



Chemical Engineering Department-BIHE

Simulation of Catalytic Pyrolysis of Waste Plastics Using Microwave Heating

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September 2022

***This dissertation is submitted for the fulfillment of a bachelor's
degree in chemical engineering***

Acknowledgments

Being a student of chemical engineering at BIHE has been one the most delightful and life-altering experiences for me. I want to thank all the members of the chemical engineering department. I have special thanks to my supervisor, Dr. Sohrab Rohani, for his kind generosity in teaching and his state of excellence. I also want to thank Dr. Saad who helped me a lot with the simulation studies carried out in this thesis. And last but not the least, I want to thank my dear family and friends whose love was heart-warming and motivating.

Abstract

The pyrolysis process is a promising method to convert waste plastics into valuable products. The catalytic process is of great importance since it operates under mild temperatures and gives a narrow range of products compared to thermal pyrolysis. Microwave heating is a rapid and volumetric heating method that can be a candidate to supply heat for pyrolysis reaction by employing microwave receptor material as the wall of the reactor. Catalysts play a crucial role in catalytic pyrolysis. HZSM-5 is an excellent catalyst for plastic pyrolysis since it favors light olefinic products as a result of its high acidity and small pore size distribution which also hinders the production of coke which is an unwanted product. Mass fraction and the size of catalyst are important areas to conduct research, as well as the velocity of carrier gas of the reaction bed. In this thesis, a microwave reactor is simulated in COMSOL, the reaction pathway and kinetics are discussed by the help of MATLAB software to solve differential equations of kinetic equations. The pyrolysis reaction is simulated in COMSOL and effects of the mass & particle size of the catalyst as well as the inlet velocity of carrier gas are investigated and discussed.

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Nomenclature

Symbols:

ϵ^* : Complex Permittivity

ϵ' : Real Part of Complex Permittivity

ϵ'' : Real Part of Complex Permittivity

$\tan(\delta)$: Loss Tangent

μ^* : Complex Permeability

μ' : Real Part of Complex Permeability

μ'' : Real Part of Complex Permeability

$\tan(\delta_\mu)$: Magnetic Loss Tangent

σ : Electrical Conductivity-S/m

C_n: n Number of Carbon Element of Olefins or Paraffins

V: Volume- m³

D: Diameter-m

L: Length-m

A: Plastic Mixture

I: Intermediate

O: Olefins

P: Paraffins

BTX: Aromatics Including Benzene, Toluene & Xylene

C: Coke

k: Rate Constant-1/min

C(i): Concentration of Species i-mol/m³

ϵ : Porosity of Catalytic Bed

ρ : Density-kg/m³

W: Mass of Catalyst-g

κ : Permeability Catalytic Bed- m^2

D_p : Catalyst Particle Diameter-m

S_e : Reactive Surface Area of Catalytic Bed- $1/\text{m}$

ε_{mf} : The Porosity at Minimum Fluidization

ψ : Sphericity

u_{mf} : Minimum Fluidization velocity-m/s

u_t : Terminal Velocity-m/s

μ : Viscosity- $\text{kg}/(\text{m}\cdot\text{s})$

C_{A_In} : Inlet Concentration of Plastic Mixture- mol/m^3

U : Inlet Velocity of Fluidizing Gas-m/s

Abbreviations:

PDF: Probability Distribution Function

SiC: Silicon Carbide

TE: Transverse Electric

TM: Transverse Magnetic

TEM: Transverse Electromagnetic

LDPE: Low-Density Polyethylene

HDPE: High-Density Polyethylene

PP: Polypropylene

PS: Polystyrene

PMMA: Poly (methyl methacrylate)

FCC: Fluid Catalytic Cracking Used in Refinery

Chapter 1

Introduction & Background

1.1 Uses, Production, and Waste Generation of Plastic Products

Plastics are widely used in the present modern time. Plastics play an important role in the enhancement of welfare in human societies. Plastics are used in different sectors including packaging, building & construction, automotive, electrical & electronic, household, agriculture, and others. Among which packaging has the most share of consumption compared to other sectors. In Europe, the percent distribution of consumption of plastics in different sectors was as depicted in the following figure in 2019.

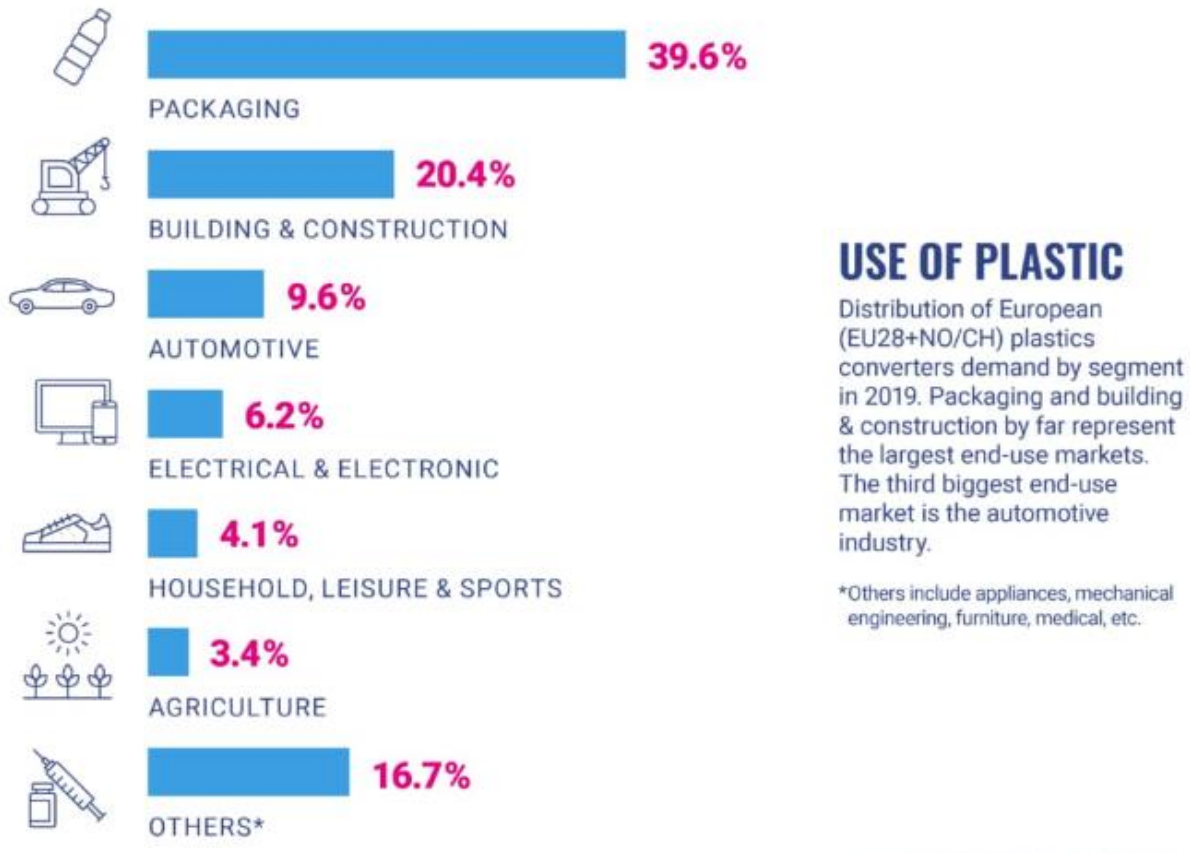


Figure 1.1: The Use of Plastic Materials in Different Sectors. [1]

