta	400C	ambient pressure	polypropylene and both low- and high-density polyethylene	Zeolite beta synthesized by the fluoride method	plastic/catalyst ratio of 50 w/w	Batch Reactor	25 mL(STP)/min N ₂ flow	Upto 70 wt%	C5-C12
35	J. Nishino et al.	2008	Pyrolysis	Catalytic degradation of plastic waste into petrochemicals using Ga-ZSM-5	450-510C	ambient pressure	polyolefin	Ga-ZSM-5 (Si/Ga = 35), obtained from Japan Chemical Industry	-	Pilot plant	-	Upto 70 wt%	-
36	Zeynep Obali et al.	2012	Pyrolysis	Catalytic degradation of polypropylene over alumina loaded mesoporous catalysts	350-480C	ambient pressure	polypropylene	mesoporous MCM-41 and SBA-15	-	Semi-Batch reactor	60 ml/min	-	C5-C18
37	J.R. Kim et al.	2001	Pyrolysis	Catalytic degradation of polypropylene: effect of dealumination of clinoptilolite catalyst	100-700C	ambient pressure	Polypropylene	Clinoptilolite (NaSCLZ4.4)	mixture of 3.0 g of PP and 0.3 g of the catalyst	Semi-Batch reactor	30 ml/min	-	C4-C13
38	S.Y. Lee et al	2001	Pyrolysis	Catalytic degradation of polystyrene over natural clinoptilolite zeolite	625-775K	ambient pressure	Polystyrene	solid acid catalysts such as silica-alumina (SA, Aldrich), ZSM-5 (RC-Penta) and NZ	-	TGA (Perkin Elmer, TGA 7)	30 ml/min	Upto 85 wt%	C5-C12
39	A.K Panda et al.	2011	Pyrolysis	Catalytic performances of kaoline and silica alumina in the thermal degradation of polypropylene	400-550C	-	Polypropylene	kaoline and silica alumina	mixture of catalyst and the polypropylene pallets in different proportion (1:2, 1:3, 1:4, 1:6, 1:10, 1:20, 1:40)	semi batch reactor	-	Upto 90 wt%	-

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N ₂ /H ₂ flowrate or ratio	Yield	Products
40	J.R Kim et al.	2001	Pyrolysis	Catalytic recycling of the mixture of polypropylene and polystyrene	0-600C	-	Polypropylene, Polystyrene	silica-alumina (SA, Aldrich), ZSM-5 (RC-Penta) and natural clinoptilolite zeolite	3.0 g of the plastics and 0.3 g	semi batch reactor	30 ml/min	-	C6-C13
41	D.Munir et al.	2017	Pyrolysis	Hydrocracking of a plastic mixture over various micro-mesoporous composite zeolites	375-425C	20 bar	plastic mixture consisted of 40% HDPE, 10% LDPE, 30% PP, and 20% PS (by wt)	Two micro-mesoporous composite catalysts as well as Al-SBA-15 and Al-SBA-16 catalysts	feed to catalyst ratio of 20:1 (by wt)	stirred batch reactor	-	Upto 85 wt%	-
42	S.Y. Lee et al	2001	Pyrolysis	Degradation of polystyrene using clinoptilolite catalysts	350-450C	-	polystyrene	solid acid catalysts such as silica-alumina (SA, Aldrich), mordenite (JRC-M20), Y-zeolite (JRC-Y5.5), ZSM-5 (RC-Penta), natural clinoptilolite zeolite (NZ) and synthesized clinoptilolite (SCLZ)	mixture of 3.0 g of PS and 0.3 g of the catalyst	semi batch reactor	30,60,100,150 ml/min	-	C5-C30
43	E.Y Hwang et al.	2001	Pyrolysis	Performance of acid treated natural zeolites in catalytic degradation of polypropylene	350,400,450 C	-	mixture of polypropylene	Five types of natural zeolite (NZ)	mixture of 3.0 g of PS and 0.3 g of the catalyst	semi batch reactor	30 ml/min	Upto 85 wt%	C2-C14
44	A.A. Garforth et al.	1997	Pyrolysis	Production of hydrocarbons by catalytic degradation of high density polyethylene in a laboratory fluidised-bed reactor	290–430C	ambient pressure	High density polyethylene	HZSM-5, Silicalite, HMOR, HUSY and SAHA	-	fluidised-bed reactor	50 ml/min	Upto 85 wt%	C1-C9
45	Hussain.G et al.	2015	Pyrolysis	Characterization of Thermo-Catalytic Degradation Products of Waste High-Density Polyethylene Using GC-MS	450C	-	High density polyethylene	MgCO ₃	catalyst/polymer ratio 0.2	Batch Reactor	He,1 mL/min	-	C7-C25
46	M.R. Herná ndez et al	2006	Pyrolysis	Effect of the temperature in the nature and extension of the primary and secondary reactions in the thermal and HZSM-5 catalytic pyrolysis of HDPE	500-800C	-	High density polyethylene	HZSM-5 zeolite from GRACE GMBH & Co. KG	varies	flash coil pyrolyzer (pyroprobe 1000),fluidised-bed reactor	-	Upto 85 wt%	C3-C7
47	R.K. Singh et al.	2016	Pyrolysis	Time and temperature depended fuel gas generation from pyrolysisof real world municipal plastic waste	0-600C	2 atm	Municipal plastic waste (Wastes like PP, PET, PS, high density PE (HDPE), LDPE, Polyamide, Polycarbonate (CD's), labelling paper)	No Catalyst,thermal degradation	-	Batch Reactor	100 ml/min	Upto 80 wt%	C1-C5
48	D.P. Serrano et al.	2004	Pyrolysis	Feedstock recycling of agriculture plastic film wastes by catalytic cracking	380-420C	-	polymeric wastes coming from used greenhouses films of Almeria (Spain), virgin low- density polyethylene ((-CH ₂ -CH ₂ -)x, Mw = 416,000) and virgin ethylene- vinyl acetate copolymer (EVA, 33 wt.% vinyl cetate content, (-CH ₂ -CHOCOCH ₃ -)x-(-CH ₂ -CH ₂ -)y). Both commercial polymers were provided by Repsol-YPF, homogenous mixture of commercial LDPE (86 wt.%) and EVA copolymer (14 wt.%)	mesoporous catalysts Al-SBA-15, Al-MCM-41 and both nanometer size HZSM-5 (n-HZSM-5) and TiAl-Beta zeolites	plastic/catalyst mass ratio = 50	Batch Reactor	100 ml/min	Upto 85 wt%	C1-C5

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N ₂ /H ₂ flowrate or ratio	Yield	Products
49	J. Aguado et al.	2006	Pyrolysis	Feedstock recycling of polyethylene in a two-step thermo-catalytic reaction system	50-700C	-	pure low density polyethylene (LDPE)	nanocrystalline n-HZSM-5 zeolite and mesostructured Al-MCM-41	5.0 g of plastic pellets with 0.5 g of catalyst	Batch Reactor	39 ml/min	Upto 80 wt%	C1-C22
50	J.-W. Kim et al	2011	Pyrolysis	Air gasification of mixed plastic wastes using a two-stage gasifier for the production of producer gas with low tar and a high caloric value	800C	-	Mixed plastic waste like polyethylene, polypropylene, PS, PVC and other minor plastics, such as PMMA and PET	Bottom reactor is filled with silica sand, which serves as a fluidized bed material. The upper reactor is filled with activated carbon or dolomite	ratio of activated carbon to the mixed plastics applied in the experiments was 1.4–2.1	Two-stage gasifier	-	-	C1-C6
51	M.-H. Cho et al.	2013	Gasification	Air gasification of mixed plastic wastes using calcined dolomite and activated carbon in a two-stage gasifier to reduce tar	900C	-	mixed plastic wastes consisted of polyethylene, polypropylene, polystyrene, polyvinyl chloride and other minor plastics, such as polymethylmethacrylate (PMMA) and polyethylene terephthalate (PET)	Calcined dolomite as a bed material and activated carbon as a tar-cracking additive	varies	bubbling fluidized bed reactor	-	-	C1-C6
52	Q. Zhou et al	2004	Pyrolysis	Catalytic degradation and dechlorination of PVC-containing mixed plastics via Al–Mg composite oxide catalysts	360,380,420 C	-	polyvinyl chloride (PVC) containing polymer mixtures, i.e. polypropylene (PP)/PVC, low-density polyethylene (LDPE)/PVC, polystyrene (PS)/PVC, and LDPE/PP/PS/PVC.	Alumina–magnesium composite oxide catalyst (Al–Mg)	10 g of sample plastics with 2 g of Al–Mg	semi batch reactor	-	Upto 80 wt%	C1-C20
53	M. A. Uddin et al	1998	Pyrolysis	Catalytic degradation of polyethylene and polypropylene into liquid hydrocarbons with mesoporous silica	380,430C	ambient pressure	polyolefinic polymers such as polyethylene (PE) and polypropylene (PP)	Mesoporous solid acid catalysts (silica–alumina, zeolite ZSM-5), silicalite, and silica-gel	varies	Batch Reactor	-	Upto 85 wt%	C5-C25
54	S. A. Sakaki et al	2014	Pyrolysis	Catalytic degradation of the mixed polyethylene and polypropylene into middle distillate products	410-450C	10 psi	Polyethylene (HDPE, LDPE) and polypropylene (PP) plastic granules	silico-alumina catalyst	varies	Batch Reactor	He,15.8 mL/min	Upto 90 wt%	C5-C12+
55	M. A. Usman et al.	2012	Pyrolysis	CATALYTIC DEGRADATION OF WATER SACHET WASTE (LPDE) USING MESOPOROUS SILICA KIT-6 MODIFIED WITH 12TUNGSTOPHOSPHORIC ACID	400C	ambient pressure	water sachet waste (which is a low density polyethylene)	Mesoporous Silica: 12-tungstophosphoric acid (HPA) and 12-tungstophosphoric acid supported on KIT-6	2g of the polymer was mixed intimately with 1g of the HPA/KIT-6	Batch Reactor	-	-	C1-C20
56	V. Wilk et al.	2013	Gasification	Conversion of mixed plastic wastes in a dual fluidized bed steam gasifier	640-850C	-	PE, PP, mixtures of PE + PS, mixtures of PE + PET and mixtures of PE + PP	No Catalyst	-	Gasification reactor	-	-	-
57	Y. Sakata et al	1999	Pyrolysis	Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts	420-450C	-	PP,PE	Silica–alumina (SA-1), Silica–alumina (SA-2), Zeolite ZSM-5, Silicalite (ZSM-5 type), Silica-gel (Q3), Mesoporous silica (PSM)	10 g of polymer pellets mixed with 1.0 g of catalyst	Batch Reactor	30 ml/min	Upto 30 wt%	C5-C25
58	B. Saha, A.K. Ghoshal	2005	Thermal Degradation	Thermal degradation kinetics of poly(ethylene terephthalate) from waste soft drinks bottles	653-788K	-	PET from waste soft drink bottles	No Catalyst	-	Thermogravimetric analysis (TGA)	-	-	-
59	J.C. Acomb et al.	2015	Pyrolysis	Effect of growth temperature and feedstock-catalyst ratio on the production of carbon nanotubes and hydrogen from the pyrolysis of waste plastics	700,800,900 C	-	LDPE	Al2O3	varies		80 ml/min	-	-

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N2/H2 flowrate or ratio	Yield	Products
60	H.-T. Lin et al	2010	Pyrolysis	Hydrocarbon fuels produced by catalytic pyrolysis of hospital plastic wastes in a fluidizing cracking process	330-450C	-	Hospital plastic waste : polyethylene (~62 wt.% PE=~38 wt.% HDPE+~24 wt.% LDPE), polypropylene (~34 wt.% PP), polyvinylchloride (~3 wt.% PVC) and with about 1 wt.% polystyrene (PS) mixtures.	Reused catalyst form FCC: Rcatc1, HUSY, ZSM-5, SAHA & silicalite (Si/Al: 2.1,17.5,13.6,3.6,1000 respectively.)	Two stage pyrolysis reactor	Fluidized bed reactor	Varies	Upto 80 wt%	C1-C9
61	W. Ding et al.	1997	Pyrolysis	Thermal and catalytic degradation of high density polyethylene and commingled post-consumer plastic waste	400-435C	1000psig	High density polyethylene and commingled post-consumer plastic waste	TiCl3,ZSM-5		Tubing & Autoclave reactor	-	Upto 70 wt%	C1-C27+
62	Karmina M. et al.	2016	Pyrolysis	Kinetic Analysis of Pyrolysis of Waste Polyolefin Mixture	350-480C	ambient pressure	Commercial mixture of high-density polyethylene (HDPE) and PP waste sample (70% HDPE and 30% PP)	ZSM-5 in powder form	5% ZSM-5 catalyst and mixture of wasted HDPE+PP	thermogravimetric Perkin Elmer TGA Diamond analyzer	3.5 L/min	-	-
63	W.X. Cheng et al.	2007	Pyrolysis	MESOPOROUS ACID SOLID AS A CARRIER FOR METALLOCENE CATALYST IN ETHYLENE POLYMERIZATION AND A CATALYST IN CATALYTIC DEGRADATION OF POLYETHYLENE	100-580C	ambient pressure	Polyethylene	HMCM-41 and AIMCM-41, and mesoporous silicoaluminophosphate molecular sieves (SAPO1 and SAPO2)	-	Glass reactor	50 L/min	Upto 70 wt%	C1-C5+
64	I. Istadi et al.	2010	Pyrolysis	Optimization of Reactor Temperature and Catalyst Weight for Plastic Cracking to Fuels Using Response Surface Methodology	480-550C	-	mixed plastic waste	modified RCC catalyst	-	fixed bed reactor	-	Upto 30 wt%	C4-C13
65	K. Gobin, G. Manos	2004	Pyrolysis	Polymer degradation to fuels over microporous catalysts as a novel tertiary plastic recycling method	300-800K	-	unstabilised linear low density polyethylene (LLDPE) in powder form	1. Zeolite-based catalysts: (a) <i>US-Y zeolite</i> (b) <i>ZSM-5 zeolite</i> (c) <i>An equimass mixture of the two above samples, US-Y and ZSM-5</i> (d) <i>Two commercial cracking catalysts, named 1 and 2, containing 20 and 40% US-Y respectively</i> 2. Clay-based catalysts: (a) <i>Saponite, with small amount of impurities, mainly sepiolite</i> (b) <i>Zenith-N, a montmorillonite (85%), 5% feldspars, 3% calcite, 2.5% quartz, illite 2% and christobalite 2%.</i> (c) <i>ATOS, a pillared derivative of the raw saponite</i> (d) <i>AZA, a pillared derivative of the montmorillonite Zenith-N</i>	Polymer and dry catalyst were 2 and 1 g, respectively.	Semi-Batch reactor	50 ml/min	Upto 75 wt%	-
66	M.H. Cho et al.	2013	Gasification	Production of low-tar producer gas from air gasification of mixed plastic waste in a two-stage gasifier using olivine combined with activated carbon	800C	-	pellet-type mixed plastic waste: comprised various types of plastic such as polyethylene, polypropylene, polystyrene, polyvinyl chloride, polymethylmethacrylate and polyethylene terephthalate	Coal-based activated carbon pellets & Natural olivine (44.2 wt% SiO2, 8.0 wt% Fe2O3, and 43.5 wt% MgO, along with other minor components such as Al2O3 and CaO)	varies	fluidized bed reactor	-	-	C1-C5+

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N2/H2 flowrate or ratio	Yield	Products
67	Yeuh-Hui Lin	2009	Pyrolysis	Production of valuable hydrocarbons by catalytic degradation of a mixture of post-consumer plastic waste in a fluidized-bed reactor	330-450C	ambient pressure	mixture of post-consumer plastic waste (PE/PP/PS/PVC)	FCC-R1, Silicalite, HUSY(Ultrastabilised Y zeolite), ZSM-5, SAHA (Amorphous silica-alumina)	varies	fluidized-bed reactor	300-900 ml/min	Upto 90 wt%	C1-C9
68	Papuga, S. V., et al	2016	Pyrolysis	TEMPERATURE AND TIME INFLUENCE ON THE WASTE PLASTICS PYROLYSIS IN THE FIXED BED REACTOR	450-525C	ambient pressure	waste plastics mixture composed of 45% polypropylene, 35% low density polyethylene, and 25% high density polyethylene	no catalyst	-	fixed bed reactor	varies	Upto 65 wt%	-
69	M.F. Ali, M.N. Siddiqui	2005	Pyrolysis	Thermal and catalytic decomposition behavior of PVC mixed plastic waste with petroleum residue	350,430C	950psi	Mixed plastic: polystyrene (PS), low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC)	8 types of catalyst: hydrocracking catalysts (HC-1, HC-2 and HC-3), ZSM-5 zeolite catalyst, FCC catalyst, presulfided NiMo/Al2O3 (NiMo) catalyst and iron oxide carbon composite catalyst.	-	micro tubular reactor	-	Upto 80 wt%	-
70	W.-C. Huang et al	2010	Pyrolysis	Thermochemical conversion of polymer wastes into hydrocarbon fuels over various fluidizing cracking catalysts	290-420C	ambient pressure	mixture of waste polymers consists of polyethylene (62 wt.% PE = 37 wt.% HDPE + 25 wt.% LDPE), polypropylene (33 wt.% PP) and about 5 wt.% polystyrene (PS) mixtures	H-ultrastabilised Y zeolite (USY), H-ZSM-5 zeolite, H-mordenite (MOR), Synclyst 25 (silica–alumina or ASA), MSM-41	varies	Fluidized bed reactor	50 ml/min	Upto 95 wt%	C2-C8
71	M.-H. Cho et al.	2014	Gasification	Two-stage air gasification of mixed plastic waste- Olivine as the bed material and effects of various additives and a nickel-plated distributor on the tar removal	800C	-	Mixed plastic waste such as polyethylene, polypropylene, polystyrene, polyvinyl chloride, PMMA (polymethylmethacrylate) and PET (polyethylene terephthalate)	Bed material: Natural olivine with composition 39.6 wt% SiO2, 26.5 wt% Fe2O3, and 27.9 wt% MgO,	-	Fluidized bed reactor	-	27.3 vol%	H2
72	S.L. Wong et al.	2017	Pyrolysis	Conversion of low density polyethylene (LDPE) over ZSM-5 zeolite to liquid fuel	400-600C	-	Virgin low density polyethylene (LDPE)	ZSM-5	0.3 g of SiC was mixed with 0.2 g of fresh catalyst	fixed bed reactor	120 ml/min	Upto 95 wt%	C5-C11
73	Mohamed M.Garib et al.	2014	Pyrolysis	CONVERSION OF PLASTIC WASTE TO LIQUID FUEL	350-450C	-	Mixed plastic waste	layered silicate catalyst (5–10% by vol)	5–10% by vol	-	-	Upto 85 wt%	-
74	P. Senthil.K et al	2015	Pyrolysis	Conversion of waste plastics into low-emissive hydrocarbon fuels through catalytic depolymerization in a new laboratory scale batch reactor	70-240C, 500-600C	-	Mixed waste plastic materials: polyethylene, polypropylene, polystyrene and polyethylene terephthalate	Activated carbon, activated carbon with granulated charcoal and activated carbon with calcium oxide	varies	Batch reactor	-	Upto 98 wt%	-
75	M. Sarker et al.	2012	Pyrolysis	A new technology proposed to recycle waste plastics into hydrocarbon fuel in USA	200-400C	-	Waste plastics (LDPE, HDPE and PP)	Activated carbon	1% by weight	Batch reactor	20 ml/min	Upto 90 wt%	C1-C9
76	S.-J. Chiu, Y.-S. Wu et al	2009	Pyrolysis	A comparative study on thermal and catalytic degradation of polybutylene terephthalate	320-400C	-	PBT (about 2.0–3.0 mm in size and cylindrical in shape)- commercial product (R1110, general grade) supplied by NanYa Plastic Co., Taiwan	catalysts include metal chloride, metal oxide, metal acetate, and metal copper powder	varies	Batch reactor	95 ml/min	-	C2-C6+
77	A.R. Auxilio et al	2017	Pyrolysis	An experimental study on thermo-catalytic pyrolysis of plastic waste using a continuous pyrolyser	300,425C	-	Plastic mixtures of high density polyethylene (HDPE), 27.5%, low density polyethylene (LDPE), 27.5%, polystyrene (PS), 17.0% and polypropylene (PP), 28.0%.	Micro-Meso: CAT-1, CAT-2, CAT-3, CAT-4 and CAT-5, (CAT-1 to CAT-4 are zeolite based catalysts with varying SiO2/Al2O3 ratio, and CAT-5 is a Kaolin clay catalyst)	-	Continuous stirred tank reactor (CSTR)	30 ml/min	-	C5-C30
78	N. Gao et al.	2014	Pyrolysis	Catalytic Degradation of LDPE and PP over MCM-49 Based Micro–Mesoporous Composites	350C	-	Low density polyethylene and polypropylene	MCM-49 zeolite with Si/Al molar ratio of 11.5	Cat/LDPE mass ratio of 1/9	Batch reactor	70 ml/min	-	-

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N ₂ /H ₂ flowrate or ratio	Yield	Products
79	J. Chattopadhyay et al.	2016	Pyrolysis	Catalytic co-pyrolysis of paper biomass and plastic mixtures (HDPE/high density polyethylene), PP (polypropylene) and PET (polyethylene terephthalate)) and product analysis	100-600C	-	Plastics (HDPE (high density polyethylene), PP (polypropylene) and PET (polyethylene terephthalate))	Cobalt based alumina, ceria and ceria-alumina catalysts	1.9 g of blend materials was mixed up with 100 mg of individual catalyst	fixed bed reactor	Ar 50ml/min	Upto 80 wt%	C2-C6+
80	Z. Sebestyén et al	2017	Pyrolysis	Catalytic Pyrolysis of Biomass and Plastic Mixtures using HZSM-5 Zeolite	100-600C	-	Mixed Plastic & Biomass waste. (PE, PP, PET, paper, cardboard, sawdust)	HZSM-5 catalyst	zeolite HZSM-5 catalyst were tested using 1:1 and 10:1 waste/catalyst ratios.	Batch reactor	-	-	-
81	A. Lopez-Urionabarrenechea et al.	2012	Pyrolysis	Catalytic stepwise pyrolysis of packaging plastic waste	440C,500C	-	Mixture of polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC), which resembles real municipal plastic waste	ZSM-5 zeolite	mass ratio of 10/1	Semi-Batch reactor	-	-	C5-C16
82	Jude A. dili et al	2016	Gasification	Catalytic supercritical water gasification of plastics with supported RuO ₂ : A potential solution to hydrocarbons–water pollution problem	450C	10-38 Mpa	Virgin plastic samples including low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP) and polystyrene (PS)	RuO ₂ /Al ₂ O ₃ catalysts had nominal RuO ₂ loadings of 5 wt%, 10 wt% and 20 wt%, while the nickel–ruthenium bimetallic catalyst contained 5 wt% RuO ₂ and 15 wt% NiO on Al ₂ O ₃ . In addition, 20 wt% and 40 wt% NiO/Al ₂ O ₃ were tested	varies	Batch reactor	-	-	-
83	M. Y. Abdelal et al	2008	Hydrolysis	Chemical Degradation of Poly(Ethylene Terephthalate)	40C for 24H	-	polyethylene terephthalate (PET)	Activating agents such as inorganic salts and phase transfer catalysts (Zinc Sulphate, Calcium Acetate, Tetraethylammonium Chloride (TEAC))	-	Batch reactor	-	Upto 50 wt%	terephthalic acid
84	T. Bhaskar et al.	2003	Thermal Degradation	Comparison of thermal degradation products from real municipal waste plastic and model mixed plastics	430C	atmospheric pressure	municipal waste plastic (MWP), PE/PP/PS/PVC/PET	No catalyst	-	Batch Reactor	10 ml/min	-	-
85	J. M. Escola et al.	2014	Pyrolysis	Conversion of LDPE into transportation fuels by a two-stage process using Ni/Al-SBA-15 as catalyst	310C	20 bar	Virgin LDPE	Ni/Al-SBA-15 catalysts with Si/Al atomic ratios within the 20–135 range	catalyst/feed ratio = 1:30	Batch Reactor	-	Upto 70 wt%	C1-C40
86	Mohammad Nahid Siddiqui	2009	Thermal Degradation	Conversion of hazardous plastic wastes into useful chemical products	420–430	450–650 psi	LDPE,HDPE,PP,PS	No catalyst	-	tubular micro-autoclave reactor	H ₂ and air flow of 40.0 and 450.0 ml/min	-	-
87	V. Wilk, H. Hofbauer et al	2013	Gasification	Conversion of mixed plastic wastes in a dual fluidized bed stream gasifier	850C	0.7-0.9 mbar	PE, PP, and mixtures of PE + PS, PE + PET and PE + PP	No catalyst	-	dual fluidized bed gasification pilot plant	-	-	-
88	Sulene A. Araújo et al.	2010	thermal decomposition	Effect of the catalyst MCM-41 on the kinetic of the thermal decomposition of poly(ethylene terephthalate)	350-500C	-	polyethylene terephthalate (PET)	MCM- 41 mesoporous catalyst	-	TG/DTA (model 2960, TA Instruments) quartz tube reactor	100 ml/min	-	-
89	Adnan et al.	2015	Pyrolysis	Effect of polyethylene terephthalate on the catalytic pyrolysis of polystyrene: Investigation of the liquid products	30-1000C	-	PET,PS	Al-Al ₂ O ₃ crystalline catalyst	20 wt%		20 ml/min	-	C6-C24

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N2/H2 flowrate or ratio	Yield	Products
90	Jon Alvarez et al.	2014	pyrolysis-gasification	Hydrogen production from biomass and plastic mixtures by pyrolysis-gasification	600-800C	-	Four different kinds of plastics were used for co-processing with the biomass: polypropylene (PP), high density polyethylene (HDPE), polystyrene (PS) and a mixture of real world plastics (RP) previously collected and recycled.	Ni/Al2O3	varies	Gasification reactor	80 ml/min	-	-
91	U. Hujuri et al	2008	Pyrolysis	Modeling pyrolysis kinetics of plastic mixtures	430-510C	-	PP,PE,PET	No catalyst	-	Thermo-gravimetric analyser	40-50 cm3/min	-	-
92	Bahador Nabgan et al.	2017	Steam reforming	Ni/Pd-promoted Al2O3-La2O3 catalyst for hydrogen production from polyethylene terephthalate waste via steam reforming	0-800C	-	polyethylene terephthalate (PET)	Ni-Pd/Al2O3-La2O3 catalyst	The feed was injected into the reactor with the steam to feed (water:phenol:PET) ratio of (1:0.107:0.003)	fixed bed reactor	10-40 ml/min	-	-
93	Erdal Eren et al.	2014	Thermal-catalytic degradationThermal	Performance of birnessite-type manganese oxide in the thermal-catalytic degradation of polyamide 6	200-1000C	-	PA6 pellets (polyamide 6)	Birnessite-type manganese oxide (BMO)	varies	PRIS Diamond TG/DTG apparatus	-	-	-
94	E. G. Fuentes-Ordonez et al.	2014	Hydrocracking	Pt/ITQ-6 zeolite as a bifunctional catalyst for hydrocracking of waste plastics containing polystyrene	263-573K	-	virgin and recycled polystyrene (PS)	Pt/Ferrierite & Pt/ITQ-6 catalyst	-	Tubular reactor	-	-	C5-C12
95	Lee et al.	2014	Pyrolysis	Pyrolysis and co-pyrolysis of Laminaria japonica and polypropylene over mesoporous Al-SBA-15 catalyst	100-600C	-	Seaweed biomass, Laminaria japonica, and a typical polymer material, polypropylene	mesoporous Al-SBA-15 catalyst	catalyst/feedstock ratio of 1/10	fixed bed reactor	50 ml/min	-	C1-C17
96	M.N. Siddiqui, H.H. Redhwi	2009	Pyrolysis	Pyrolysis of mixed plastics for the recovery of useful products	430-440C	5.5-6 Mpa	polystyrene (PS) with low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), poly-ethylene terephthalate (PET)	Hydroprocessing Catalyst: MoO3 content=13.9 to 17.0 wt.%, NiO content=4.4 to 5.6 wt.%, Nominal Size=1/16 in. cylindrical extrudate, Avg. Bulk Density=44 lb/ft3, Loss on Ignition (500 °C)=2.2 wt.%, Crush Strength=12 lb, Avg. Diameter=0.06 to 0.072 in. and Avg. Length=0.09 in	varies	Tubular micro autoclave reactor	hydrogen and air flow of 40.0 and 450.0 ml/min	-	-
97	T. Yoshioka et al.	2004	Pyrolysis	Pyrolysis of poly(ethylene terephthalate) in a fluidised bed plant	510-730C	-	Poly-ethylene terephthalate (PET)	No catalyst	varies	Fluidized bed reactor	-	-	C1-C6+
98	Neena George and Thomas Kurian	2015	Thermal Degradation	Sodium Carbonate Catalyzed Aminolytic Degradation of PET	335C	-	Poly-ethylene terephthalate (PET)	non-toxic catalyst (sodium carbonate)	varies	-	-	-	-
99	E. Valanciene et al.	2015	Pyrolysis	The influence of zeolite catalyst on kinetics and thermodynamics of polypropylene waste thermal degradation	303-823K	-	Polypropylene	Zeolite-regenerated NaceRTM FCC (“Grace”, USA) catalyst	varies	Thermogravimeter TGA 4000 (PerkinElmer, USA)	20 ml/min	-	-
100	A. López et al.	2011	Pyrolysis	Pyrolysis of municipal plastic wastes II: Influence of raw material composition under catalytic conditions	440C	-	HDPE, PP, PS, PET, PVC , PE film, pp film, Other packaging materials Tetra-brik, Inappropriate materials Paper, Wood, Glass, Inerts	Commercial ZSM-5 zeolite	plastic/catalyst ratio of 10/1	Semi-Batch reactor	50 ml/min	-	C5-C16

No.	Author	Year	Process	Title	Temp.	Pressure	Type of raw material	Type of Catalyst	Catalyst/Waste Ratio	Size/Type of Reactor	N ₂ /H ₂ flowrate or ratio	Yield	Products
101	M.F. Ali, M.N. Siddiqui	2005	Pyrolysis	Thermal and catalytic decomposition behavior of PVC mixed plastic waste with petroleum residue	430C	-	Mixed Plastic Waste: polystyrene (PS), low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC)	Eight Catalyst: hydrocracking catalysts (HC-1, HC-2 and HC-3), ZSM-5 zeolite catalyst, FCC catalyst, presulfided NiMo/Al ₂ O ₃ (NiMo) catalyst and iron oxide carbon composite catalyst	-	Glass reactor	-	-	-

Appendix-II (A)

MSDS of Catalyst used, ZSM-5 and BZ

SAFETY DATA SHEET

SECTION 1: IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifier

Product Name CBV 2314
Alternative names ZEOLITE AMMONIUM ZSM-5 POWDER
CAS No. 1318-02-1
EINECS No.
REACH Registration No. 01-2119455853-31-0011

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified use(s) Catalyst.

1.3 Details of the supplier of the safety data sheet

Company Identification Zeolyst International
280 Cedar Grove Road
Conshohocken
PA 19428-2240
USA
Telephone: +1 610-651-4200
E-Mail (competent person) sds.uk@pqcorp.com

1.4 Emergency telephone number

Emergency Phone No. Zeolyst +1 610-651-4200
Chem Trec +1 800-424-9300

SECTION 2: HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

GHS Classification Not classified as dangerous for supply/use.

EC Classification Not classified as dangerous for supply/use.

Hazards summary May cause irritation to skin and eyes. May cause irritation to the respiratory system.

SECTION 3: COMPOSITION/INFORMATION ON INGREDIENTS

Regulation (EC) No. 1272/2008 (CLP)

Ingredient(s)	%W/W	CAS No.	EINECS No. / REACH Registration	Hazard symbol(s) and hazard statement(s)
Zeolite	100	1318-02-1	215-283-8	Not classified.

SECTION 4: FIRST AID MEASURES

4.1 Description of first aid measures

Eye Contact If substance has got into the eyes, immediately wash out with plenty of water for at least 15 minutes. If symptoms develop, obtain medical attention.

Skin Contact Wash affected skin with plenty of water. Continue to wash the affected area for at least 15 minutes. If symptoms develop, obtain medical attention.

Inhalation	Remove patient from exposure, keep warm and at rest. If symptoms develop, obtain medical attention.
Ingestion	Do not induce vomiting. Wash out mouth with water. Obtain medical attention.
4.2 Most important symptoms and effects, both acute and delayed	May cause irritation to skin and eyes. May cause irritation to the respiratory system.
4.3 Indication of any immediate medical attention and special treatment needed	Flush the contaminated area of body with large amounts of water.

SECTION 5: FIRE-FIGHTING MEASURES

5.1 Extinguishing media	
Suitable Extinguishing Media	Normal extinguishing media. As appropriate for surrounding fire.
Unsuitable extinguishing Media	None known.
5.2 Special hazards arising from the substance or mixture	Not applicable. Inorganic powder or granules.
5.3 Advice for fire-fighters	Wear suitable protective clothing. Impervious gloves and boots. Chemical goggles (EN 166).

SECTION 6: ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures	Wear suitable protective clothing. Wear eye/face protection. An approved dust mask should be worn if dust is generated during handling.
6.2 Environmental precautions	Prevent entry into drains.
6.3 Methods and materials for containment and cleaning up	Contain spillages. Dampening with water can reduce dust. Sweep or preferably vacuum up and collect in suitable containers for recovery or disposal.
6.4 Reference to other sections	See Section: 8

SECTION 7: HANDLING AND STORAGE

7.1 Precautions for safe handling	Avoid generation of dust. Avoid contact with skin and eyes. Wash thoroughly after handling. Do not eat, drink or smoke at the work place. Wear protective equipment to comply with good occupational hygiene practice.
7.2 Conditions for safe storage, including any incompatibilities	Keep container tightly closed and dry. Store in a cool/low-temperature, well-ventilated (dry) place.
7.3 Specific end use(s)	Not available.

SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

SUBSTANCE.	Occupational Exposure Limits
	UK EH40: Dust Total inhalable: WEL 10mg/m ³ 8h TWA. Respirable: WEL 4mg/m ³ 8h TWA. ACGIH: Particulates not otherwise classified Inhalable TLV 10mg/m ³ 8h TWA. Respirable: TLV 3mg/m ³ 8h TWA. OSHA: Inert or Nuisance Dust Total dust : PEL 15mg/m ³ 8h TWA. Respirable fraction : PEL 5mg/m ³ 8h TWA.

8.2 Exposure controls

8.2.1 Appropriate engineering controls

Provide adequate ventilation, including appropriate local extraction if dusts, fumes or vapours are likely to be evolved. Engineering methods to prevent or control exposure are preferred. Methods include process or personnel enclosure, mechanical ventilation (dilution and local exhaust), and control of process conditions. Emergency shower and eye wash facilities should be readily available.

8.2.2 Personal Protection

Respiratory protection

Avoid inhalation of dusts. Wear suitable respiratory protective equipment if working in confined spaces with inadequate ventilation or where there is any risk of the exposure limits being exceeded.

Eye/face protection

Safety spectacles. Goggles.

Skin protection

Wear suitable protective clothing and gloves. Plastic or rubber gloves. For example EN374-3. Wear suitable overalls.

8.2.3 Environmental Exposure Controls

Use with local exhaust ventilation.

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

Appearance	Powder. White.
Odour	Odourless.
Odour Threshold (ppm)	Not available.
pH (Value)	Not applicable.
Freezing Point (°C)	Not applicable.
Melting Point (°C)	> 1000
Boiling Point (°C)	Not applicable.
Flash Point (°C) [Closed cup]	Not applicable.
Evaporation rate	Not applicable.
Flammability (solid, gas)	Not applicable.
Explosive Limit Ranges	Not applicable.
Vapour Pressure (mm Hg)	Not applicable.
Vapour Density (Air=1)	Not applicable.
Density (g/ml)	>1
Solubility (Water)	Insoluble.
Solubility (Other)	Not available.
Partition Coefficient	Not available.
Auto Ignition Point (°C)	Not applicable.
Decomposition Temperature (°C)	Not available.
Viscosity (mPa. s)	Not available.
Explosive properties	Not applicable.
Oxidising Properties	Not applicable.
9.2 Other information	Not available.

SECTION 10: STABILITY AND REACTIVITY

10.1 Reactivity	Not to be expected.
10.2 Chemical stability	Stable.
10.3 Possibility of hazardous reactions	Contact with water generates heat Ammonia may be released on contact with strong bases.
10.4 Conditions to avoid	Keep away from heat.
10.5 Incompatible materials	None
10.6 Hazardous decomposition product(s)	Ammonia , Nitrogen oxides

SECTION 11: TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity

Ingestion	Low oral toxicity, but ingestion may cause irritation of the gastrointestinal tract.
Inhalation	Avoid inhalation of dusts. Existing medical conditions (eg. asthma, bronchitis) may be aggravated by exposure to dust. Effects of dust may be greater, and occur at lower levels of exposure in smokers compared to non-smokers.
Skin Contact	Dust may have a drying effect on the skin.
Eye Contact	Dust may cause discomfort and mild irritation.
Sensitisation	It is not a skin sensitiser.
Mutagenicity	There is no evidence of mutagenic potential.
Carcinogenicity	IARC assessment: Similar material (synthetic zeolite) is not classifiable as to its carcinogenicity to humans (Group 3).
Reproductive toxicity	No evidence of reproductive toxicity or developmental toxicity.
STOT - single exposure	Not available.
STOT - repeated exposure	Not available.
Other information	Not available.

SECTION 12: ECOLOGICAL INFORMATION

12.1 Toxicity	No environmental hazards have been reported or known.
12.2 Persistence and degradability	No data.
12.3 Bioaccumulative potential	No data. The product has low potential for bioaccumulation.
12.4 Mobility in soil	No data.
12.5 Results of PBT and vPvB assessment	Not classified as PBT or vPvB.
12.6 Other adverse effects	None known.

SECTION 13: DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods	Disposal should be in accordance with local, state or national legislation. Not a hazardous waste under RCRA Sec.3001. This material is not classified as hazardous waste under EC Directive 2008/98/EC (and amendments). This material is not classified as hazardous waste under the Hazardous Waste (England and Wales) Regulations SI 2005 No. 894. This material is not classified as hazardous waste under the Hazardous Waste (England and Wales) Regulations SI 2005 No. 894.
------------------------------	--

SECTION 14: TRANSPORT INFORMATION

14.1 UN number	Not classified as dangerous for transport.
14.3 Transport hazard class(es)	Not applicable.
14.4 Packing group	Not applicable.
14.5 Environmental hazards	Not classified as a Marine Pollutant.
14.6 Special precautions for user	No special packaging requirements.
14.7 Transport in bulk according to Annex II of MARPOL73/78 and the IBC Code	

SECTION 15: REGULATORY INFORMATION

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture	
---	--

TSCA Inventory Status: Reported/Included.
AICS Inventory Status: Reported/Included.
DSL/NDSL Inventory Status: Reported/Included.
1,0,0

15.2 Chemical Safety Assessment Not applicable.

SECTION 16: OTHER INFORMATION

This SDS was last reviewed: 09/2014

The following sections contain revisions or new statements: All sections.

Information contained in this publication or as otherwise supplied to Users is believed to be accurate and is given in good faith, but it is for the Users to satisfy themselves of the suitability of the product for their own particular purpose. Zeolyst International gives no warranty as to the fitness of the product for any particular purpose and any implied warranty or condition (statutory or otherwise) is excluded except to the extent that exclusion is prevented by law. Zeolyst International accepts no liability for loss or damage (other than that arising from death or personal injury caused by defective product, if proved), resulting from reliance on this information. Freedom under Patents, Copyright and Designs cannot be assumed.

SAFETY DATA SHEET

SECTION 1: IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifier

Product Name CP811C-300 ZEOLITE H-BETA POWDER
Alternative names ZEOLITE BETA POWDER

CAS No. 1318-02-1
REACH Registration No. 01-2119455853-31

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified use(s) Catalyst.

1.3 Details of the supplier of the safety data sheet

Company Identification Zeolyst International
280 Cedar Grove Road
Conshohocken
PA 19428-2240
USA
Telephone: +1 610-651-4200
E-Mail (competent person) sds.uk@pqcorp.com

1.4 Emergency telephone number

Emergency Phone No. Zeolyst +1 610-651-4200
Chem Trec +1 800-424-9300

SECTION 2: HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

GHS Classification Not classified as dangerous for supply/use.

EC Classification Not classified as dangerous for supply/use.

2.2 Label elements

Signal word(s) Not applicable.

Hazard statement(s) Not applicable.

Precautionary statement(s) Not applicable.

2.3 Other hazards Dust may have a drying effect on the skin.

SECTION 3: COMPOSITION/INFORMATION ON INGREDIENTS

Regulation (EC) No. 1272/2008 (CLP)

Ingredient(s)	%W/W	CAS No.	EINECS No. / REACH Registration	Hazard symbol(s) and hazard statement(s)
Zeolite	100	1318-02-1	215-283-8	Not classified.