Based on a study in 2015, 6300 Mt of plastics had been generated. Which makes plastics one of the most man-made materials. [2]

Despite the undeniable role of plastics in human activities, these materials are relatively new in genesis. The production of plastics was not initiated before 1950 and the use of plastics outside the military was not commercialized before the end of World War II. The annual production of plastics from 1950 to 2020 is depicted in the following figure.

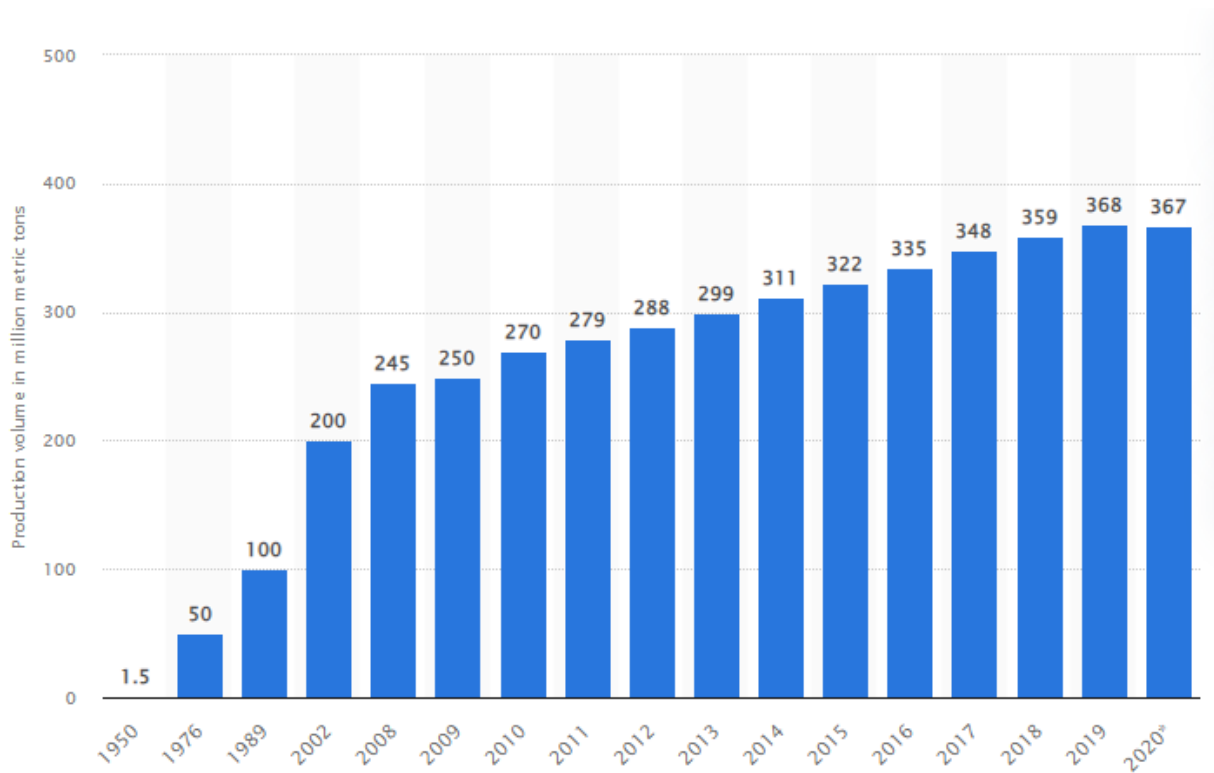


Figure 1.2: The Annual Production of Plastics (million metric tons) From 1950 to 2020. [3]

The production of plastics is inevitably followed by waste generation. Plastics manufactured for packaging usually have a short life cycle and are used one-time only. The log-normal of probability distribution function (PDF) of plastics plotted against life cycle is as below. [2]

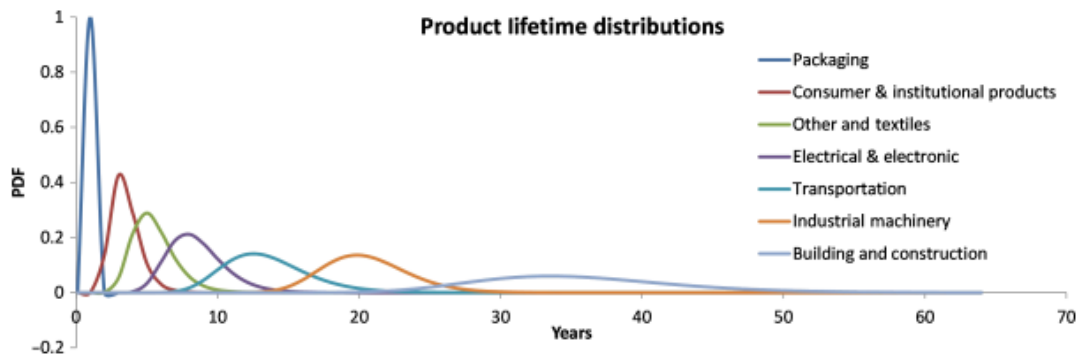


Figure 1.3: PDF vs. Life Cycle of Different Plastic Products Sectors.

The above figure also indicates that plastics for the packaging sector have the shortest life cycle compared to the plastics used in other sectors. With all this information, one can conclude a huge amount of waste plastics generated annually. Most commonly used plastics are not biodegradable; hence these materials remain on the land for decades. [2]

The following figure indicates the total annual waste of plastics and also per capita in 10 countries in millions of metric tons and kg/year, respectively, in 2016. [1]

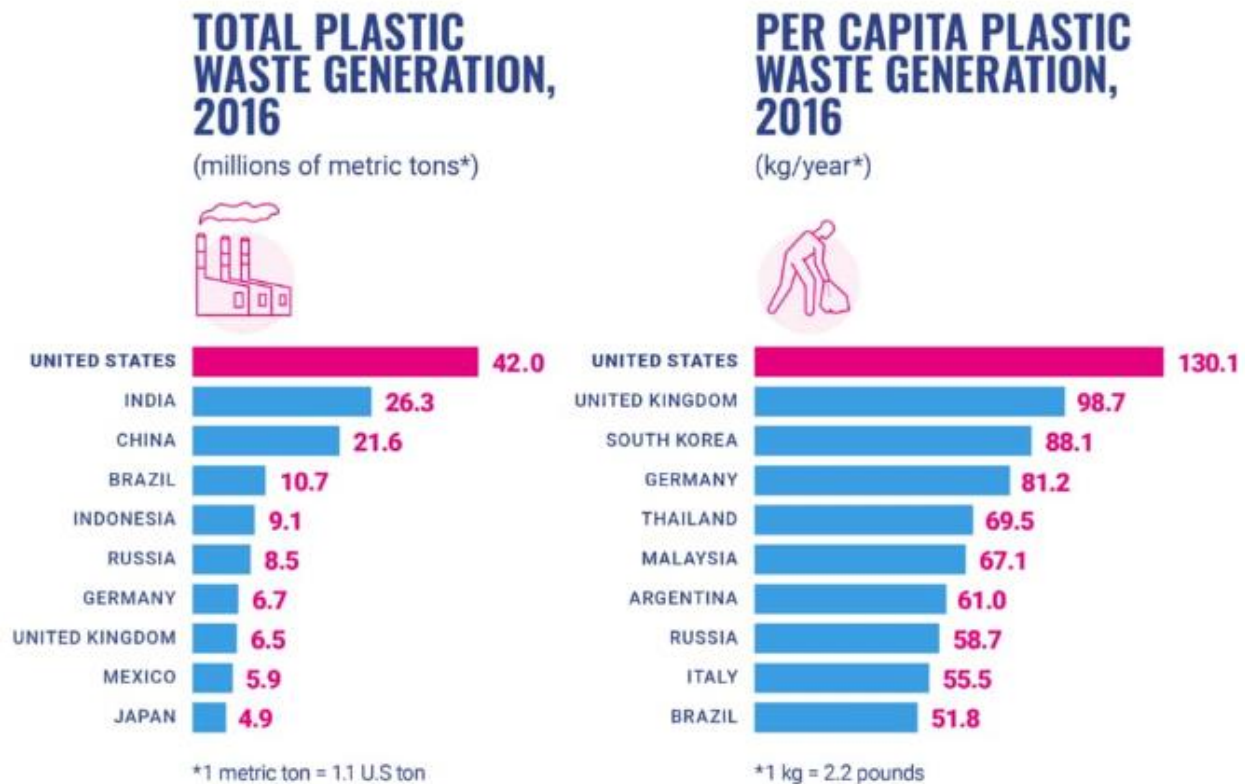


Figure 1.4: Total and Per Capita Waste Plastic Generated in 10 Countries in 2016

In conclusion, the amount of waste plastics generated annually in the whole world is considerable and may lead to challenges in waste management which makes recycling of plastics an important and promising field of research.

1.2 Waste Plastic Management

There are some methods to manage waste plastics such as landfilling, incineration, and recycling (mechanical or chemical). Landfilling is the most widely used method for waste plastic management. Due to the low biodegradability of plastics which was mentioned before, landfill is not the best choice since land depletion is inevitable. Incineration is an attractive solution for waste plastic management since plastics have a high calorific value, 40-48 MJ/kg [4,5]. And their incineration will result in energy recovery and electricity production. However, incineration results in the emission of toxic gases such as dioxane and furan, and carbon dioxide which threaten the health of humans and animals and contribute to global warming. [6,7].

Mechanical recycling is proceeded via melting and molding the thermoplastics. The drawbacks of this method are that plastic mixtures cannot be employed, high operating costs, low-quality products and low profitability. [8]

Chemical recycling which is also known as feedstock recycling and tertiary recycling breaks down polymers into monomers or other chemicals. Solvolysis is a chemical method for recycling plastics but polyolefins such as polyethylene

and polypropylene are known as addition polymers which cannot be treated by solvolysis for decomposition purposes. [9]

Gasification is a process in which feedstock is partially oxidized and syngas which consists of hydrogen and carbon monoxide (H_2+CO) are produced. Syngas may be used as fuel directly or undergo a Fischer-Tropsch reaction to yield hydrocarbon fuels or chemicals. [8]

Pyrolysis is conducted by heating the feedstock in the absence of oxygen. [10] Pyrolysis is used for fuel production from biomass. Plastics are also a possible feedstock for the pyrolysis process. Pyrolysis of plastics may be conducted without a catalyst (thermal pyrolysis) as well as in the presence of a catalyst (catalytic pyrolysis). [8] Pyrolysis of plastics is of special interest to this thesis and will be discussed in detail in the form of a literature review and simulation of a pyrolysis process.

As was mentioned earlier, plastic wastes are mostly landfilled rather than incinerated or recycled. By 2015, 9% of total waste plastics generated were recycled, 12% were incinerated and 79% were landfilled. [2]