SECTION 4: FIRST AID MEASURES

4.1 Description of first aid measures

Eye Contact	If substance has got into the eyes, immediately wash out with plenty of water for at least 15 minutes. If symptoms develop, obtain medical attention.
Skin Contact	Wash affected skin with plenty of water. Continue to wash the affected area for at least 15 minutes. If symptoms develop, obtain medical attention.
Inhalation	Remove patient from exposure, keep warm and at rest. If symptoms develop, obtain medical attention.
Ingestion	Do not induce vomiting. Wash out mouth with water. Obtain medical attention.
4.2 Most important symptoms and effects, both acute and delayed	May cause irritation to skin and eyes. May cause irritation to the respiratory system.
4.3 Indication of any immediate medical attention and special treatment needed	Flush the contaminated area of body with large amounts of water.

SECTION 5: FIRE-FIGHTING MEASURES

5.1 Extinguishing media	
Suitable Extinguishing Media	Normal extinguishing media. As appropriate for surrounding fire.
Unsuitable extinguishing Media	None known.
5.2 Special hazards arising from the substance or mixture	Not applicable. Inorganic powder or granules.
5.3 Advice for fire-fighters	Wear suitable protective clothing. Impervious gloves and boots. Chemical goggles (EN 166).

SECTION 6: ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures	Wear suitable protective clothing. Wear eye/face protection. An approved dust mask should be worn if dust is generated during handling.
6.2 Environmental precautions	Prevent entry into drains.
6.3 Methods and materials for containment and cleaning up	Contain spillages. Dampening with water can reduce dust. Sweep or preferably vacuum up and collect in suitable containers for recovery or disposal.
6.4 Reference to other sections	See Section: 8

SECTION 7: HANDLING AND STORAGE

7.1 Precautions for safe handling	Avoid generation of dust. Avoid contact with skin and eyes. Wash thoroughly after handling. Do not eat, drink or smoke at the work place. Wear protective equipment to comply with good occupational hygiene practice.
7.2 Conditions for safe storage, including any incompatibilities	Keep container tightly closed and dry. Store in a cool/low-temperature, well-ventilated (dry) place.
7.3 Specific end use(s)	Not available.

SECTION 8: EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

SUBSTANCE.	Occupational Exposure Limits
	UK EH40: Dust Total inhalable: WEL 10mg/m ³ 8h TWA. Respirable: WEL 4mg/m ³ 8h TWA. ACGIH: Particulates not otherwise classified Inhalable TLV 10mg/m ³ 8h TWA. Respirable: TLV 3mg/m ³ 8h TWA. OSHA: Inert or Nuisance Dust Total dust : PEL 15mg/m ³ 8h TWA. Respirable fraction : PEL 5mg/m ³ 8h TWA.

8.2 Exposure controls

8.2.1 Appropriate engineering controls

Provide adequate ventilation, including appropriate local extraction if dusts, fumes or vapours are likely to be evolved. Engineering methods to prevent or control exposure are preferred. Methods include process or personnel enclosure, mechanical ventilation (dilution and local exhaust), and control of process conditions. Emergency shower and eye wash facilities should be readily available.

8.2.2 Personal Protection

Respiratory protection

Avoid inhalation of dusts. Wear suitable respiratory protective equipment if working in confined spaces with inadequate ventilation or where there is any risk of the exposure limits being exceeded.

Eye/face protection

Safety spectacles. Goggles.

Skin protection

Wear suitable protective clothing and gloves. Plastic or rubber gloves. For example EN374-3. Wear suitable overalls.

8.2.3 Environmental Exposure Controls

Use with local exhaust ventilation.

SECTION 9: PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

Appearance	Powder. White.
Odour	Odourless.
Odour Threshold (ppm)	Not available.
pH (Value)	Not applicable.
Freezing Point (°C)	Not applicable.
Melting Point (°C)	> 1000
Boiling Point (°C)	Not applicable.
Flash Point (°C) [Closed cup]	Not applicable.
Evaporation rate	Not applicable.
Flammability (solid, gas)	Not applicable.
Explosive Limit Ranges	Not applicable.
Vapour Pressure (mm Hg)	Not applicable.
Vapour Density (Air=1)	Not applicable.
Density (g/ml)	>1
Solubility (Water)	Insoluble.
Solubility (Other)	Not available.
Partition Coefficient	Not available.
Auto Ignition Point (°C)	Not applicable.
Decomposition Temperature (°C)	Not available.
Viscosity (mPa. s)	Not available.
Explosive properties	Not applicable.
Oxidising Properties	Not applicable.
9.2 Other information	Not available.

SECTION 10: STABILITY AND REACTIVITY

10.1 Reactivity

Not to be expected.

10.2 Chemical stability

Stable.

10.3 Possibility of hazardous reactions	Contact with water generates heat
10.4 Conditions to avoid	Keep away from heat.
10.5 Incompatible materials	None
10.6 Hazardous decomposition product(s)	None known.

SECTION 11: TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity

Ingestion	Low oral toxicity, but ingestion may cause irritation of the gastrointestinal tract.
Inhalation	Avoid inhalation of dusts. Existing medical conditions (eg. asthma, bronchitis) may be aggravated by exposure to dust. Effects of dust may be greater, and occur at lower levels of exposure in smokers compared to non-smokers.
Skin Contact	Dust may have a drying effect on the skin.
Eye Contact	Dust may cause discomfort and mild irritation.
Sensitisation	It is not a skin sensitiser.
Mutagenicity	There is no evidence of mutagenic potential.
Carcinogenicity	IARC assessment: Similar material (synthetic zeolite) is not classifiable as to its carcinogenicity to humans (Group 3).
Reproductive toxicity	No evidence of reproductive toxicity or developmental toxicity.
STOT - single exposure	Not available.
STOT - repeated exposure	Not available.
Other information	Not available.

SECTION 12: ECOLOGICAL INFORMATION

12.1 Toxicity	No environmental hazards have been reported or known.
12.2 Persistence and degradability	No data.
12.3 Bioaccumulative potential	No data. The product has low potential for bioaccumulation.
12.4 Mobility in soil	No data.
12.5 Results of PBT and vPvB assessment	Not classified as PBT or vPvB.
12.6 Other adverse effects	None known.

SECTION 13: DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods	Disposal should be in accordance with local, state or national legislation. Not a hazardous waste under RCRA Sec.3001. This material is not classified as hazardous waste under EC Directive 2008/98/EC (and amendments). This material is not classified as hazardous waste under the Hazardous Waste (England and Wales) Regulations SI 2005 No. 894.
-------------------------------------	--

SECTION 14: TRANSPORT INFORMATION

14.1 UN number	Not classified as dangerous for transport.
14.3 Transport hazard class(es)	Not applicable.
14.4 Packing group	Not applicable.
14.5 Environmental hazards	Not classified as a Marine Pollutant.
14.6 Special precautions for user	No special packaging requirements.

**14.7 Transport in bulk according
to Annex II of MARPOL73/78 and
the IBC Code**

SECTION 15: REGULATORY INFORMATION

15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

TSCA Inventory Status: Reported/Included.

AICS Inventory Status: Reported/Included.

DSL/NDSL Inventory Status: Reported/Included.

1,0,0

15.2 Chemical Safety Assessment Not applicable.

SECTION 16: OTHER INFORMATION

This SDS was last reviewed: 05/2015

The following sections contain revisions or new statements: All sections.

Information contained in this publication or as otherwise supplied to Users is believed to be accurate and is given in good faith, but it is for the Users to satisfy themselves of the suitability of the product for their own particular purpose. Zeolyst International gives no warranty as to the fitness of the product for any particular purpose and any implied warranty or condition (statutory or otherwise) is excluded except to the extent that exclusion is prevented by law. Zeolyst International accepts no liability for loss or damage (other than that arising from death or personal injury caused by defective product, if proved), resulting from reliance on this information. Freedom under Patents, Copyright and Designs cannot be assumed.

Appendix-II(B)

Characterization of BZ and ZSM-5

(BET adsorption isotherm)

Table (A2.1): Structural properties of the BZ catalyst

Catalyst	S_g (m ² /g)	v_{mp} (cm ³ /g)
BZ (Si/Al-300)	581.9	0.210

S_g is surface area calculated by using Brunauer-Emmett-Teller (BET) method, v_{mp} is micropore volume obtained using t-plot. The value of surface area shown in Table(11) is taken from the company website.

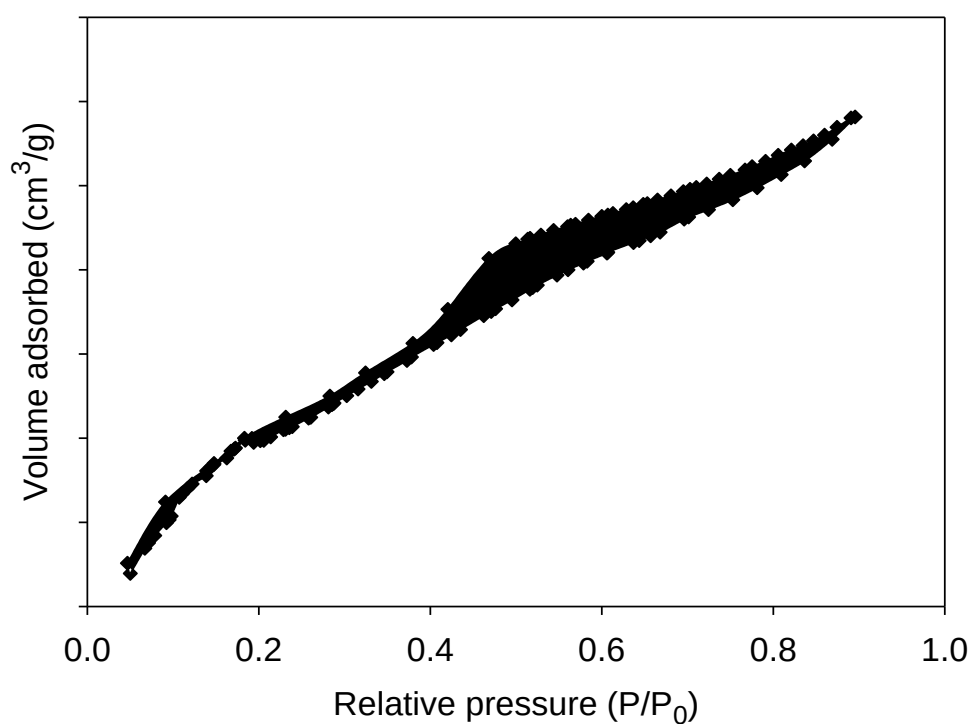


Fig. (A2.2): N₂-adsorption/desorption isotherms of BZ

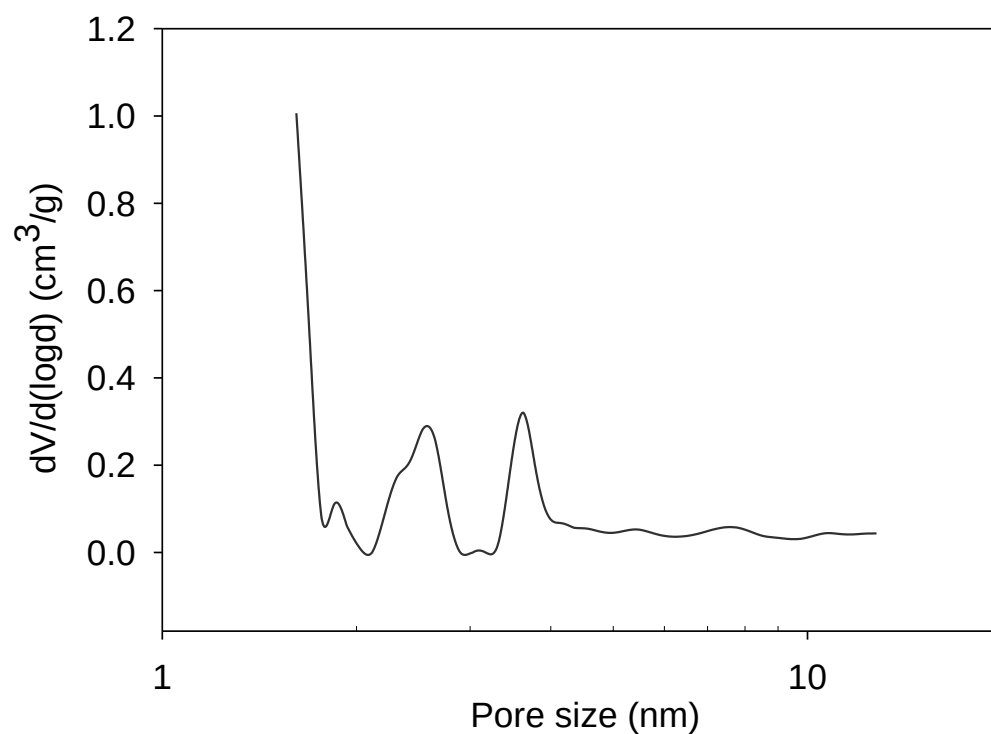


Fig. (A2.3): Pore volume of BZ

Table (A2.2): Structural properties of the ZSM-5 catalyst

Catalyst	S_g (m^2/g)	v_{mp} (cm^3/g)
HZM-5 (Si/Al-23)	339.2	0.127

S_g is surface area calculated by using BET method, v_{mp} is micropore volume obtained using t-plot. The value of surface area shown in Table(11) is taken from the company website.

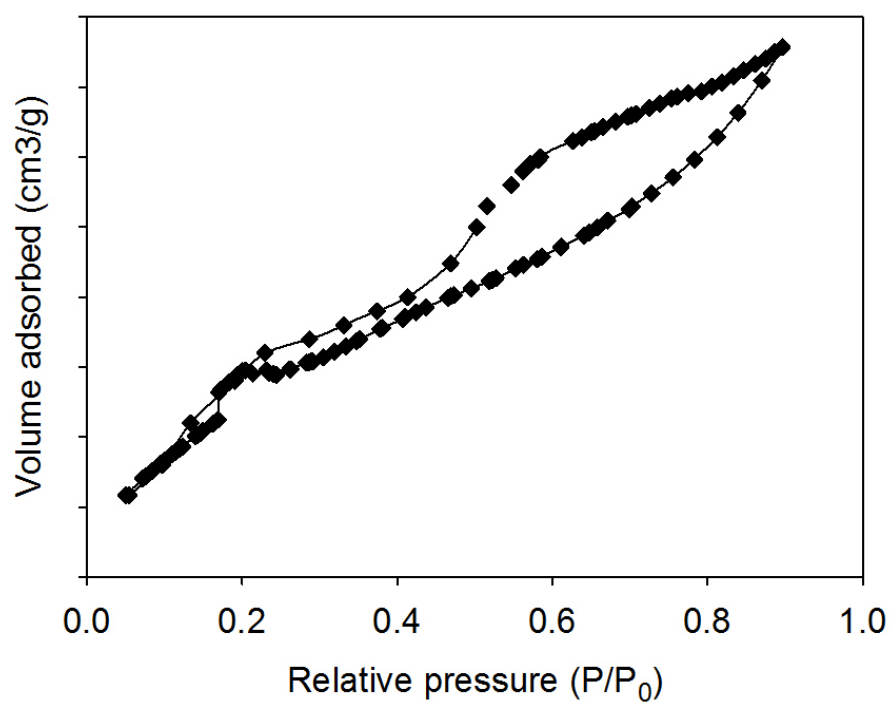


Fig. (A2.4): N₂-adsorption/desorption isotherms of ZSM-5

Appendix-II (C)

List of chemicals used

Table (A2.3): List of chemicals used

<i>Chemical</i>	<i>Supplier</i>	<i>Catalogue</i>	<i>Assay,%</i>
Sodium Hydroxide	Research lab	1310-73-2	99%
Hydrochloric acid	Research lab	7647-01-0	34-37
Ammonium Chloride	BDH	12125-02-9	99.5
Aluminum Hydroxide	BDH	21645-51-2	47
n-Heptane	BDH	142-82-5	98
n-Hexane	BDH	110-54-3	95.5
Methanol	BDH	12055-62-8	99.8
Tetrahydrofuran	BDH	109-99-9	99
Nitric Acid	BDH	7697-37-2	68-70
Aluminum Nitrate	BDH	7784-27-2	99.9