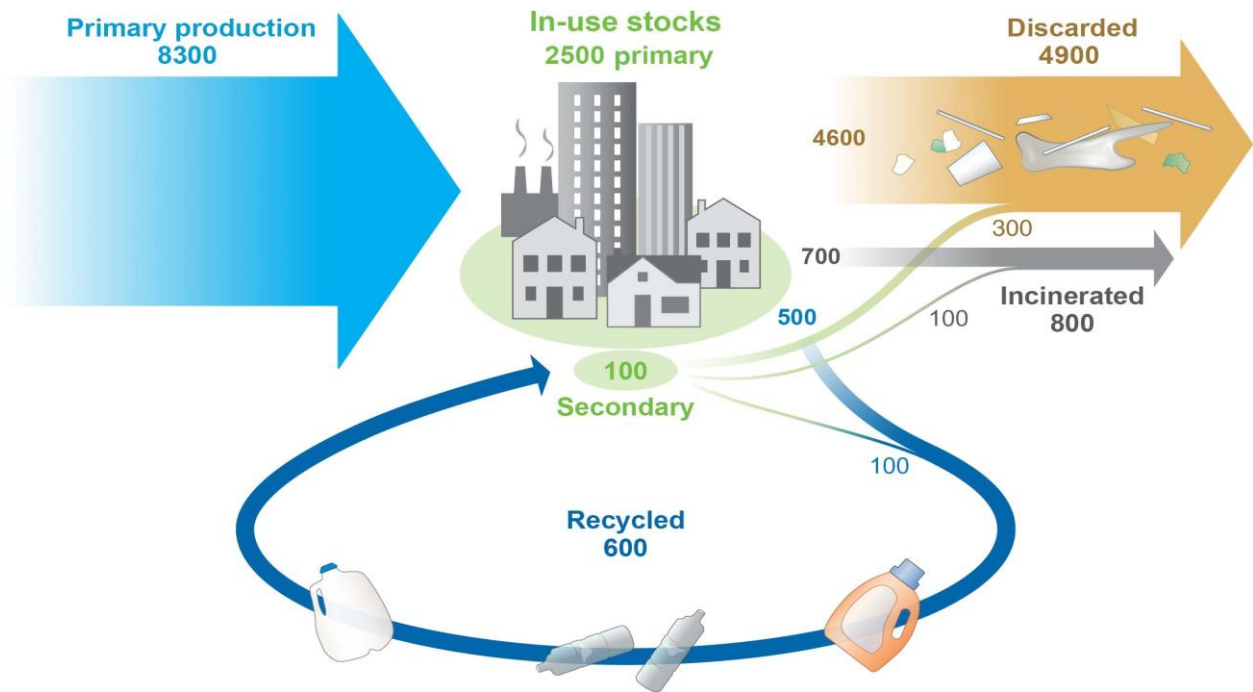


Figure 1.5: Production, Use and Waste Management of Plastics.

Cumulative plastics waste generation in million metric tons from 1950-2015 with a projection of future prediction is illustrated in the following figure:

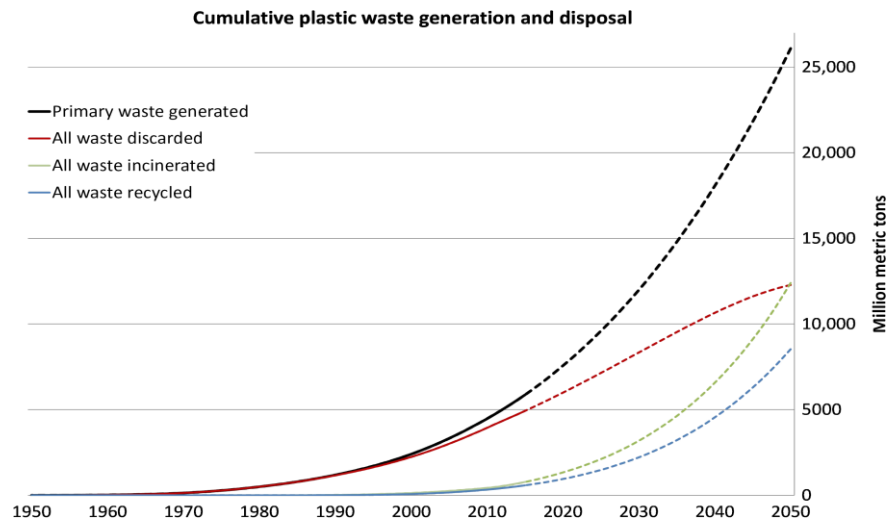


Figure 1.6: Cumulative Plastic Waste Generation and Disposal.

The above figure also indicates the larger share of landfilling in the fate of waste plastics generated. One may conclude that feedstock recycling is an interesting and promising topic to conduct research on to overcome the problems associated with the waste plastic generation and to avoid the land depletion and emission of toxic gasses caused by landfilling and incineration, respectively.

1.3 Oil, Gas & Coal Depletion

The source of monomers which are the raw materials of the polymerization process is fossil hydrocarbons which are limited in nature and inevitably will be depleted and consumed almost fully. The below figure predicts the end life of coal, gas and oil. [11]

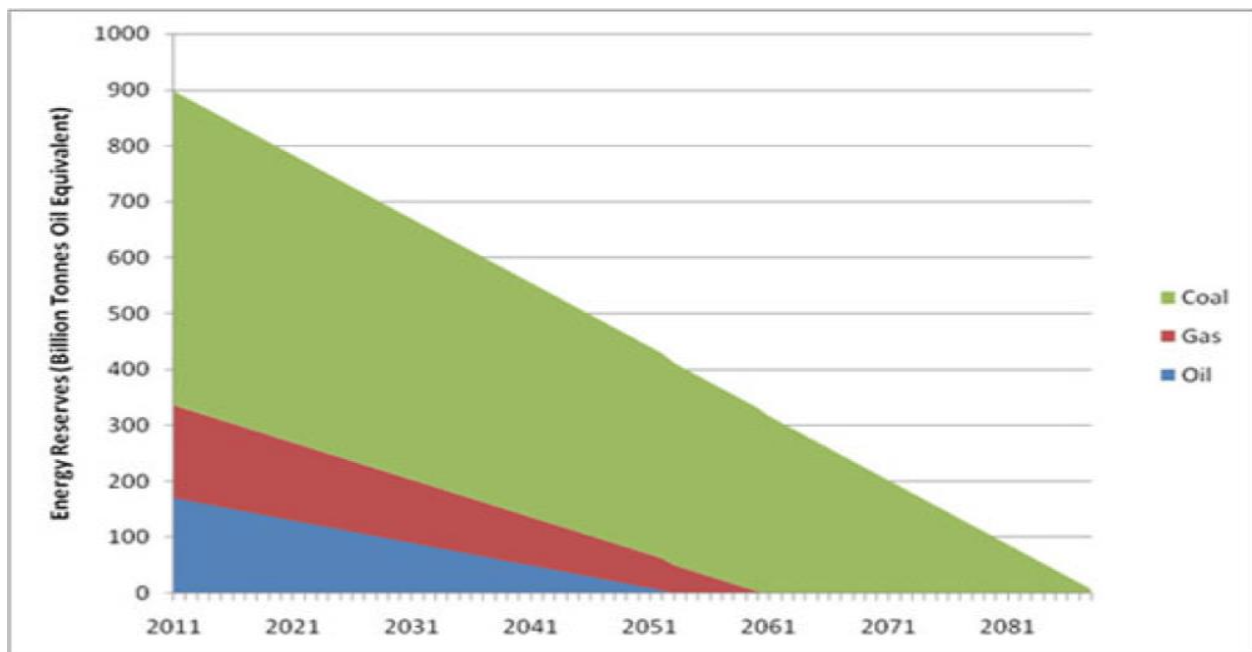


Figure 1.7: The Prediction of the Time of Full Consumption of Coal, Gas and Oil

The importance of plastics in today's modern society was indicated earlier and a world without them is unimaginable. Since the source of these materials is being depleted rapidly, recycling waste plastics to obtain monomers sounds promising and necessary. In the following sections, a scheme is proposed for "Renewable Carbon".

1.4 Microwave Heating

As mentioned earlier, pyrolysis involves heating the feedstock. Microwave heating may be a candidate for the heating source of the plastic pyrolysis process. Since the 1980s microwave reactors have attracted attention as an interesting heating method due to the advantages of microwave heating compared to conventional heating. Microwave heating is a selective and volumetric method which means materials with special electric and magnetic properties heat up and heating occurs within the material itself. Microwave heating usually offers a reduction in reaction time. In microwave heating, microwave irradiation is used to heat the target material. Electromagnetic irradiation of microwave reactors is between 300 MHz and 300 GHz. However, irradiations with the frequency of 915 MHz, 2.45 GHz, and 5.85 GHz are used frequently for chemical processes to avoid any interference with irradiations associated with communication and broadcast. [12]. Different aspects of microwave heating will be discussed in more detail in Chapter 2.

Advantages of microwave heating:

- 1) Volumetric heating makes it an efficient heating method compared to conventional heating methods which are conductive or convective heating (surface heating). [19,20]
- 2) Reaching high temperatures in a short time. [21]

Disadvantages of microwave heating:

- 1) Although selective heating is an advantage in many cases, in plastic pyrolysis a third material must be introduced to the reaction chamber since plastics are transparent to microwave irradiation and do not warm up by microwave irradiation directly.
- 2) More complex apparatus which makes it more expensive than the conventional heating apparatuses. [8]

1.5 Thesis objectives

- 1) Different microwave heating phenomena are discussed and a suitable microwave receptor material for plastic pyrolysis is selected. Also, microwaves used for the different processes are reviewed.
- 2) A literature review of thermal and catalytic pyrolysis of plastics is conducted.
- 3) Microwave heating is simulated using COMSOL.
- 4) A reaction of catalytic plastic pyrolysis with associated kinetics is selected and kinetic equations are solved using MATLAB, the reaction progress is illustrated with respect to time, and results are discussed.
- 5) The same catalytic process mentioned is simulated in COMSOL and the effects of mass & size of catalyst and velocity of carrier gas are investigated and discussed.

Chapter 2

Microwave Heating Phenomena & Applications

2.1 Microwave Irradiation

As stated, the frequency of microwave irradiation is between radio and infrared frequencies. With the wavelength of 1m to 1mm in a vacuum. With the frequency of 2.45 GHz of having a wavelength of 12.25 cm in the vacuum which is the typical frequency of microwaves used in households and industries. [12].

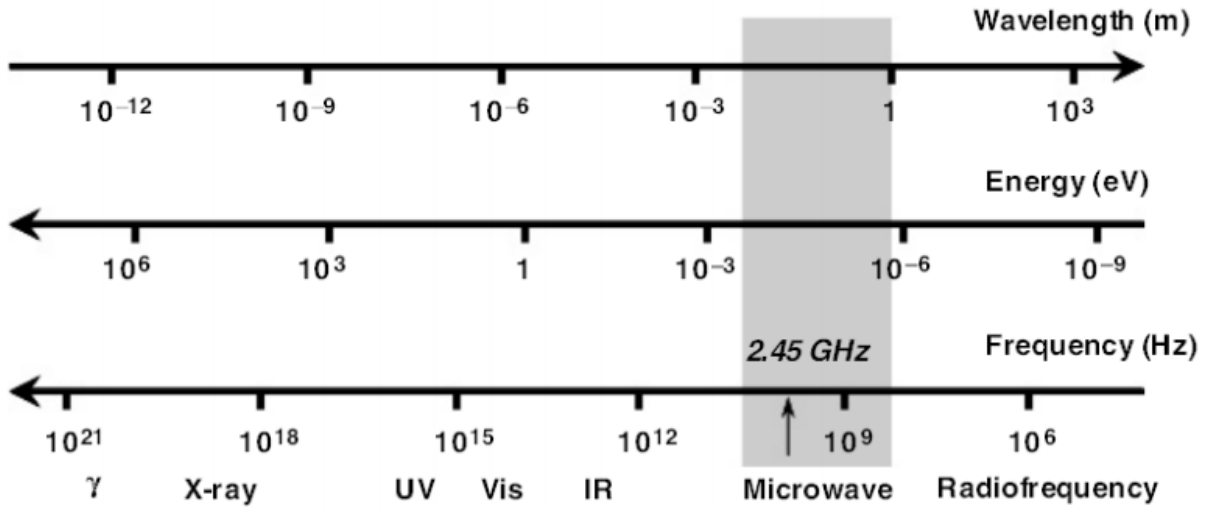


Figure 2.1: The Electromagnetic Spectrum with Microwave Highlighted. [13].

The energy of microwave irradiation is too low to break chemical bonds and cause the chemical reaction to proceed [13]. In the following section reactor heating mechanism by microwave energy is discussed.

2.2 Microwave Heating Phenomena

Gases do not heat up by microwave irradiation, liquids that are ionic or have dipole moments are good microwave receptors and when they are placed in an external alternating electrical field, the movement and translation of dipoles and ions which have a tendency of alignment with the external field, causes friction and loss of energy in the form of heat [12].

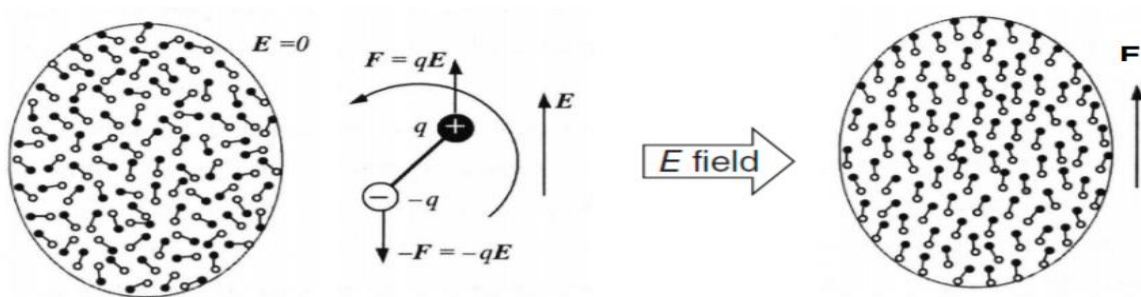


Figure 2.2: External Electrical Field Effect on the Dipoles of A Polar Substance. [12].

Solid materials are divided into 4 groups based on their interaction with microwave irradiation characteristics.