Appendix-III

GCMS data for preliminary experiment-1

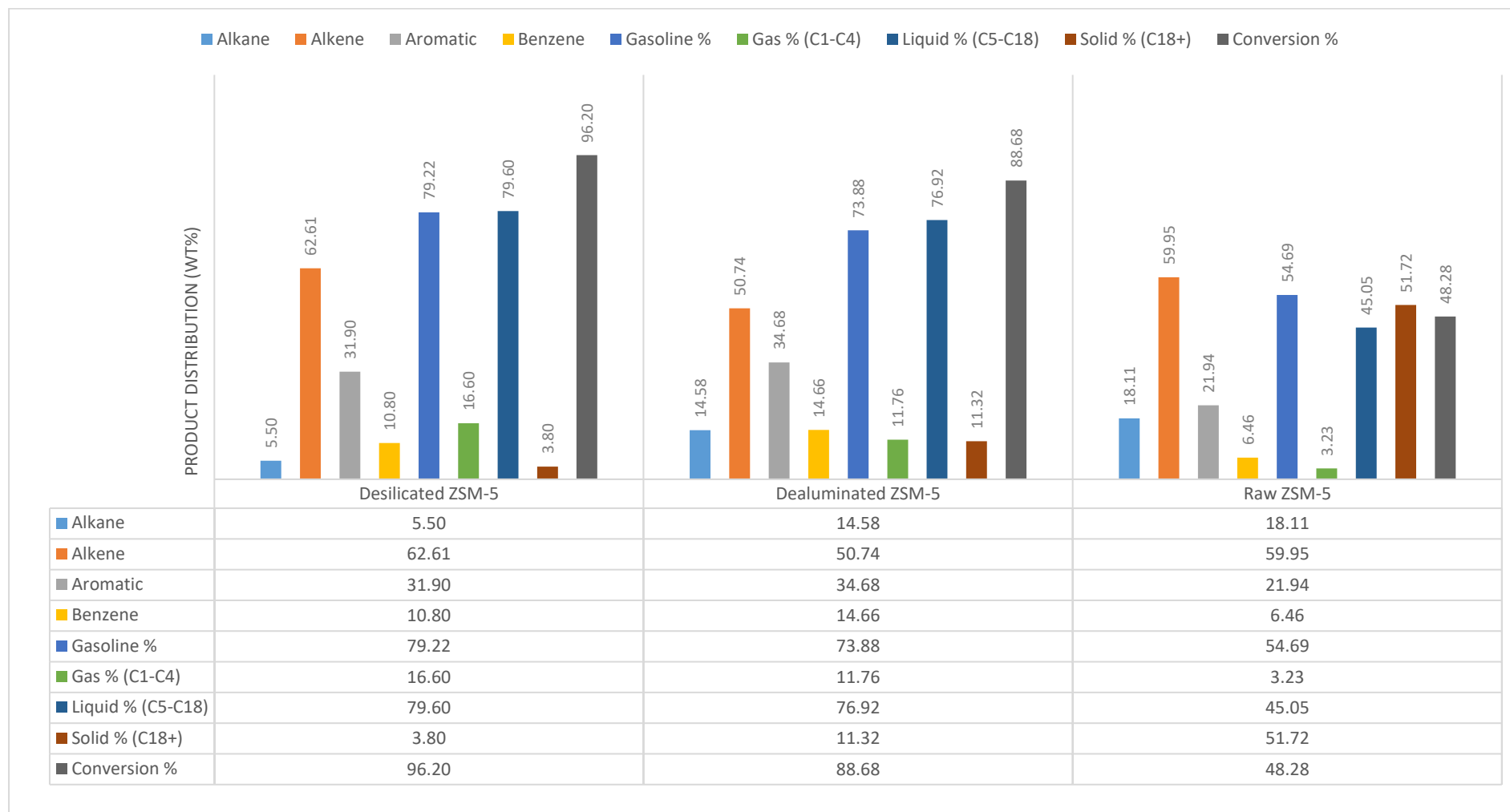


Fig. (A3.1): GCMS detailed data of preliminary experiments-1

Appendix-IV

GCMS data for preliminary experiment-2

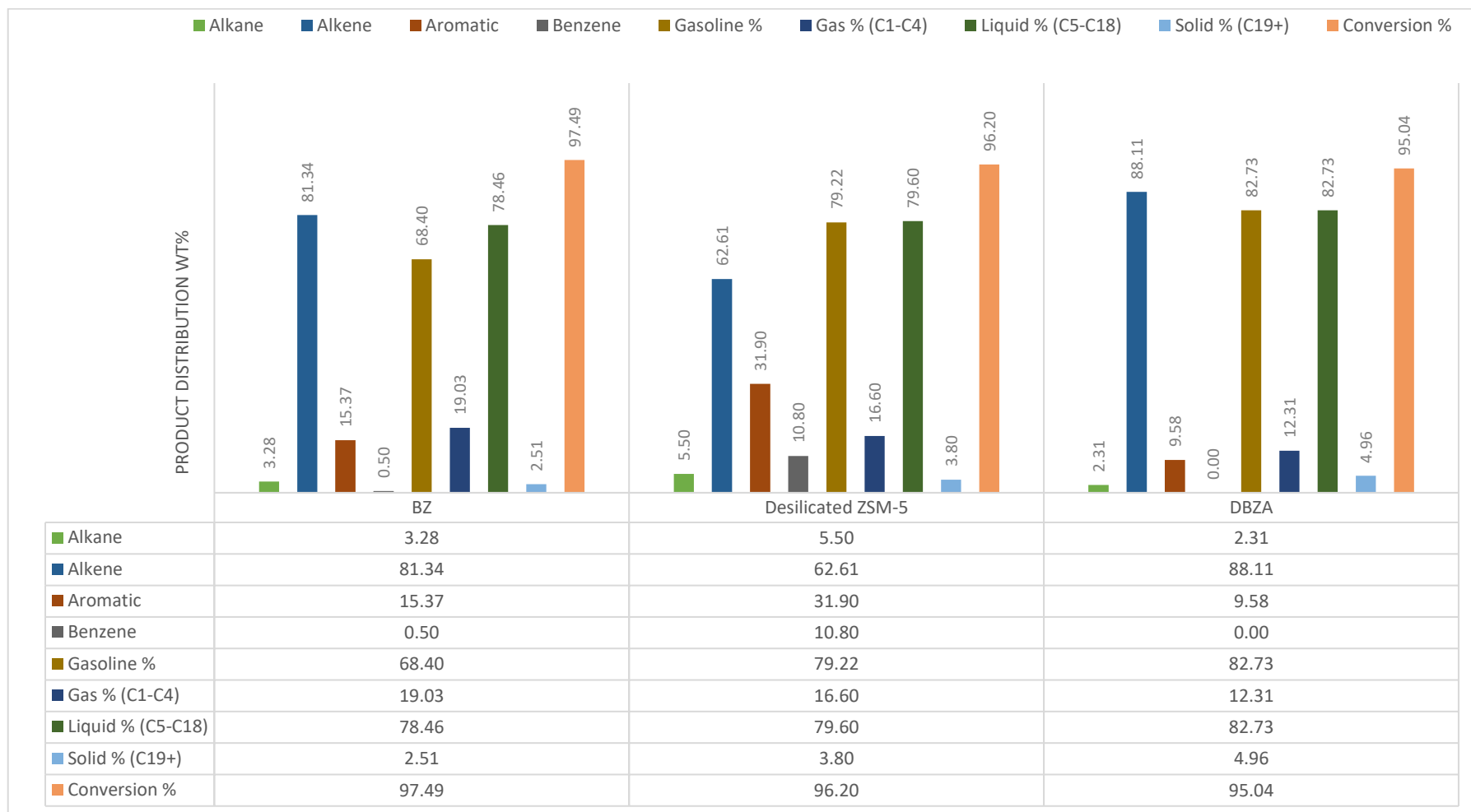


Fig. (A4.1): GCMS detailed data of preliminary experiment-2

Appendix-V

GCMS data for catalyst synthesis optimization

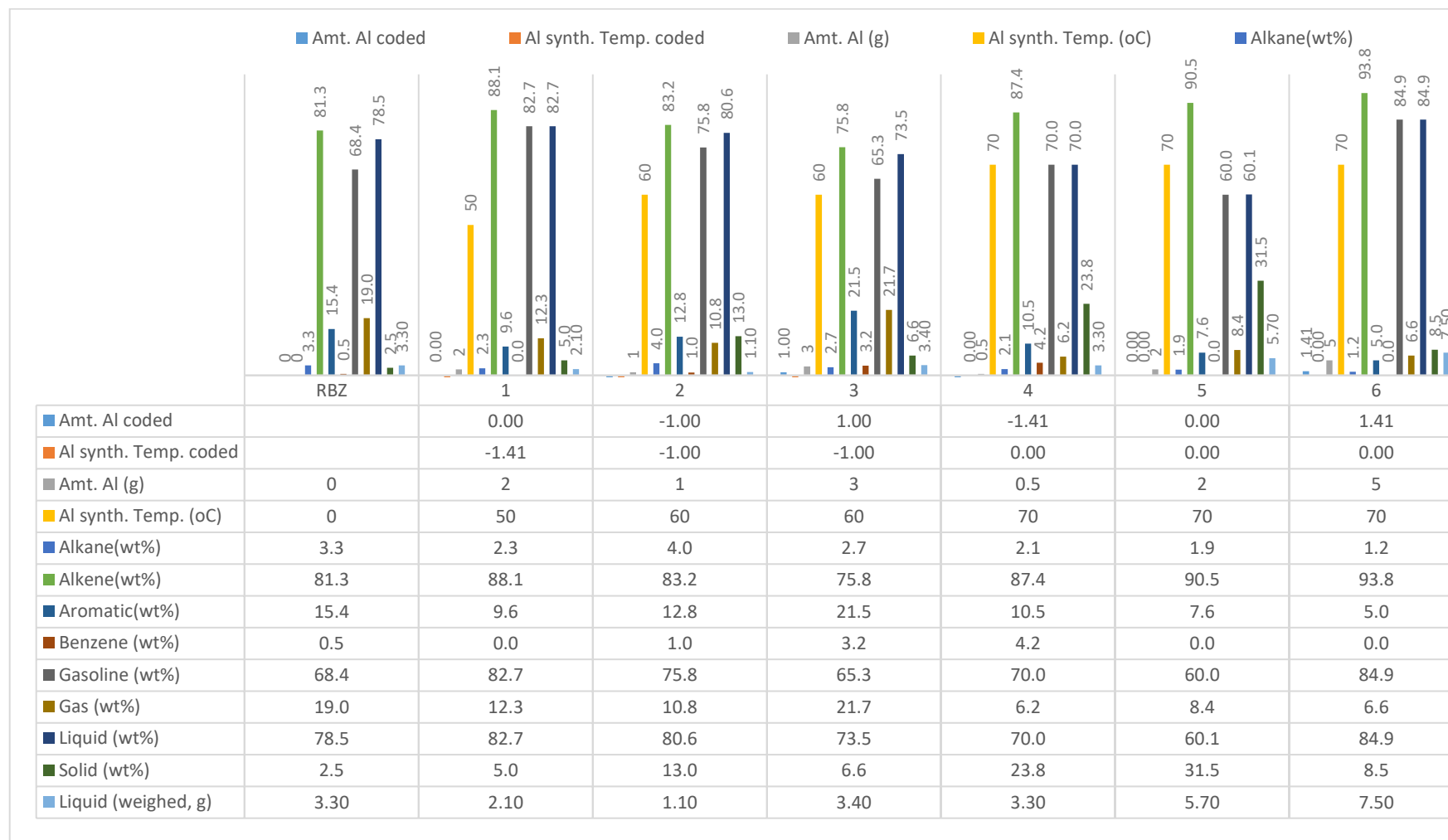


Fig. (A.5-1): GCMS detailed data of catalyst optimization experiments

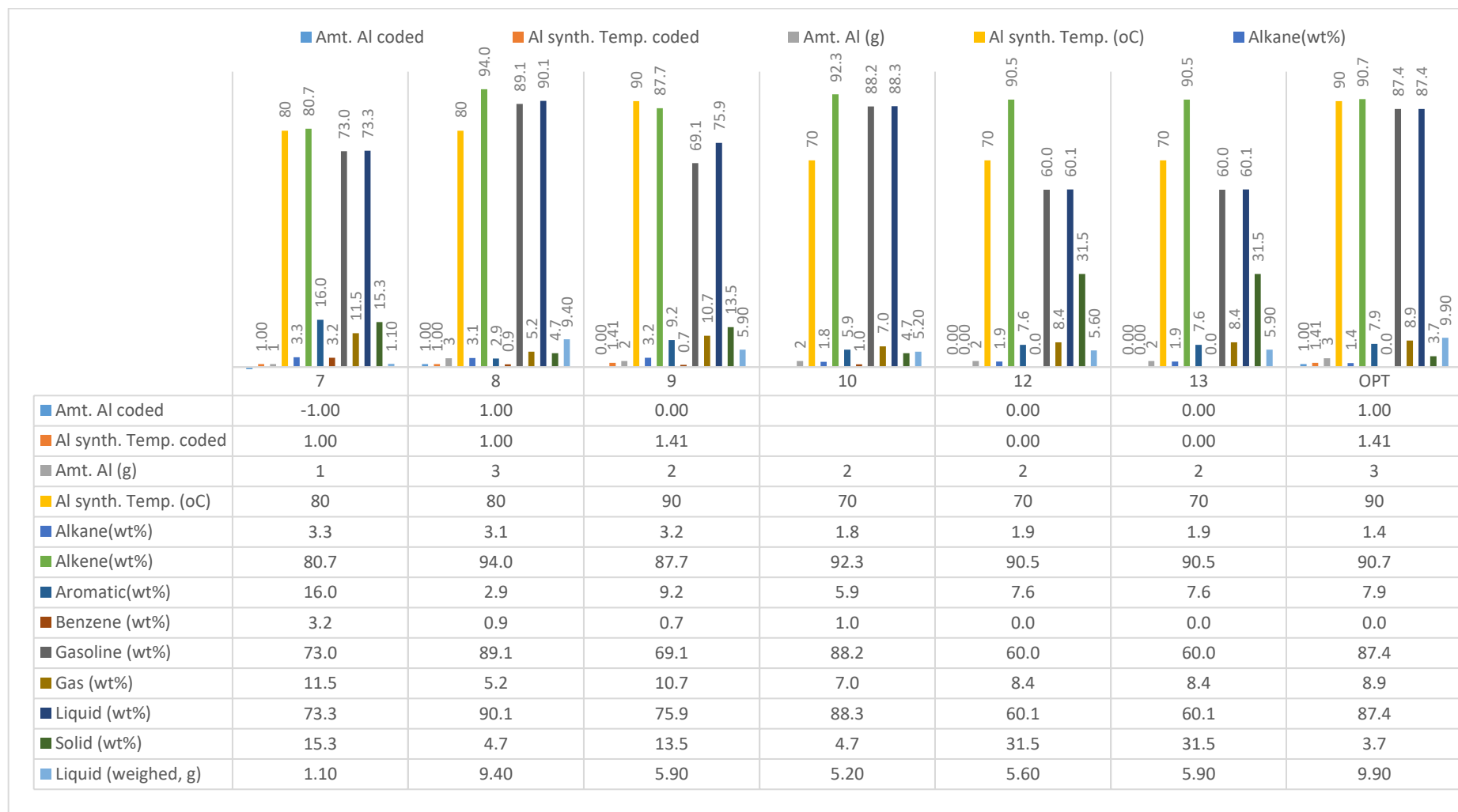


Fig. (A.5-2): GCMS detailed data of catalyst optimization experiments

Appendix-VI

Observations on desilication of BZ

Observations on Desilication of Beta Zeolite

To begin with desilication of beta zeolite in itself was tricky, as on performing the desilication of the zeolite, it would immediately dissolve out or in other words dissolution of the Silica in the zeolite structure occurs where the majority of the lattice structure has collapsed. As seen in the figure (A.6.1), in a situation where Si/Al ratio is above 200 the same amount of sodium hydroxide leads to excessive silica dissolution and very little or nothing of the zeolite structure is left. This was physically indicated in two ways during experiments carried out, one the solution turning brown in color and second on filtration using whatman filter nothing is achieved and everything passes through the filter. As seen in figure (1)-d, the solution that has been dissolved can be clearly seen as it gives it a distinguished brown color during synthesis.

The range of 1g Beta Zeolite in 5ml Sodium Hydroxide (1/5) to 1g Beta zeolite in 70ml Sodium Hydroxide (1/70) was explored. For exploring the ratio range concentration and temperature were fixed at 0.5M and 65°C respectively. And as for the ratio of beta zeolite to solution 1/5, 1/10, 1/15, 1/20, 1/30, 1/40, 1/50, 1/60 & 1/70 were carried out. Out of which all ratios lead to dissolution of the beta zeolite except 1/5 and 1/10.

Hence it was intended to carry out optimization of the catalyst such that Temperature of synthesis varies at levels 65, 75 and 85°C, ratio of beta Zeolite to solution varying at levels 1/5, 1/7 and 1/10, varying concentration of 0.1 to 0.5M. Once optimum is achieved exploration of alumina impregnation was to be carried out. However, this **couldn't happen** as on using the only desilicated catalyst lead to liquified wax formation within the tubular reactor which lead to numerous issues like

- Blockage of nitrogen/hydrogen gas inflow

- Blockage of outflow channel meant for gas yield to sweep out to condenser
- Rupture of pipe connecting to reactor and condenser
- Stubborn wax residue on the glass tubular reactor, making cleaning process cumbersome.

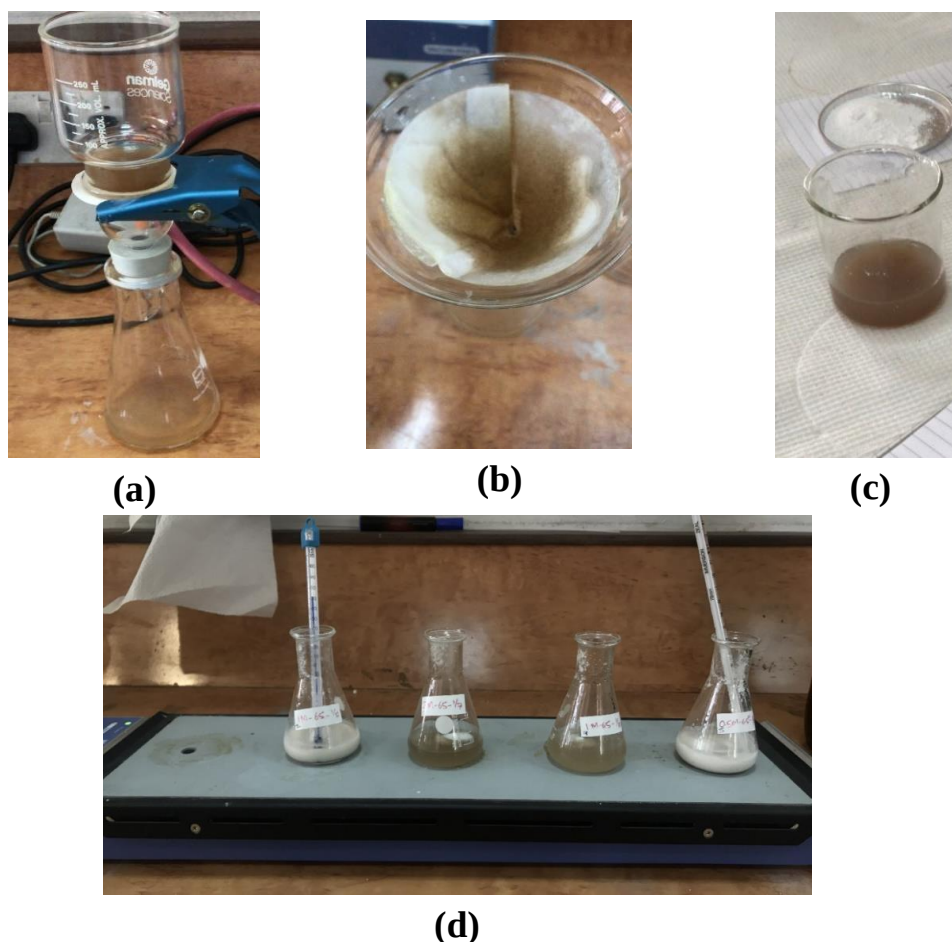


Fig. (A.6-1): (a) Dissolved BZ passing through the filter (b) Dissolved BZ after passing through the filter paper (c) Dissolved filtrate achieved (d) BZ being synthesized at defined temperature

The reasons cited above lead to halt this set of experimental research, as seen in the figures (A.6.2). To counter this issue and optimize the catalyst employment, alumina impregnation of the catalyst that has been desilicated is carried out, on doing so improved the issue of wax formation.

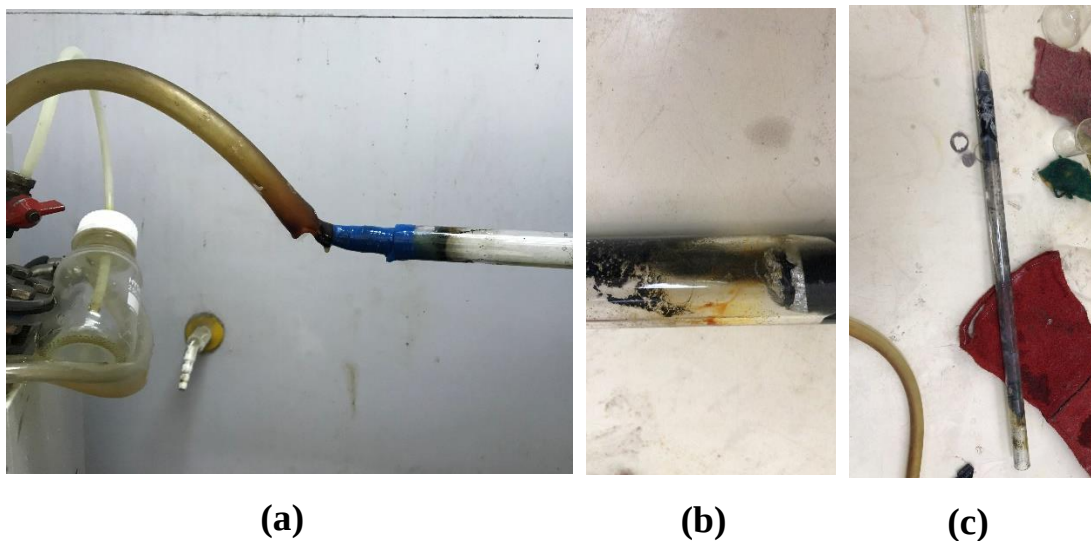


Fig. (A.6-2): (a) Connection Pipe Rupture (b) Blockage of the gas inlet (c) Wax accumulated in the tubular glass

For few prepared samples at various parameters involved in desilication of betazeolite; SEM, EDS and XRD was carried out. The figure (A.6.3) shows the set of samples meant for SEM, EDX, XRD analysis and the table (A.6.1) shows the detailed description of the parameters involved in the desilication catalyst preparation procedure.

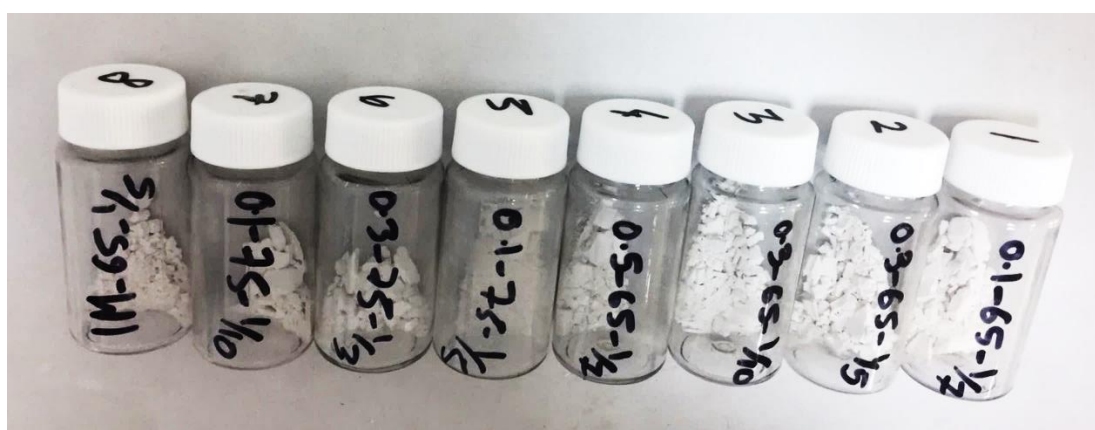


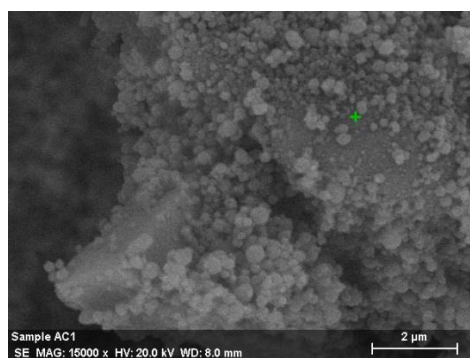
Fig. (A.6-3): Desilicated Beta Zeolite Catalyst Samples

**Table (A.6-132): List of Desilicated Beta Zeolite
at different parametric settings**

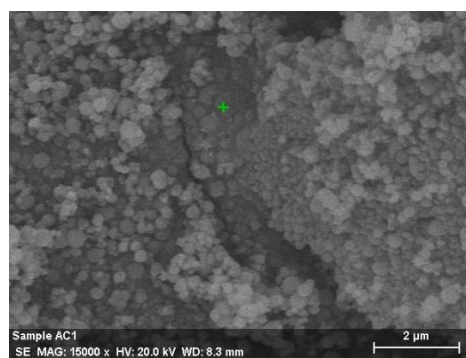
Sample No.	Sodium Hydroxide Molarity (M)	Temperature Synthesized (°C)	Ratio of Zeolite to Sodium Hydroxide Solution
1	0.1	65	1/7
2	0.3	65	1/5
3	0.3	65	1/10
4	0.5	65	1/7
5	0.1	75	1/5
6	0.3	75	1/3
7	0.1	75	1/10
8	1	65	1/5

**Table (A.6-2): Summary of EDX data on Desilication
of Beta Zeolite**

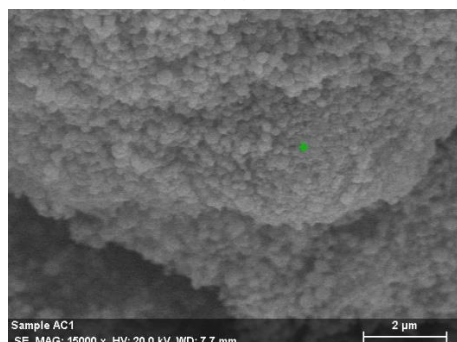
Sample No.	1	2	3	4	5	6	7	8
Wt. Composition(%)								
Oxygen	96.0	91.3	65.8	87.4	74.2	63.7	60.95	58.52
Silica	2.8	6.2	22.3	8.8	21.1	20.3	25.35	17.48
Aluminum	1.1	0.6	1	0.6	0.7	0.62	1	1
Sodium		1.1	3.6	1.8	4.1	3.02		3.92
Nitrogen		0.6		1.4				
Copper		0.3		0.09				
Flourine			8.2			12.41	13.7	20.08
Si/Al ratio	2.7	10.3	22.3	14.9	32.4	32.7	25.35	17.48



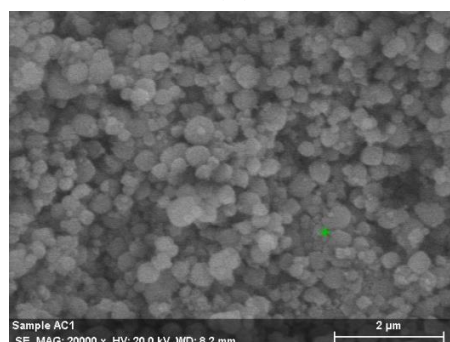
(a)



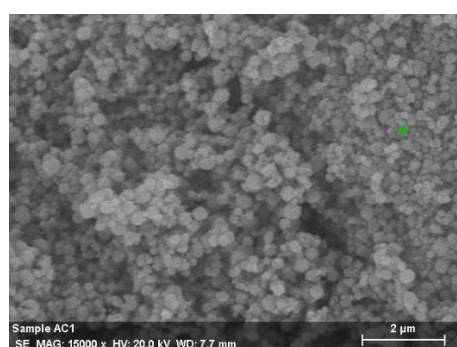
(b)



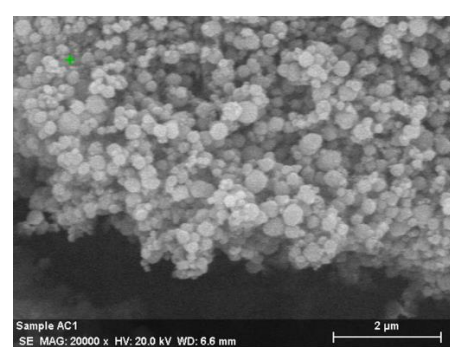
(c)



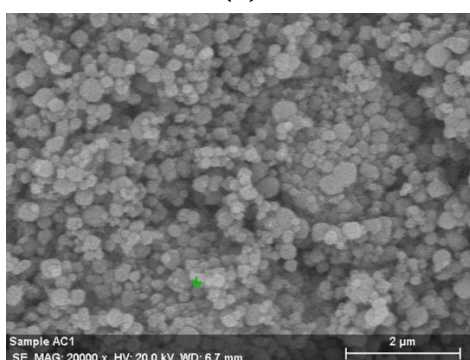
(d)



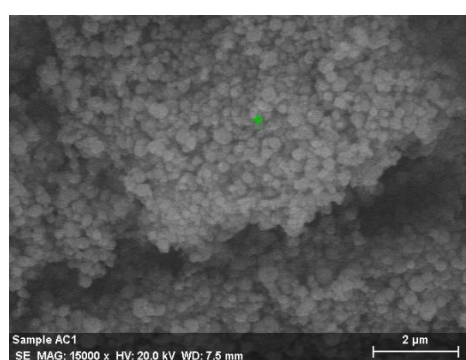
(e)



(f)



(g)



(h)

Fig. (A.6-4): SEM images of Desilicated samples from (a) as sample-1 to (h) as sample-8 in respective order

As expected, Silica and Oxygen are found to compose majority of zeolite besides Alumina also being prevalent, although not as much due to presence of very low amount of alumina in parent beta zeolite. The commercially purchased beta zeolite contained silica and oxygen in the form of SiO_4 tetrahedra, with a very low amount of aluminum. The presence of nitrogen, chlorine and other elements in some of the SEM-EDX spectra are likely to be due to anions left over from the catalyst preparation steps. From the EDX data, it is seen that the Si/Al ratio varies with variation in different parameters involved in catalyst preparation, hence it is difficult to assess the impact of each factor on each other as these are just a partial set of data part of a whole set of design of experiment that was intended to be carried out.

Nevertheless, the Silica Alumina ratio of a catalyst is not the only measure of a decent catalyst. Catalytic sites must have high activity and be accessible to incoming molecules and hence knowledge of surface areas and pore sizes of the catalysts will help to give a greater insight into their effectiveness. Unfortunately, due to unavailability of Nitrogen Adsorption/Desorption instrument, pore size, pore volume, pore area etc couldn't be calculated. Fourier Transform-Infrared (FTIR) spectrometry of adsorbed pyridine, allows an assessment of the number and strength of acidic active sites which couldn't be carried out as well due to unavailability.

Appendix-VII

Kinetic analysis graphs

FOR HIERARCHICAL BETA ZEOLITE:

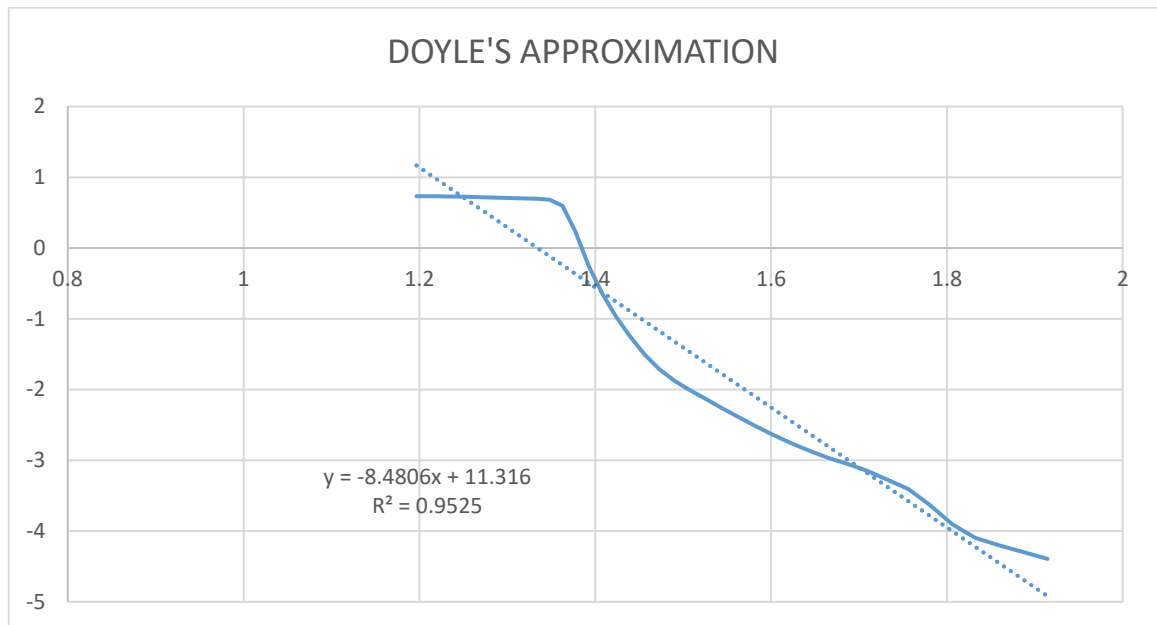


Fig. A.7-1: Plot of $\ln(-\ln(1-x))$ vs $1/T$ (K) for Doyle's approximation

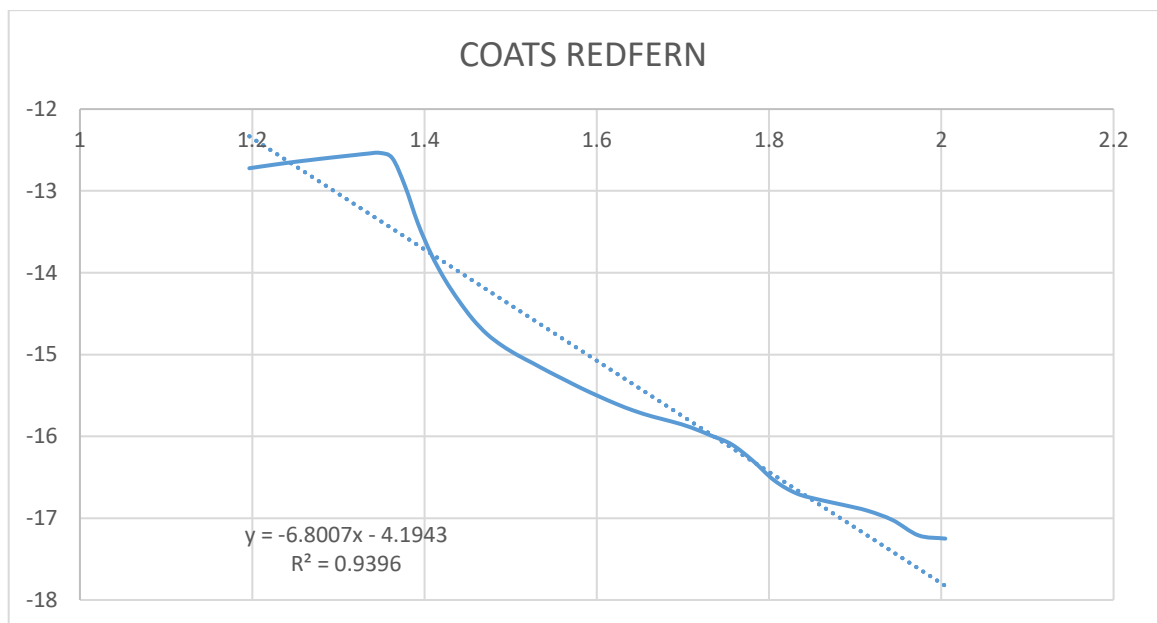


Fig. A.7-2: Plot of $\ln(-\ln(1-x)/T^2)$ vs $1/T$ (K) for Coats redfern approach

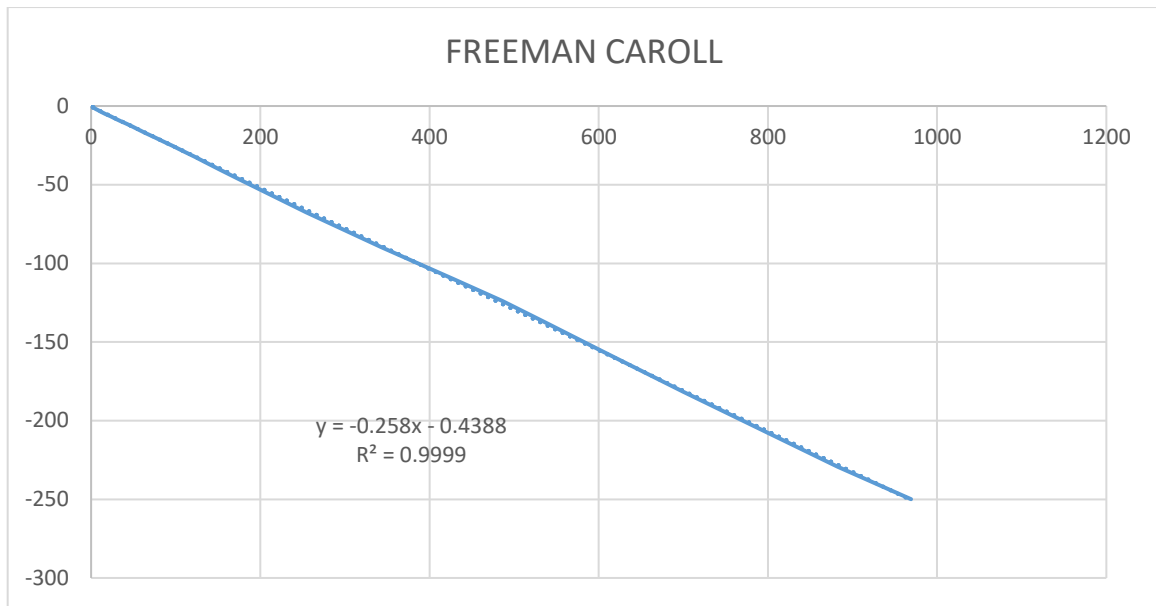


Fig. A.7-3: Plot of $\ln((d\alpha)/dt)/\ln(1-\alpha)$ vs $(1/T)/\ln(1-\alpha)$ for Freeman caroll's approach

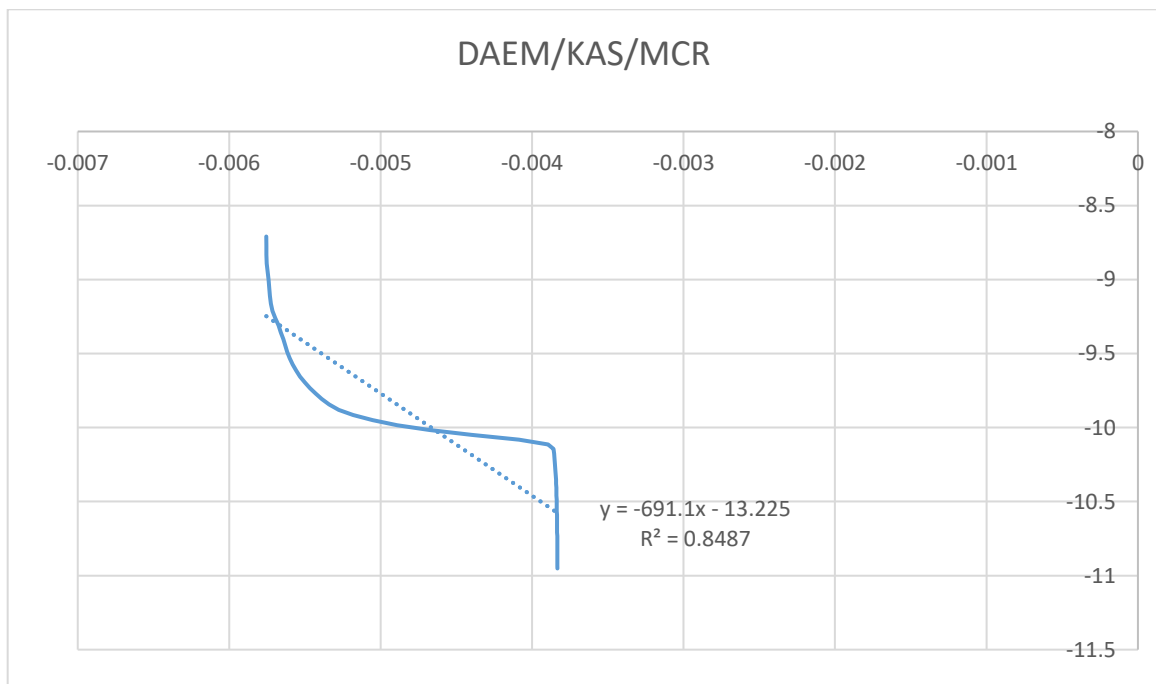


Fig. A.7-4: Plot of $\ln(\beta/T^2)$ vs $1/T$ (K) for DAEM/KAS/MCR

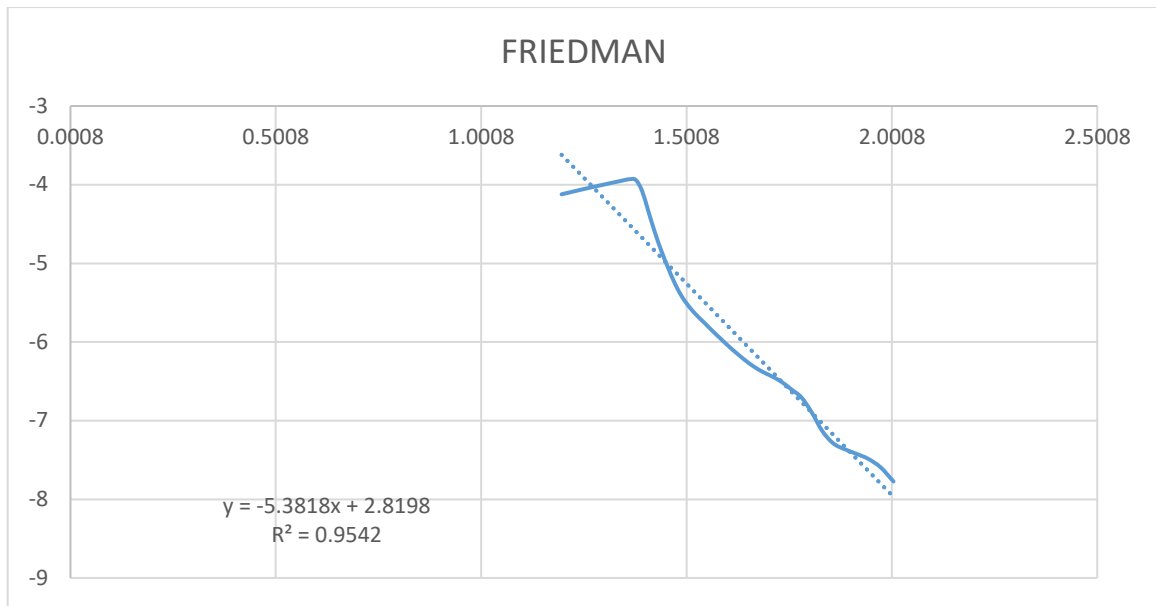


Fig. A.7-5: Plot of $\ln(dx/dt)$ vs $1/T$ (K) for Friedman approach

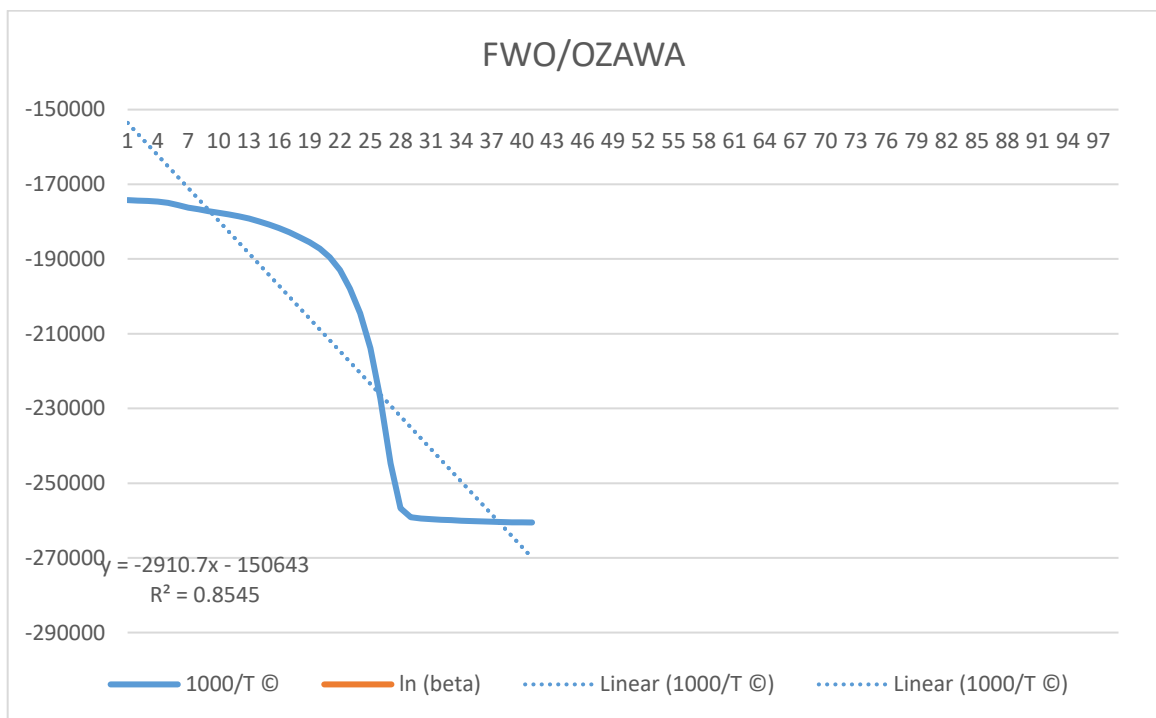


Fig. A.7-6: Plot of $\ln(\beta)$ vs $1/T$ (K) for FWO & OZAWA approach

FOR BETA ZEOLITE:

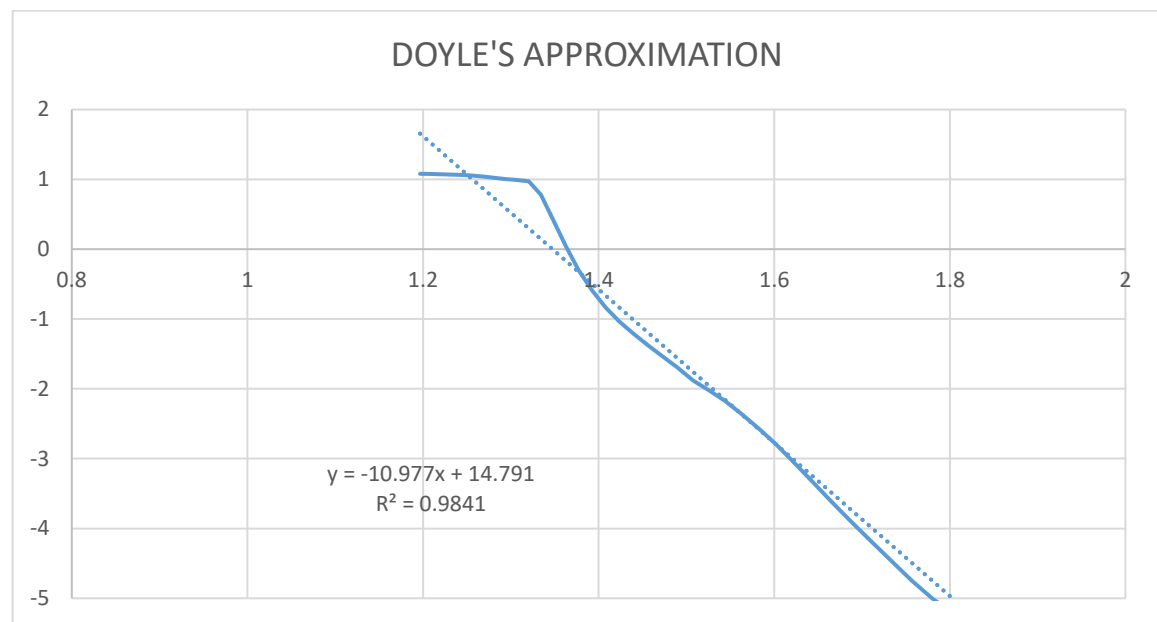


Fig. A.7-7: Plot of $\ln(-\ln(1-x))$ vs $1/T$ (K) for Doyle's approximation

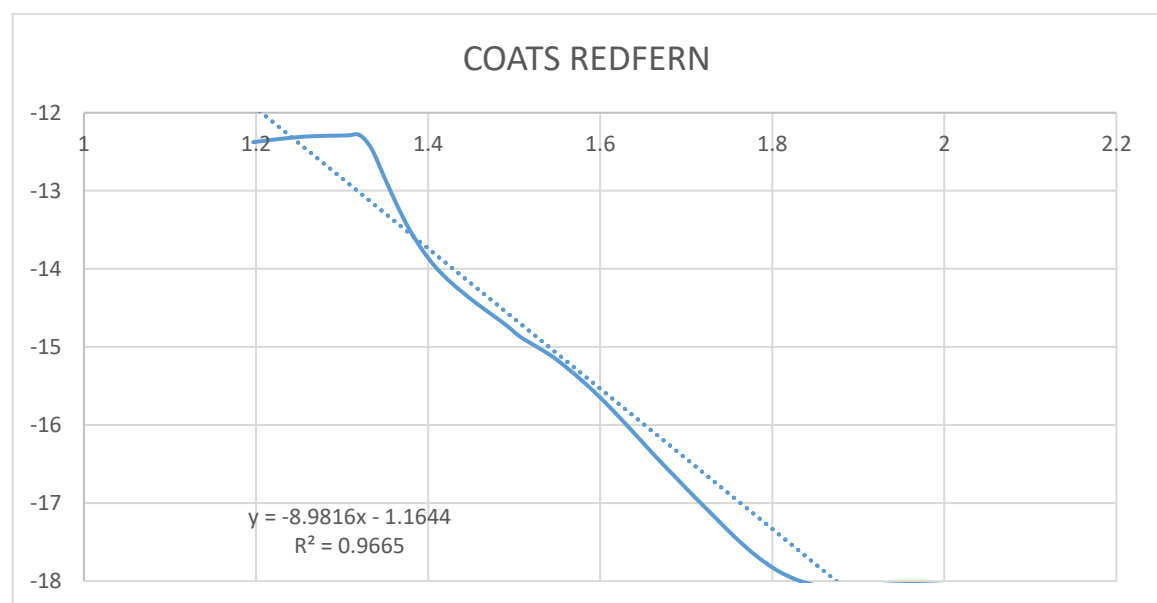


Fig. A.7-8: Plot of $\ln(-\ln(1-x)/T^2)$ vs $1/T$ (K) for Coats redfern approach

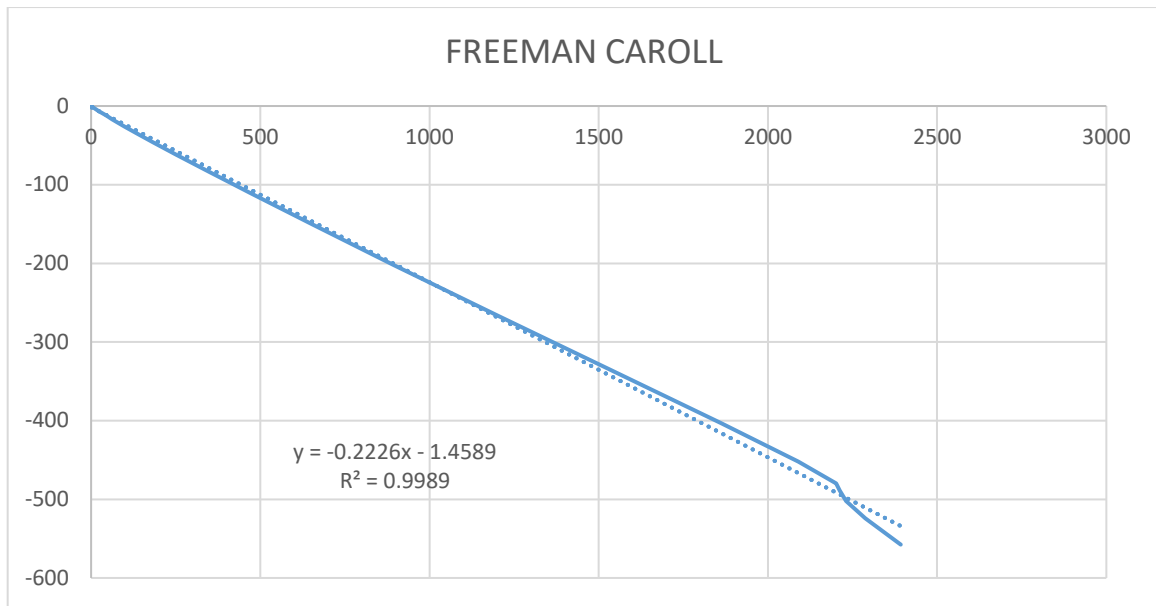


Fig. A.7-9: Plot of $\ln((d\alpha)/dt)/\ln(1-\alpha)$ vs $((1/T))/\ln(1-\alpha)$ for Freeman caroll's approach

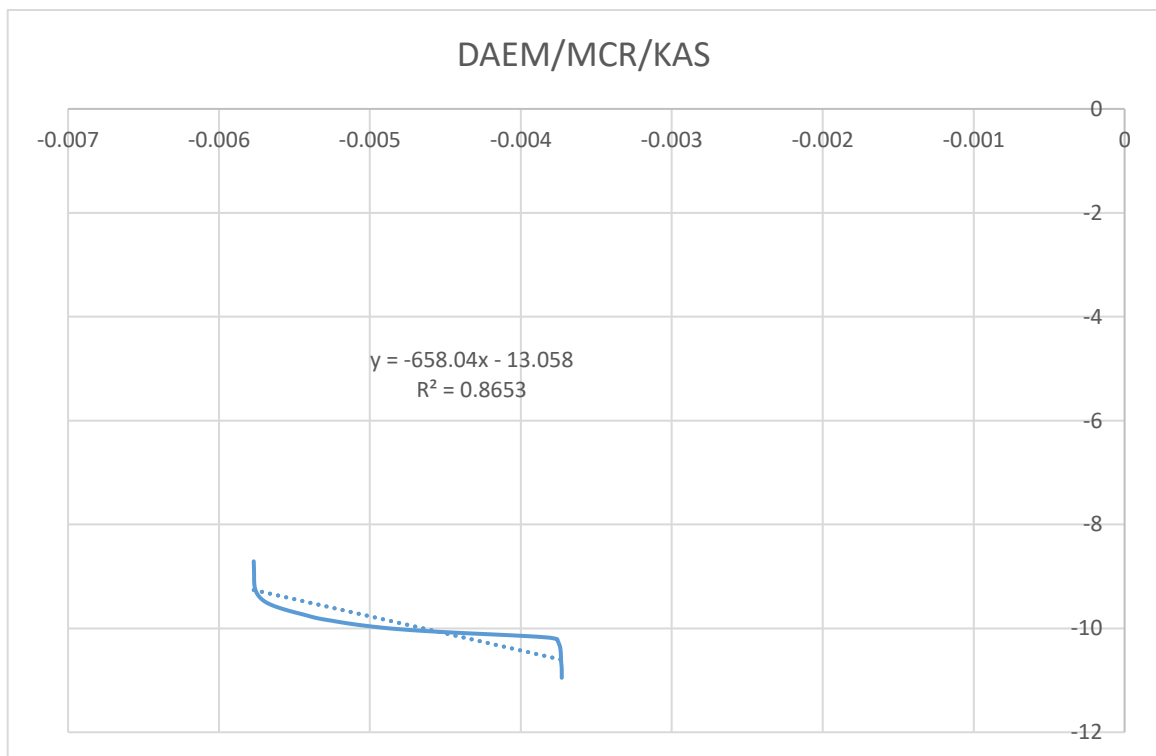


Fig. A.7-10: Plot of $\ln(\beta/T^2)$ vs $1/T$ (K) for DAEM/KAS/MCR

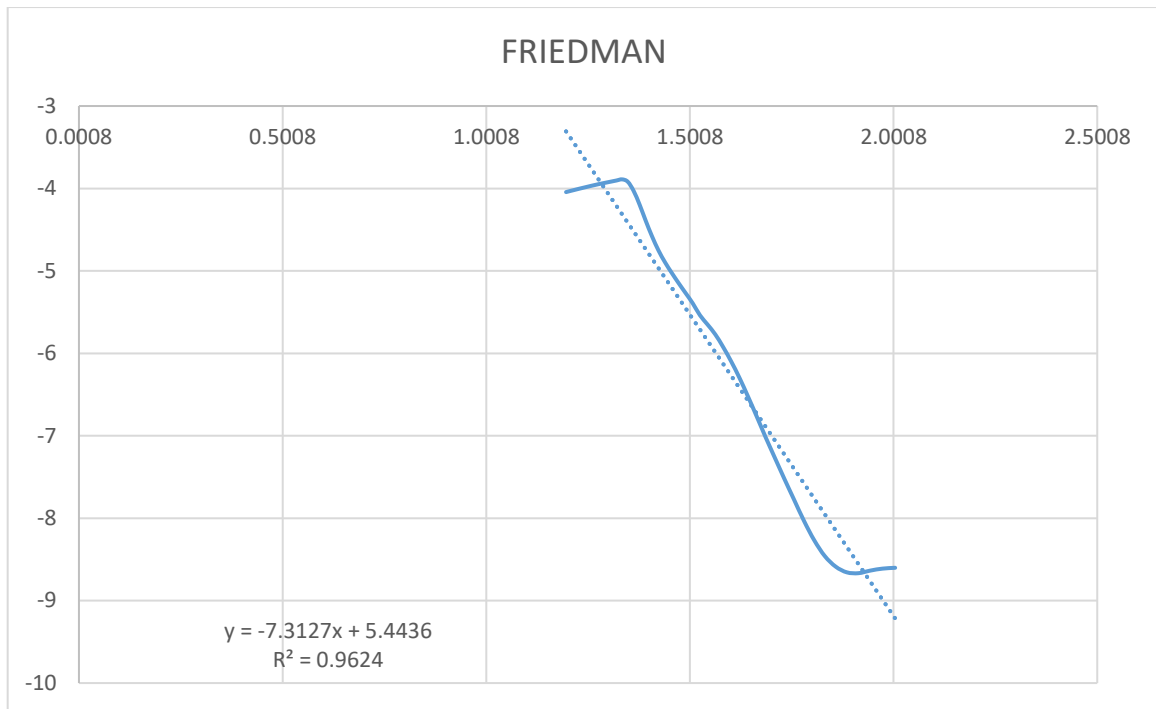


Fig. A.7-11: Plot of $\ln(dx/dt)$ vs $1/T$ (K) for Friedman approach

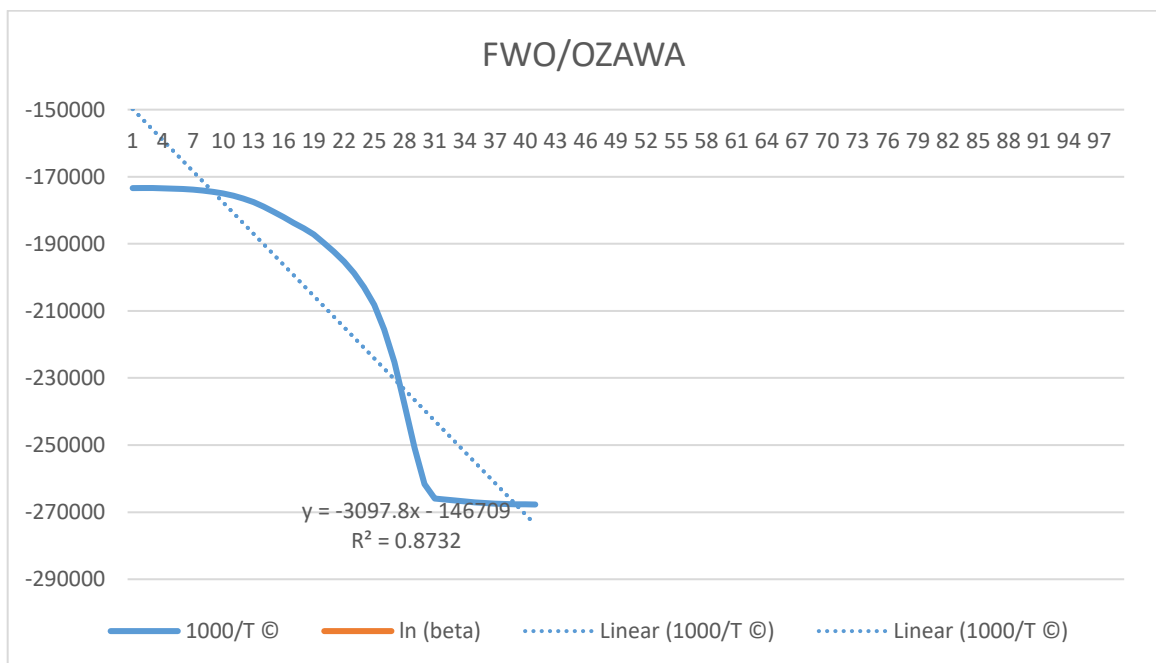


Fig. A.7-12: Plot of $\ln(\beta)$ vs $1/T$ (K) for FWO & OZAWA approach

FOR ZSM-5 ZEOLITE:

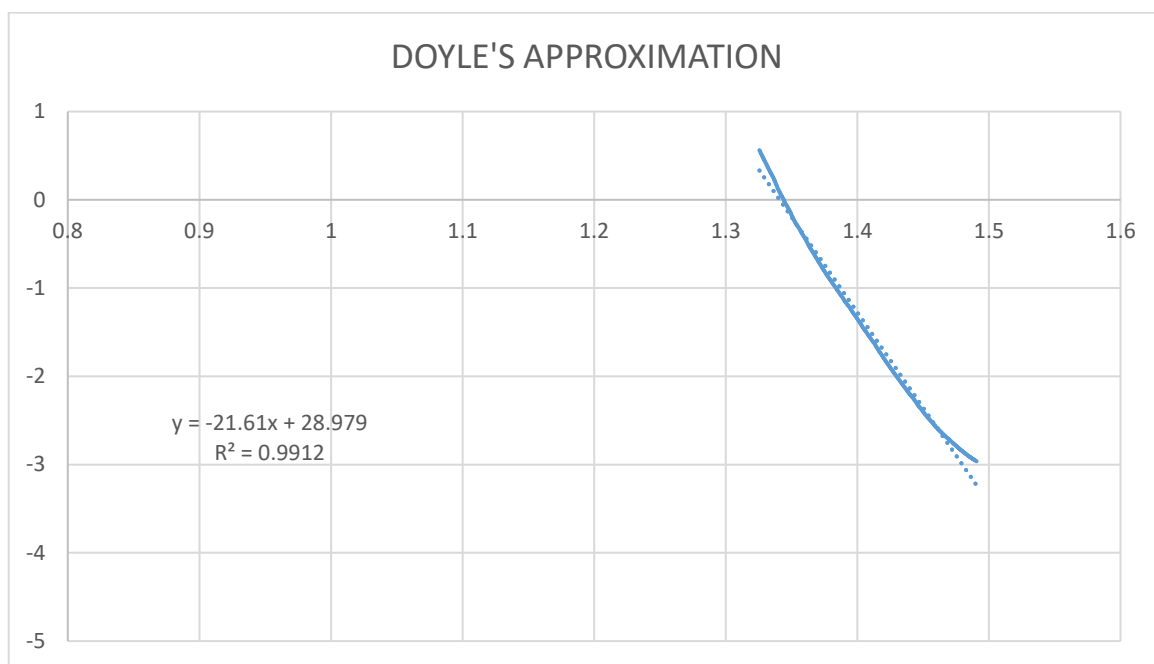


Fig. A.7-13: Plot of $\ln(-\ln(1-x))$ vs $1/T$ (K) for Doyle's approximation

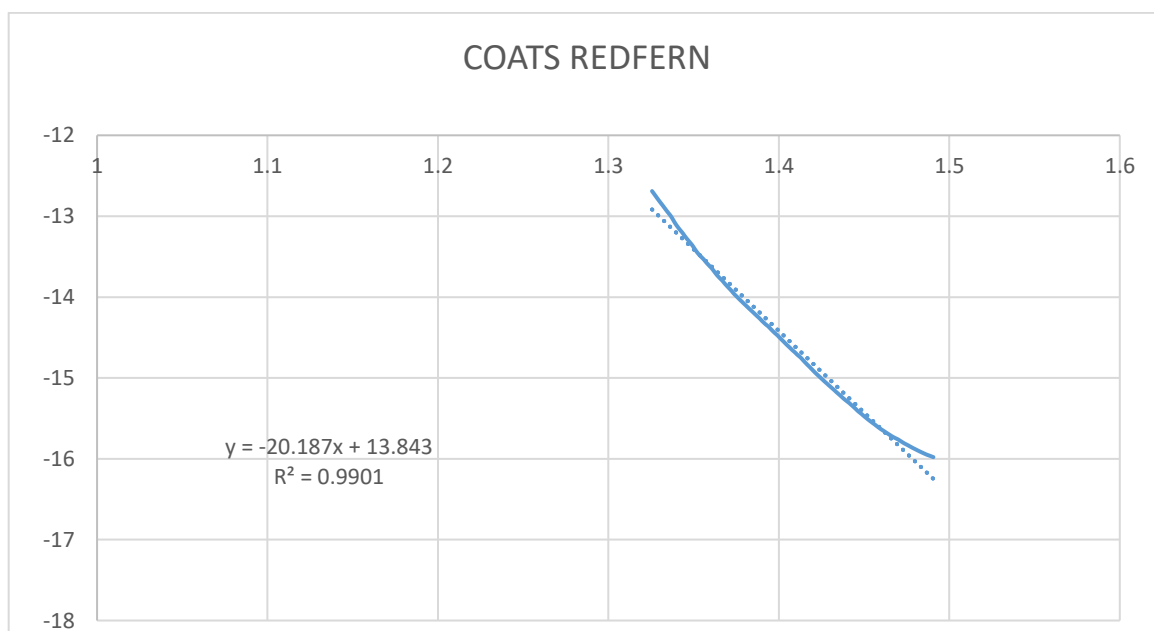


Fig. A.7-14: Plot of $\ln(-\ln(1-x)/T^2)$ vs $1/T$ (K) for Coats redfern approach