- 1) Perfect conductors: reflecting microwaves from the surface. Examples are metals and graphite.
- 2) Insulators: transparent to microwave irradiation which cause them unable to be heated by microwaves. Examples are plastics such as polyethylene.
- 3) Dielectric lossy materials: absorb microwave irradiation and get heated. An example is silicon carbide (SiC).
- 4) Magnetic lossy materials: magnetic loss happens due to realignment of magnetic materials with respect to altering the magnetic field of microwave generator (magnetron) [12].

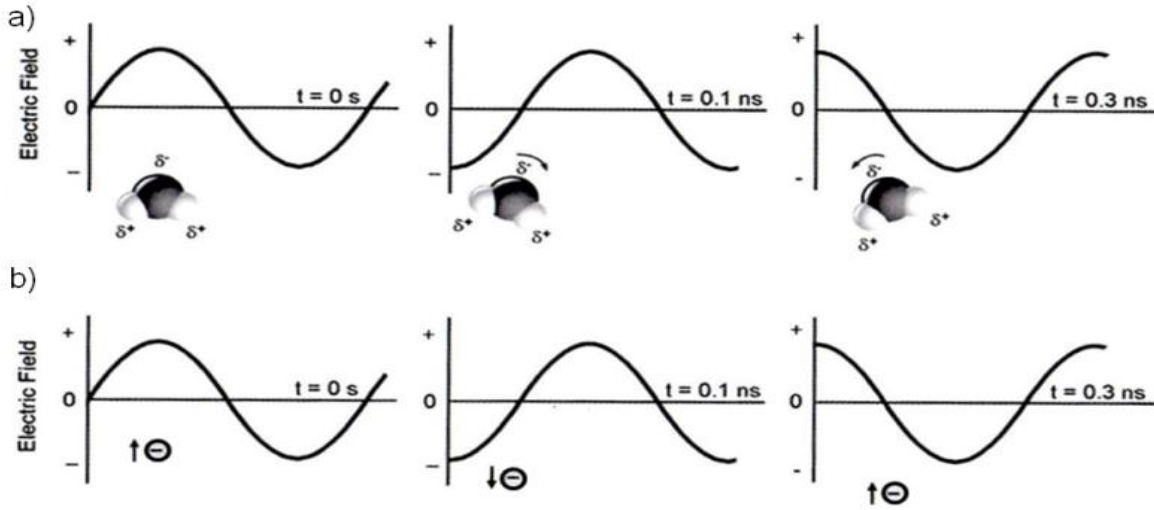


Figure 2.3: Realignment of Ions and Dipoles While Being Held in Microwave Cavity. [13]

Perfect conductors like metals heat up when placed in the microwave. Alternating electrical field results in a larger current density near the surface and the flow of current causes heating. The density of current decreases with increasing depth which is called the skin effect [12].

Dielectric lossy materials heat up when placed in the microwave by storing the electrical energy by dipoles and subsequent energy loss in the form of heat as resistance to the movement of dipoles with respect to the exerted electrical field. In this case, complex permittivity is introduced.

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

Where ε' represents the ability to store electrical energy by dipoles and ε'' represents the ability of molecules to release the stored energy as heat. Hence, a loss factor is introduced.

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

The higher the loss factor, the more readily the material is heated by microwave.

Magnetic lossy materials which consist of a magnetic dipole, heat up in microwaves similarly to the dielectric lossy material with the difference that an external alternating magnetic field interacts with materials instead of the electrical field. Magnetic energy is stored within the materials and energy loss in the form of heat due to the resistance to the movement of magnetic dipoles in the realignment process. In this case, complex permeability is introduced.

$$\mu^* = \mu' - j\mu''$$

Where μ' represents the ability to store magnetic energy within the material and μ'' represents the amount of energy that can be released as heat. Hence magnetic loss tangent is introduced.

$$\tan \delta_{\mu} = \frac{\mu''}{\mu'}$$

The higher the magnetic loss tangent, the more readily the material is heated by microwave.[12]

2.3 Penetration Depth

A key factor to be considered in microwave heating is penetration depth, which is the depth where the power of the microwave reduces to 37% of initial power. This depth is high for transparent materials and lower for microwave receptors. Penetration depth is a function of temperature and frequency. [12,13].

2.4 Specific Vs. Thermal Effects of Microwaves

The reason of advantages of microwave heating compared to conventional heating have been the subject of controversy. Some researchers believe microwaves heat up the reaction species to a high bulk temperature in a short period of time while under pressure and cause the reaction to proceed at high speed. However other groups believe there are specific effects associated with microwaves other than thermal effects which offer direct interaction of microwave irradiation with molecules. For example, stabilizing the polar transition state of reaction due to the presence of an electrical field generated by a microwave generator. To investigate which group is right, Obermayer and his research team stated that silicon carbide which is an excellent microwave receptor absorbs the radiation and heats up, and makes a shield against radiation reaching the reaction solution. In a reaction run, this research group used silicon carbide as a reaction vessel and in another run, a Pyrex vessel which is transparent to the microwave irradiation, and reaction species were in direct contact with microwave irradiation. All operating conditions such as temperature and residence time were identical in order for results to be comparable. The results were nearly identical suggesting that specific or non-thermal effects are not associated with microwave heating. [13,14]

2.5 Modes of Microwave

Single mode microwaves have a single microwave generator at the excitation point. Multi-mode microwaves have multiple microwave generators at the excitation point. The reaction volume of single-mode microwaves is limited, to a maximum of 200 mL [12].

2.6 Mode type of reactors

Based on the direction of the magnetic and electric field in the x-y-z plane, transverse electric (TE), transverse magnetic (TM), and transverse electromagnetic (TEM) modes are known. In TE, the electric field in the z-direction is zero. In TM magnetic field in the z-direction is zero and in TEM both magnetic and electric fields are zero in the z-direction. [16]

2.7 Microwave Heating

As stated before, the interest of this thesis is to research about pyrolysis of plastics using microwave heating. Since plastics are not microwave receptors, a third material that can be heated up by microwave must be introduced. Silicon carbide is an excellent dielectric lossy material which its loss factor dependence on temperature is negligible. With assumed complex permittivity of [15]:

$$\varepsilon^* = 20.08 - j * 1.5 \quad j = \sqrt{-1}$$

And conductivity of:

$$\sigma = 0.16 \frac{S}{m}$$

2.8 Applications of Microwave Heating

Microwaves have been used for organic synthesis as well as pyrolysis of different feedstocks. A brief review is presented here.

2.8.1 Pyrolysis of Tires

Yatsun et al. [17] pyrolyzed tires in a microwave and investigated the composition of the gaseous products.