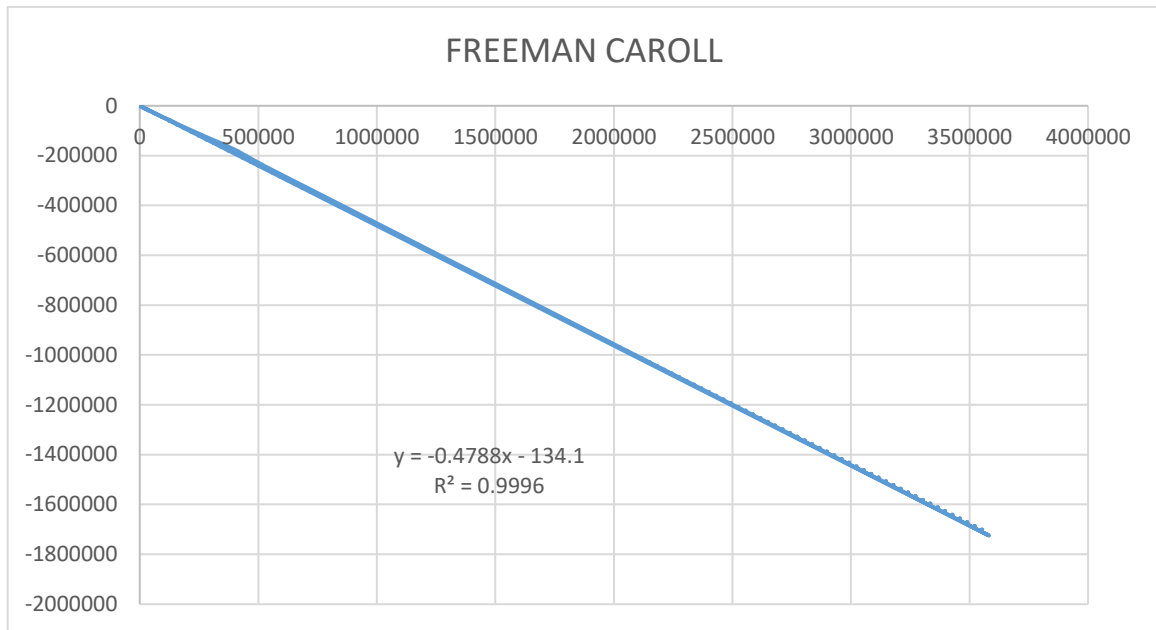


Fig. A.7-15: Plot of $\ln((d\alpha)/dt)/\ln(1-\alpha)$ vs $((1/T))/\ln(1-\alpha)$ for Freeman caroll's approach

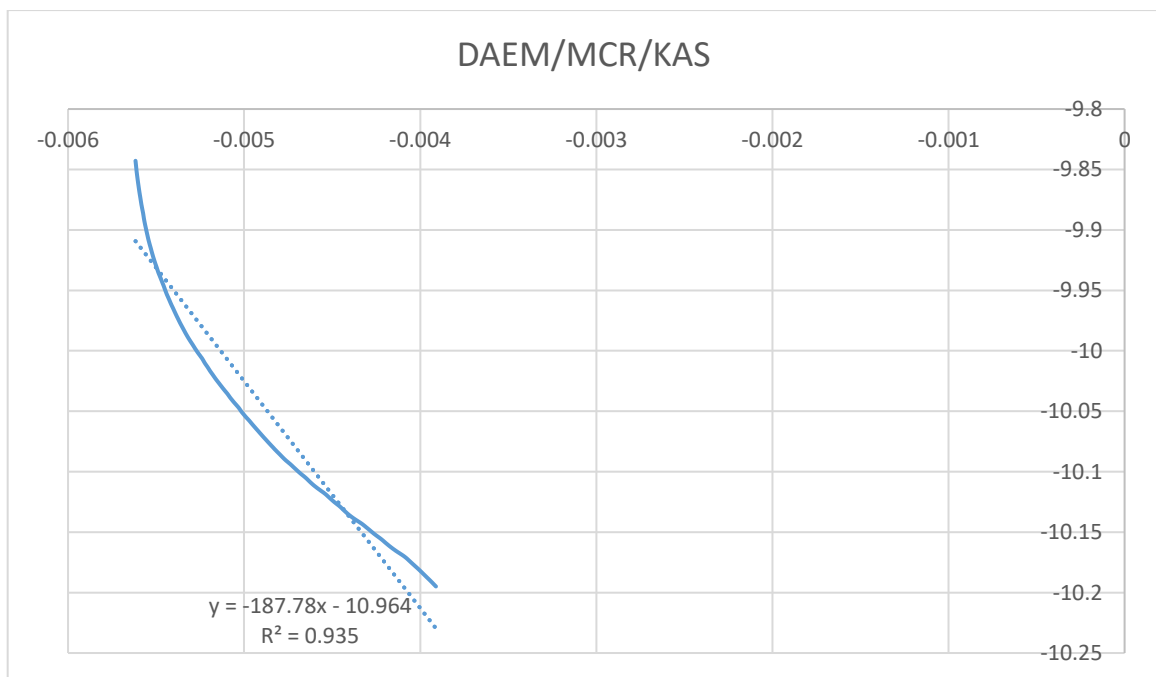


Fig. A.7-16: Plot of $\ln(\beta/T^2)$ vs $1/T$ (K) for DAEM/KAS/MCR

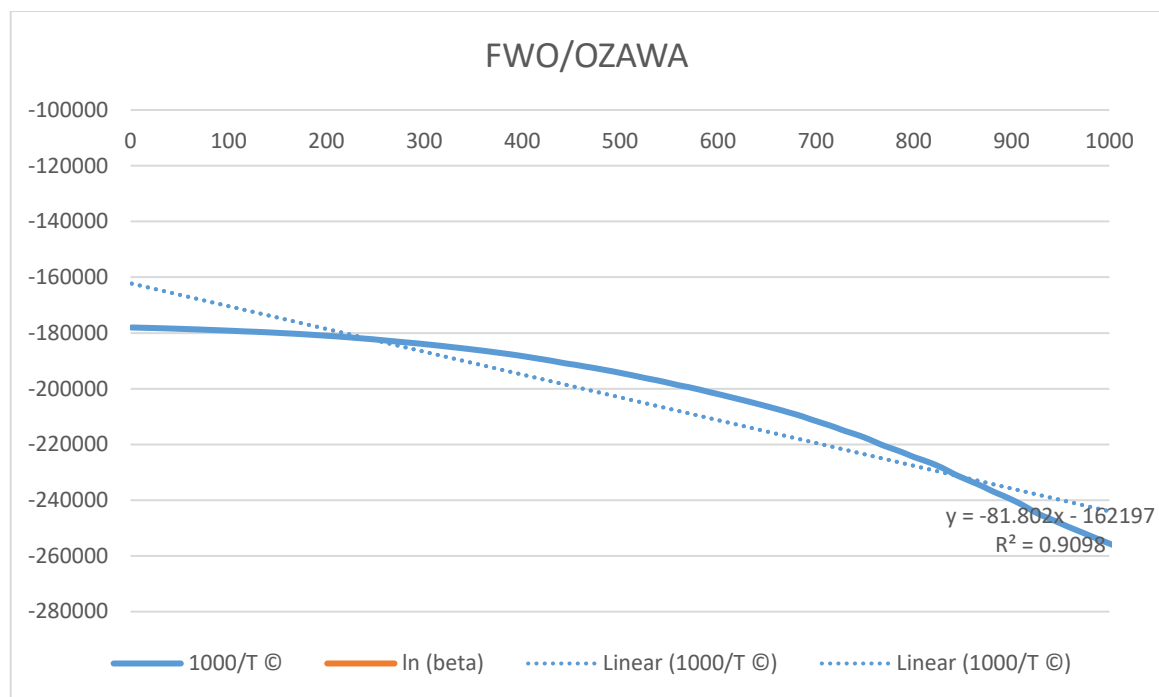


Fig. A.7-17: Plot of $\ln(\beta)$ vs $1/T$ (K) for FWO & OZAWA approach

Appendix-VIII

Catalyst & liquid products characterization techniques

Catalyst & liquid products characterization techniques

Numerous techniques were adopted to analyze the products achieved and the prepared catalyst. Details of them are as follows:

A8.1 Gas chromatography–mass spectrometry (GC-MS)

GCMS or Gas chromatography–mass spectrometry is an analytical approach which combines the 2 features of gas chromatography and mass spectrometry of any given liquid sample to evaluate its contents, in our case liquid product oil is employed to analyze its contents and quality. Samples in very small amounts (about 5ml) are placed in a small bottle and placed in the GCMS setup as seen in Figure (A8.1). The data is given out in .txt form which gives out the components detected and its percentage.



Fig. (A8.1) GCMS setup for liquid fuel analysis

The liquid products from both preliminary and design of experiment stages were analyzed by gas chromatography mass spectrometry to identify the optimum product samples of higher gasoline yields. The oil samples need to be filtered from solid particles that might cause a

blockage in the GC-MS column. The filtration process was performed with whatman filter paper of 0.8μ with activated carbon placed over it to pass through it to absorb any moisture. In the given setup the carrier gas is helium. The programmed initial temperature is held at 70°C for 3 minutes and a final temperature of 250°C that stays for a total time of about 10 minutes. The heating rate between these temperatures is $10^{\circ}\text{C}/\text{min}$. The GC-MS unit used in this project is in the unit operations laboratory of chemical engineering department at University of Bahrain.



Fig. (A8.2): Ultrasonic bath used for fuel with waxes

In situation where wax is to be analyzed it is first mixed with methanol or n-hexane after which it is placed in an ultrasonic bath as seen in Figure (A8.2) for the bonds to break after which they are placed in a centrifuge as seen in Figure (A8.3) for thorough mixing, both these equipments are placed in lab 28-123.



Fig. (A8.3): Centrifuge used for mixing n-hexane with waxes

A8.2 EDS (Energy Dispersive X-ray Spectroscopy)

EDS is an analytical technique used for obtaining the elemental compositions of a sample along with the concentrations of the identified elements. When a sample is targeted with a centralized beam of electrons, an x-ray spectrum is formed because of the emissions by the sample. This spectrum is utilized to obtain a localized chemical analysis. The analysis can either be qualitative and/or quantitative. By qualitative, only the identification of the lines in the spectrum is performed, to recognize the elements of the sample and by quantitative the line intensities are measured for each sample thus getting the concentrations of the elements. EDS and Scanning Electron Microscopy (SEM) are usually integrated into one equipment using which both can be done. This system has a sensitive x-ray detector, a liquid nitrogen tower for cooling, and program to pool and analyze the data. An EDS detector comprises of a crystal which absorbs the energy of incoming x-rays by ionization, giving out a free electron in the crystal that becomes conductive and gives out an electrical charge. The electrical pulses correspond to the characteristic x-rays of the element, which is depicted through a schematic in Figure (A8.4).

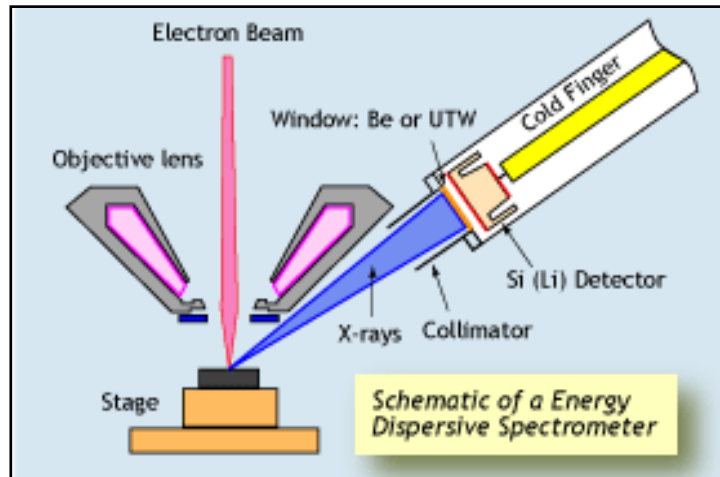


Fig. (A8.4): Schematic of EDS (McSwiggen et al., 2018)

A8.3 SEM (Scanning Electron Microscopy)

SEM (Scanning Electron Microscopy) technique utilizes a beam of high energy electrons with significant amount of kinetic energy.



Fig. (A8.5): SEM-EDS equipment

The beam is pointed on the sample from a scan coil, the electrons inside the beam slows and due to this mechanism, many electrical signals are produced on the surface of the solid sample. Each interaction is registered generating an image. The signals reveal the external morphology

(texture); composition of the sample and also tells about the crystalline or amorphous structure of the materials present in the sample. SEM images are two dimensional and can be obtained on a screen. A sample of only 1cm to 5 microns in width can be used to generate images which can be magnified from 20X to approximately 30000X. The EDS-SEM machine as seen in Figure (A8.5) is placed at physics department of University of Bahrain, Sakheer. In preparation for energy dispersive X-ray (EDX) analyses and scanning electron microscopy (SEM), characteristic samples of zeolite representative of each variation being explored have been dispersed on adhesive carbon tape which in turn was mounted on and ground to an aluminum stub using silver dag. The latter assembly was then gold-coated to facilitate obtaining maximum electron yield. In an effort to minimize undesirable charging effects and enhance imaging quality the variable pressure (VP) mode on an environmental Evo LS 10 Carl Zeiss scanning electron microscope utilizing a LaB6 filament was adopted. The VP mode was set such that a typical extended chamber pressure of 50 Pa and an aperture of 100 μ m were used. Improved resolution was sought by deploying an accelerating voltage of 20 kV with reduced beam/probe currents as low as 30 pA. Lacking a variable pressure secondary electron (VPSE) detector and to avoid the risk of arcing with conventional SE detectors the topographical nature of the nano structural features did not readily offer themselves for critique. As such imaging was restricted to high yield back scattered electron mode. EDX analyses were conducted with the aid of a Bruker BSD detector with a resolution of 127 eV whilst maintaining recommended count levels at 5- 6 KCPS through optimization of beam alignment and maximizing probe current without compromising resolution.

A8.4 XRD (X-ray diffraction)

The XRD equipment used for this project was Ultima IV X-ray diffraction generator by Rigaku as seen in Figure (A8.6). X-ray diffraction is the most widely used x-ray based analytical technique.



Fig. (A8.6): XRD Apparatus, Rigaku

The sample under observation is taken in a powder form, which consists of fine grains of crystalline structure. When an X-Ray beam is focused on the sample, part of the beam is absorbed by the sample, the rest of it gets either scattered, diffracted or refracted. The part of the beam which is diffracted measures the distance between planes of atoms by applying Bragg's Law (1921) and can be written as follows:

$$n\lambda = 2d\sin\theta \quad (\text{A8.4.1})$$

where,

n- Order of diffracted beam

λ - Wavelength of incident X-ray beam

d- Distance between adjacent planes of atom (d-spacing)

θ - Incident angle of X-ray beam

The average crystallite size of zeolite catalysts was calculated according to the Debye-Scherrer's formula (Smail et. al, 2019):

$$Crystallite\ size(D) = \frac{k\lambda}{B\cos\theta} \quad (A8.4.2)$$

where,

k- shape factor of particle (0.9, Scherrer's constant)

λ - Wavelength of incident X-ray beam (0.1541nm)

B- full width at half maxima of the diffraction peaks (FWHM in radians)

θ - Incident angle of X-ray beam (peak position in radians)

These d-spacings characteristics sets are generated in the X-ray scan, which provides pattern of the minerals present in the sample. On comparison with the standard reference patterns the minerals present in the sample can be easily identified. The XRD machine is placed at Chemistry department of University of Bahrain, Sakheer.

A8.5 TGA (Thermogravimetric Analyzer)

The kinetics of the catalytic hydrocracking of plastic waste reaction is to be study via thermogravimetric analyzer (TGA). Thermal gravimetric analysis (TGA) was run on a TA Q-500 instrument as seen in Figure (A8.7) with the sample held in a platinum pan under nitrogen flow with 10°C/min heating rate. The outcome of a TGA is in the form of a data that comprises of weight loss with temperature and time. The sample that needs to be analyzed is placed on a pan in very small quantity. In our study, about 10mg of mixed plastic were prepared in a particular ratio of various types of plastics which were further shredded and mixed with a measured amount of catalyst as per the catalyst to plastic ratio. Using this data kinetic parameters like activation energy can be calculated from various well-known models. This setup does not exist at University of Bahrain (UOB) and is the curtsy of King Fahd University of Petroleum and Minerals (KFUPM) for their generous favour in analysis of our samples.

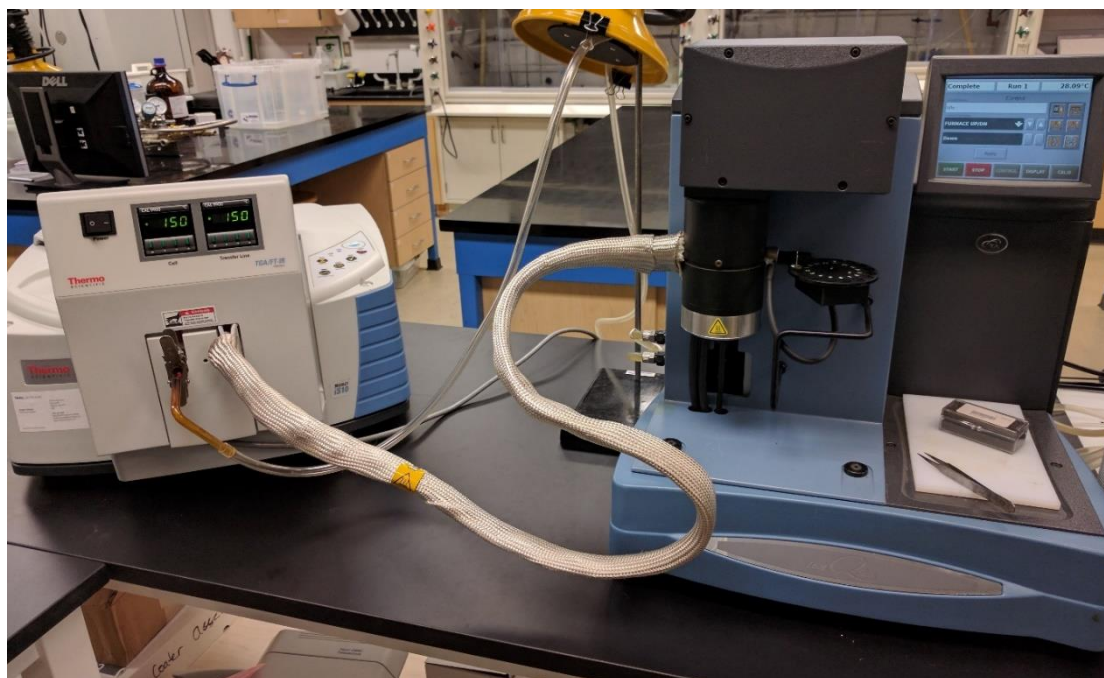


Fig. (A8.7): Thermogravimetric Analyzer (TGA)

Appendix-IX

Various other methods of Hierarchical Zeolite preparation

A9.1 Irradiation

This method of top-down approach was introduced by Valchev et al. (2011) in his study which demonstrated the possibility of addition of secondary porosity of uniform parallel mesopores which extended through entire zeolite crystal. This methodology involves 2 steps. First, the addition of radiated ions like uranium to zeolite to create paths within the zeolite crystal. Second, wash the radiated zeolite with hydrofluoric acid and then water. Consequently, mesopores of 50nm parallel arranged between the pores were created as seen in the Figure (A9.1), where ‘a’ is the thickness and ‘r’ is the radius of the pores (Feliczak-Guzik, 2018; Valthev et al., 2011).

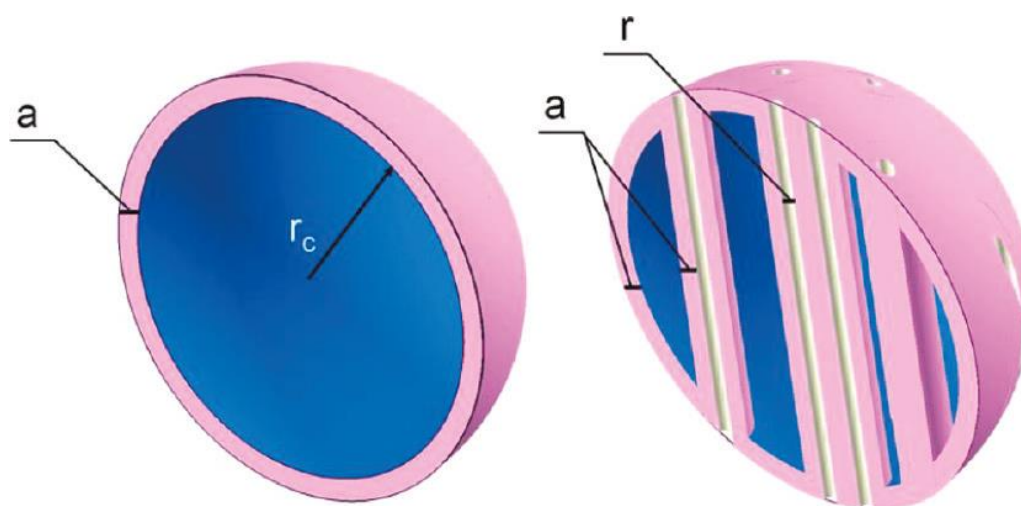


Fig. (A9.1): Zeolite at left before and at right after catalytic reaction (Valthev et al., 2011)

A9.2 Hard templating

This method of bottom-up approach prepares hierarchical zeolites via engineering micro/mesopores domain usually with template materials. Carbon based materials (like carbon black, carbon nano tubes, carbon nanofibers, carbon aerogel, mesoporous carbon etc) are usually used in hard templating due to their availability and adaptability. Carbonized rice-

husk, Calcium carbonate, pyrolyzed wood, polystyrene and other polymeric materials have also been reported to be used for templating (Li et al., 2014; Zhang et al., 2016)

Jacobsen et al. (2000) from very popular Danish catalyst firm ‘Haldor Topose’ published innovative study in the preparation of mesoporous zeolite ZSM-5 single crystals with intracrystalline mesoporosity in the synthesis of nanosized zeolites ZSM-5 in the confined space within the pores of carbon black as seen in Figure (A9.2).

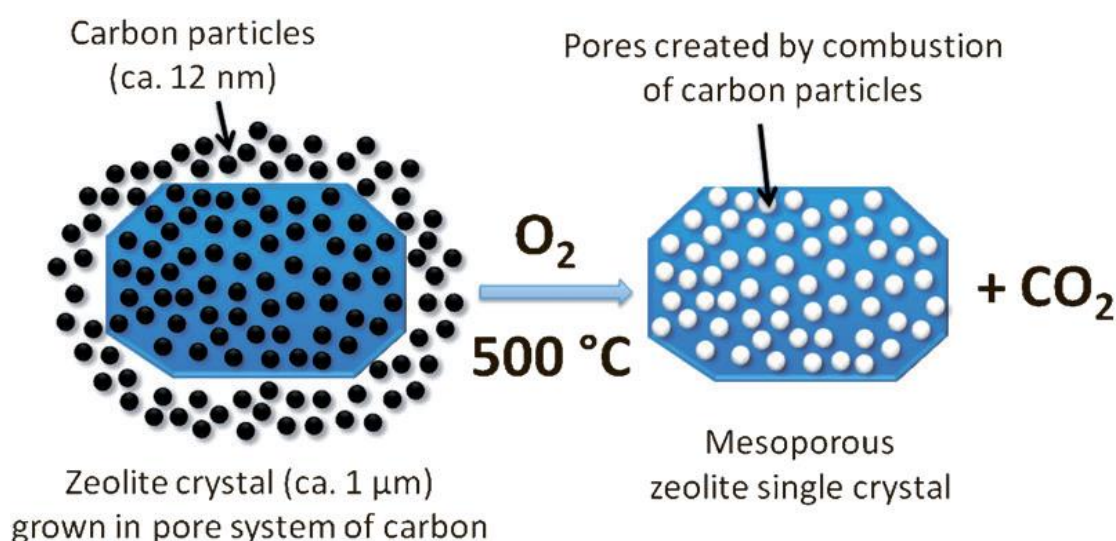


Fig. (A9.2): Hard template mesoporous zeolite crystal (Jacobsen et al., 2000)

A9.3 Soft templating

This method of ‘Bottom-up’ approach involves involve the use of cationic surfactants, mesoscopic-cationic polymers, block polymers, silylated polymers or surfactants, polymeric aerogels, starch, bacteria etc. The most commonly used ones involve the use ‘block copolymers’ as they are easily available and relatively cheap. Zhou et al. (2011) in their research employed the used of copolymers like Pluronic F127, Pluronic P123 and Brij for the synthesis of hierarchical zeolites. Zhou et al. (2013) in their study used co-polymer F127 as well as cetyltrimethylammonium bromide

as co-template for synthesis of ZSM-5 zeolite. Acknowledgements solutions like these that has aggregated crystallites occurrences that created bigger mesopores passages in zeolites structure (Feliczak-Guzik, 2018; Li et al., 2014; Na & Somorjai, 2015; Peng et al., 2012; Zhou et al., 2013; Zhou et al., 2011). Serrano et al. (2009) in their study for synthesis of hierarchical zeolites ZSM-5, beta, A, mordenite, TS-1 obtained secondary porosity by removing zeolite SDA and silanization agent by calcination, in which ammonium-moiety is not required to be involved in organ silane molecule as depicted in Figure (A9.3). The organ silane molecular act as mesoporosity producer and crystal growth inhibitor (Zhang et al., 2016).

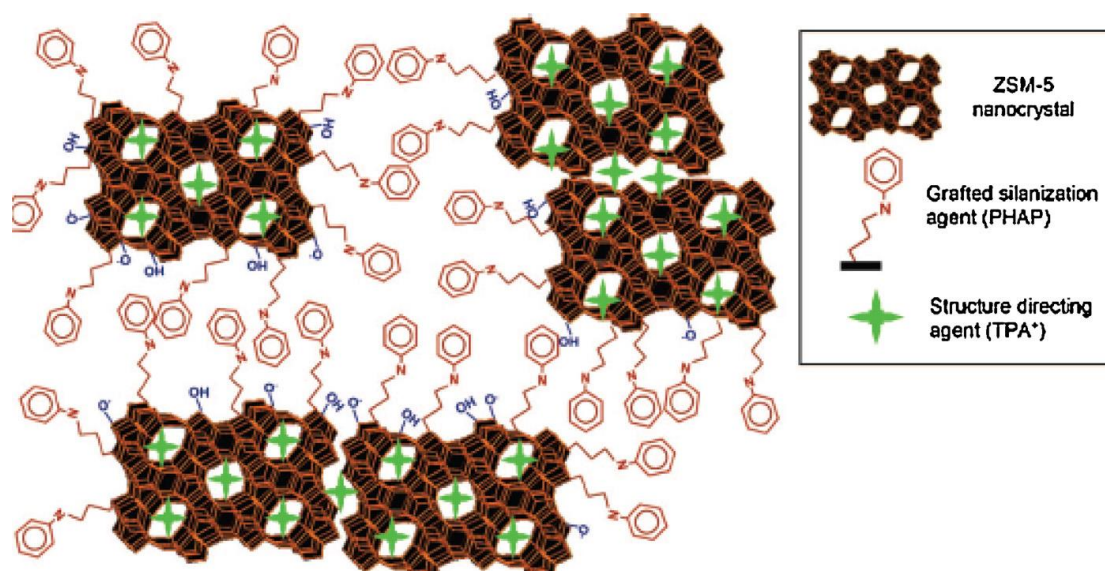


Fig. (A9.3): Sketch of crystallization of hierarchical zeolites by organosilane surface functionalization (Serrano et al., 2009; Zhang et al., 2016)

A9.4 Surfactant templating or recrystallization

In this method of top-down approach, well controlled mesoporosity can be introduced into the zeolitic structure by using cationic surfactants like CTAB (cetyltrimethylammonium bromide) or CTAC (cetyltrimethylammonium chloride) together with mild condition of synthesis (like dilute sodium hydroxide solution at low temperature for a

short time), which is recrystallization of microporous zeolites to micro/mesoporous zeolites. The preparation of hierarchical zeolite using this approach is simple which doesn't have usual flaws of desilication like damage of the zeolite crystal itself or momentous loss of silica (Feliczak-Guzik, 2018; Hartmann et al., 2016; Koohsaryan & Anbia, 2016; Li et al., 2014). Ivanova et al (2014) used this approach to study the mechanism of this process, their research shows that during desilication alkaline medium, large inter/intra-crystalline pore were formed after Silica-Oxygen-Silica bond were broken initially. CTAB molecules diffuses in these spaces, CTA cations exchanged with Sodium and micelles were formed. Lastly, the cluster of silicon species adjoining micelles result in single-phase zeolite with a bimodal porous structure as seen in Figure (A9.4).

A9.5 Zeolitization of materials & assembly of nano sized zeolites

This method of bottom-up approach involves either altering the amorphous-pore-walls of mesoporous-silica consisting materials like silicates, aluminosilicates, silica monoliths, diamite etc to zeolites, or assembling units into mesoporous-materials with nano-crystalline-pore-walls. Mesopores in hierarchical zeolites can be in 3 forms. It can be either intercrystalline or intracrystalline or both between within the crystals. Intercrystalline-mesoporous-structures in hierarchical zeolites can be attained by governing the circumstances enabling crystallization, like in Figure (A9.5). They tend to have improved properties compared to zeolites as nano sized zeolite crystals are characterized by bigger outer surface area and the occurrence of mesopores amongst nanocrystals fast-tracking the mobility of reactants and products (Feliczak-Guzik, 2018; Koohsaryan & Anbia, 2016; Li et al., 2014).

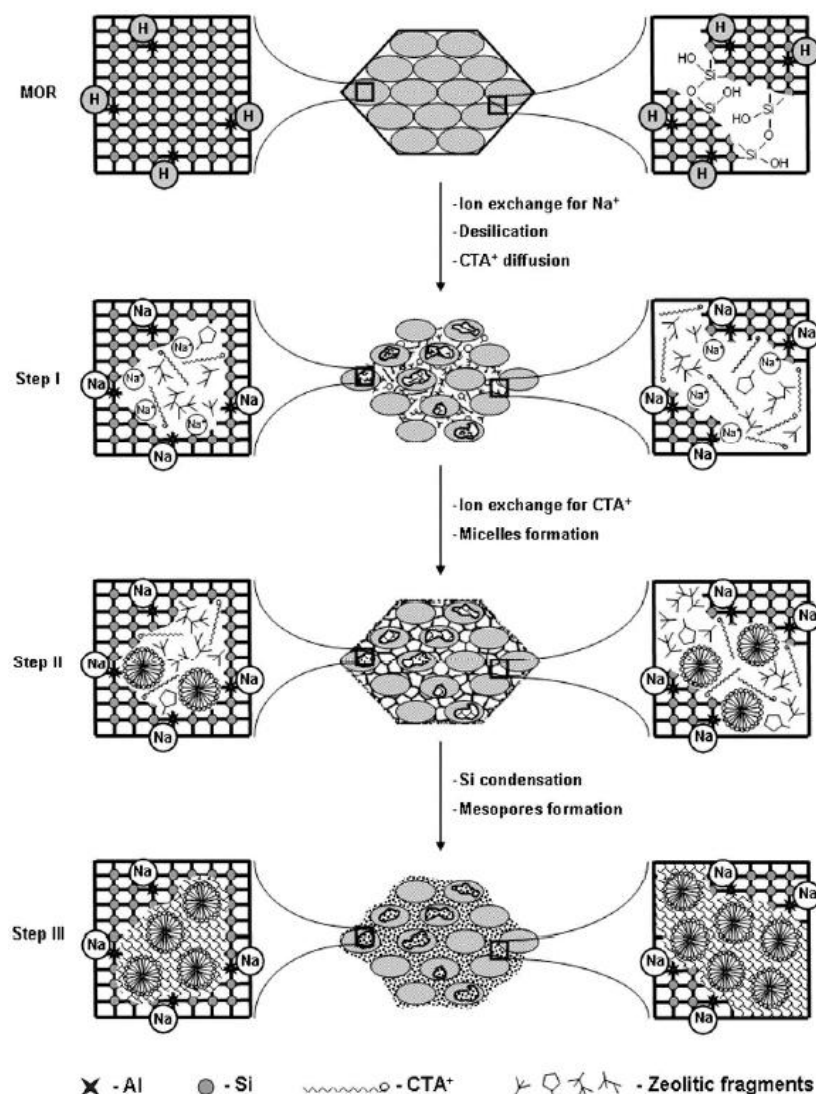


Fig. (A9.4): Mechanism of desilication/recrystallization to micro-mesoporous structure (Ivanova et al., 2014)

Study carried by Lysenko et al. (2011) and Yue et al. (2008) aided to renovate mesoporous zeolites structures with amorphous-pore-walls. Transformation of dry-gel accompanied by organic microporous SDA (structure directing agent) directed to creation of ordered-mesoporous zeolites like SBA-15 or MCM-41, exposing their walls to restricted crystallization leading to form zeolitic structure via steam assisted conversion as seen in Figure (A9.5). This technique leads to formation of intercrystalline mesopores.

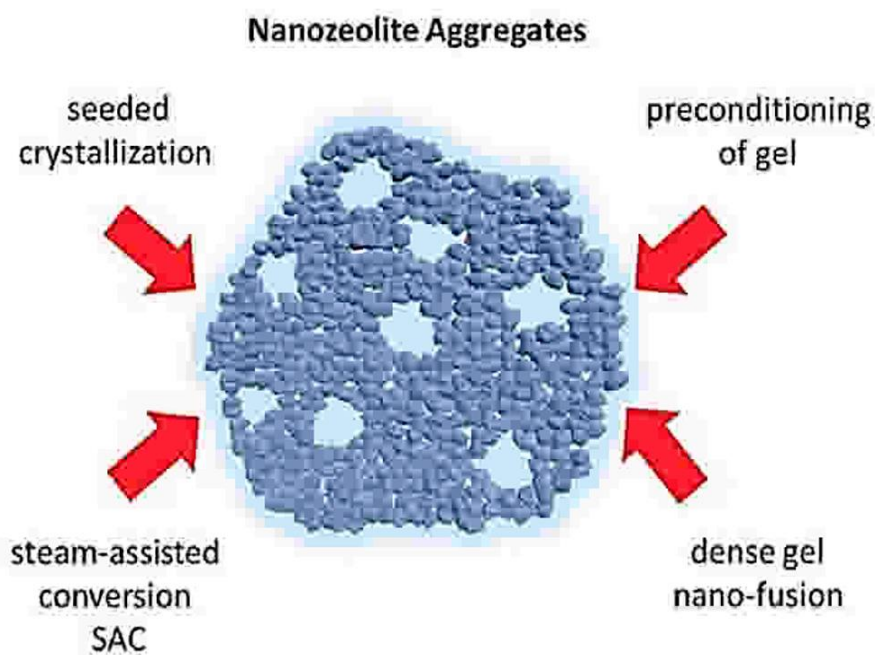


**Fig. (A9.5): Assembly of nanozeolites to form mesoporous zeolites
(Moller & Bein, 2013; Koohsaryan & Anbia, 2016)**

ملخص الدراسة

يهدف هذا المشروع إلى تكسير خليط المخلفات البلاستيكية باستخدام الهيدروجين لإنتاج وقود سائل مفيد. استُخدم في هذه الدراسة خليط من المخلفات البلاستيكية تحتوي على نسبة ٢٤,٧% من البولي إيثيلين منخفض الكثافة، و ٢٩,٨% بولي إيثيلين مرتفع الكثافة، و ١٠,٥% بولي بروبيلين، و ٣٤,٨% بولي ستيرين. يُعد هذا المشروع فريد من نوعه، إذ يتم تحسين المحفزات والعمليات المستخدمة لها بإضافة الزيوليت الهرمي المحفز إلى التفاعل لتحليل خليط البلاستيك من المخلفات، واستُخدم في عملية التحسين طريقة الاستجابة السطحية (Response Surface Methodology) مع تصميم مركب مركزي (Central Composite Design). أجريت للتجارب التمهيدية لتوفير المحفزات تحت ضغط الغرفة العادي (١ بار)، أما بالنسبة لتحسين متغيرات العمليات استُخدم نظام ضغطٍ مختلفٍ. وأُجريت التجارب التمهيدية باستخدام زيوليت سكوني موبيل ٥- الهرمي (ZSM-5) والبيتا زيوليت (Beta Zeolite). أعطى البيتّا زيوليت منزوع السيليكا المشبع بأكسيد الألومنيوم (الألومينا) (Desilicated alumina impregnated beta zeolite) أفضل النتائج فيما يخص إنتاج الوقود السائل، وقد يرجع ذلك إلى المسامية الزائدة. حقق ذلك الإجراء نجاحًا ملحوظًا، فعند استخدام ٢٠ جم من مخلفات البلاستيك المخلوطة كتغذية، أشارت النتائج إلى الحصول على ٩,٩ جم (لكل ١ جم من المحفز) من الوقود السائل عند استخدام محفز البيتّا زيوليت الهرمي المحسن الذي نزعنا منه السيليكا باستخدام ٠,١ مولار من هيدروكسيد الصوديوم عند درجة حرارة ٧٥ مئويةً وأضيف إليه ٣ جم من الألومينا لكل ٥ جم من زيوليت (٢٢% المنيوم أوكسايد لكل زيولت) عند درجة حرارة تصل إلى ٩٠ مئويةً بالمقارنة بالبيتّا زيوليت الخام الذي لم ينتج سوى ٢,١ جم من الوقود السائل. تم إجراء تلك التجارب باستخدام نسبة محفز إلى البلاستيك تبلغ ١ : ٢٠ عند درجة حرارة تصل إلى ٤٠٠ درجة مئوية. ثم استُخدم المحفز المحسن في تحسين العمليات. المتغيرات التي وقع الاختيار عليها من أجل تحسين العمليات هي درجة الحرارة (٣٦٠-٤٤٠ درجة مئوية)، الضغط (١ - ٤٠ بار)، ونسبة المحفز إلى البلاستيك (١ : ٥ - ٤٠ : ١). تشير النتائج إلى أن الضغط ونسبة المحفز إلى البلاستيك ليست لهما الدلالة الإحصائية المهمة ذاتها مقارنة بالتغيرات في درجة الحرارة التي لها دلالة إحصائية أهم. ومن نتائج هذه الدراسة، الحصول على كمية زيت تصل إلى ١١,٢٧ (لكل 1 جم من المحفز) جم في الظروف المحسنة التالية: درجة حرارة تصل إلى ٤٢٠ مئويةً، و ٢٠ ضغط جوي، ونسبة محفز إلى بلاستيك تبلغ ١ : ٣٠. وبلغت قيمة R^2 النموذجين في الدرجة الثانية لتحسين العمليات والمحفز ٩١% و ٩٥% على التوالي، مما يشير إلى التوافق مع البيانات التجريبية. تم استخدام عدد من الطرق الرياضية التفاضلية والتكاملية بناءً على بيانات التحليل الوزني الحراري (Thermogravimetric analysis) لمحفزات الزيوليت سكوني موبيل-٥ والبيتّا زيوليت الهرمي (Mesoporous beta zeolite). واتضح أن قيم طاقة التنشيط للزيوليت سكوني موبيل-٥ ١٧٠,٨٠-٩١,٦٨ كيلوجول/مول، و ٨٦,٨٠-٥١,١٠ كيلوجول/مول بالنسبة للبيتّا زيوليت، و ٦٧,٤٠-٤٤,٧٤ كيلوجول/مول للبيتّا زيوليت الهرمي، بناءً على الطرق الرياضية المستخدمة. كما اتضح أنه عند استخدام البيتّا زيوليت الهرمي تتطلب العملية طاقة تنشيط أقل بالمقارنة بالبيتّا زيوليت الخام أو الزيوليت سكوني موبيل-٥.

جامعة البحرين

قسم الهندسة الكيميائية

كلية الهندسة



تحويل النفايات البلدية البلاستيكية إلى وقود سائل باستخدام محفزات الزيوليت الهرمية: دراسات معدلات التفاعل و تحسين الإنتاجية

أطروحة مقدمة في إطار الوفاء الجزئي بمتطلبات درجة ماجستير العلوم في الهندسة الكيميائية

إعداد

فيصل ممتاز أحمد

الرقم الجامعي: ٢٠١٠١٣٦١

إشراف

د. محمد فيصل عرفان

(أستاذ مساعد)

جامعة البحرين

مملكة البحرين

يوليو ٢٠٢٠