Table 2.1: Composition of the Gaseous Product of Microwave Pyrolysis of Tires by Yatsun et al. [17]

Composition of pyrolysis gas

Component	Amount of component (vol. %) in samples			
	1	2	3	4
<i>n</i> -C ₅ H ₁₂	1.32	0.85	0.17	0.06
<i>i</i> -C ₅ H ₁₂	3.68	2.87	0.53	0.23
<i>cis</i> -C ₄ H ₈	0.09	0.04	0.02	0.01
<i>trans</i> -C ₄ H ₈	0.43	0.29	0.08	0.03
<i>n</i> -C ₄ H ₁₀	0.72	0.34	0.12	0.04
<i>i</i> -C ₄ H ₁₀	3.83	3.51	0.89	0.41
C ₃ H ₈	1.43	1.3	0.48	0.26
C ₃ H ₆	4.27	3.18	1.1	0.61
H ₂ S	0.44	0.37	–	–
C ₂ H ₆	4.2	3.45	1.62	1.65
CO ₂	9.85	9.16	4.54	3.72
CH ₄	17.42	13.03	6.71	5.89
H ₂	48.3	56.87	68.03	73.66
CO	1.86	1.69	0.66	0.38

2.8.2 Pyrolysis of Engine Oil

Lam et al. [18,19,20]. conducted the pyrolysis of fresh and waste engine oil in microwave and investigated the effect of temperature.

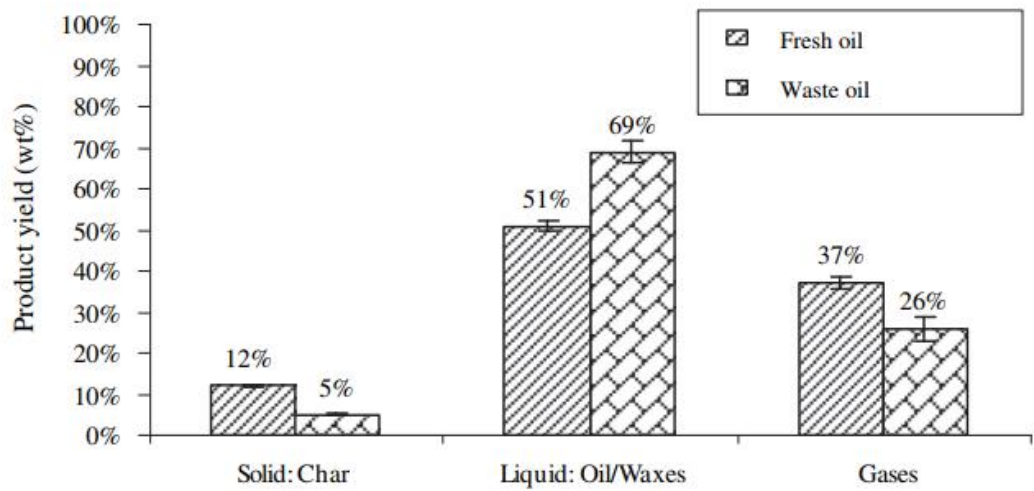


Figure 2.4: Product Yield of Pyrolysis of Engine Oil by Lam et al. [18,19,20].

2.8.3 Pyrolysis of Waste Plastic

Ludlow-Palafox and Chase [21] pyrolyzed high-density polyethylene (HDPE) in a microwave reactor with carbon as a microwave receptor. The scheme of the reactor they used is as below:

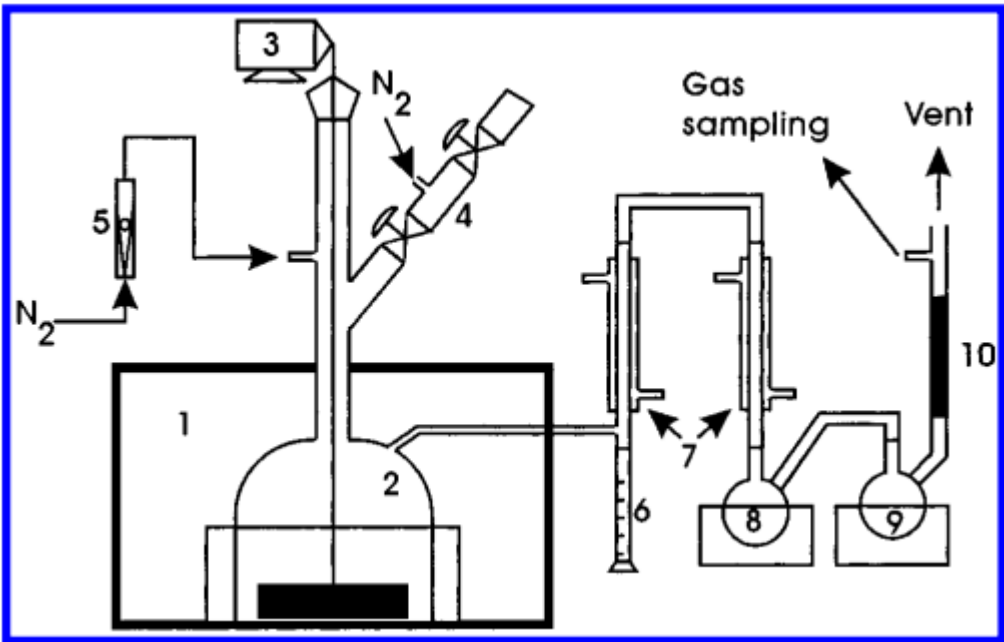


Figure 2.4: Product Yield of Pyrolysis of Engine Oil by Lam et al. [18,19,20].

At 500 °C, the yield of gaseous, oil/wax, and solid yield was 19, 81 and 0, respectively and at

600 °C was 20.9, 79.1 and 0, respectively. [21]

Russel et al. [22] pyrolyzed HDPE in the microwave using activated carbon and coke in a temperature range 400-600 °C. The results obtained are as below:

Table 2.2: % Yields of the Product of Microwave-Assisted Pyrolysis of HDPE on Activated Carbon and Coke by Russel et al. [22]

	Activated Carbon					Coke				
Pyrolysis Temperature	400 °C ^a	450 °C	500 °C	550 °C	600 °C	400 °C ^a	450 °C	500 °C	550 °C	600 °C
Carbons:										
1	2.8%	2.9%	3.1%	5.3%	6.8%	4.6%	3.6%	6.1%	4.5%	5.8%
2	28.8%	27.2%	30.9%	37.6%	40.5%	46.1%	39.9%	42.3%	45.6%	54.0%
3	55.2%	59.0%	55.9%	49.6%	49.0%	45.1%	49.6%	43.3%	36.4%	31.5%
4	13.3%	9.4%	9.2%	4.8%	3.8%	4.3%	6.9%	8.3%	13.5%	8.6%
5		1.6%	1.0%	2.7%						
Of which:										
n-Alkane	85.0%	69.7%	67.8%	62.7%	56.9%	57.9%	51.6%	55.5%	62.4%	66.9%
n-Alkene	15.0%	26.3%	28.4%	32.8%	39.6%	40.7%	41.5%	38.8%	33.5%	27.8%
iso-Alkene		2.4%	2.9%	1.8%	1.6%		4.3%	2.5%	2.5%	4.0%
iso-Alkane		1.6%	1.0%	2.6%	1.9%	1.4%	2.6%	3.2%	1.6%	1.2%

It is observed that by increasing the temperature, the product distribution favors lighter hydrocarbons. [22]

Zhang et al. [24] pyrolyzed LDPE in a microwave reactor using activated carbon as a catalyst to obtain jet fuel as the major product. Seven different activated carbon samples were used (6 commercial and 1 homemade).

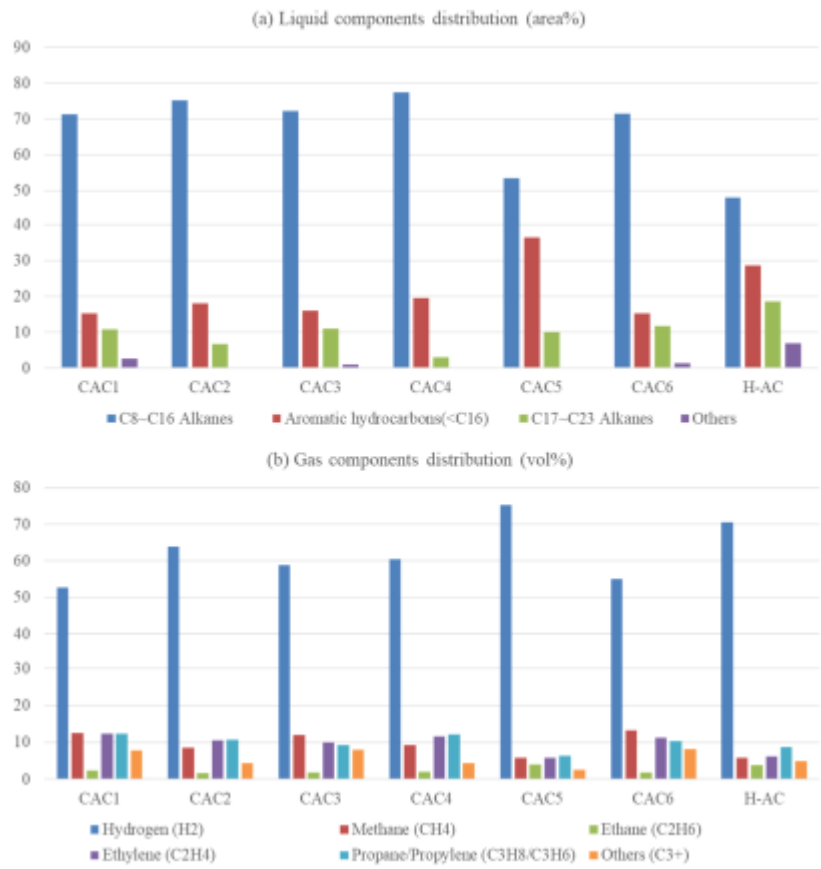


Figure 2.6: Liquid and Gas Product of Microwave-Assisted Pyrolysis of LDPE With 7 activated carbons by Zhang et al. [24]

It was observed that the main product in the liquid phase was C8-C16 hydrocarbon in all runs. [24]

Zhang et al. [23] pyrolyzed LDPE in a microwave reactor and passed the products obtained through a heated jacket filled with ZSM-5 catalyst. The scheme of the experimental set-up of this research group is as below:

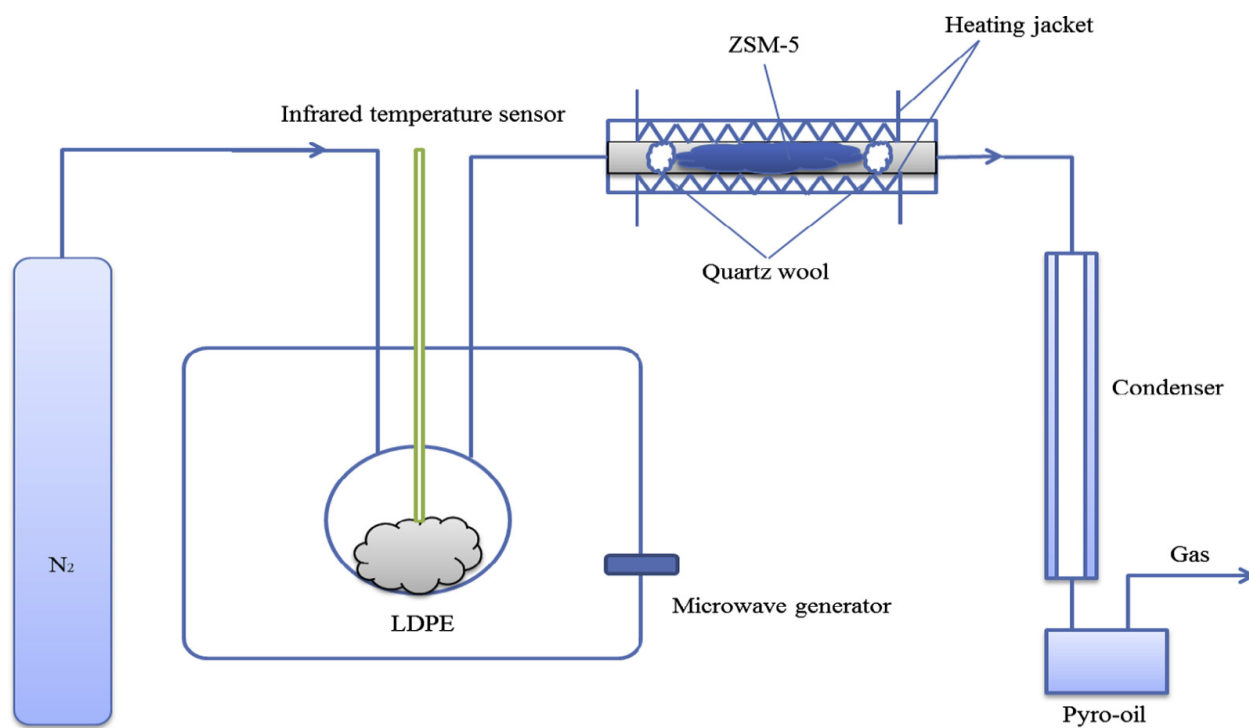


Figure 2.7: Scheme of Microwave-Assisted Pyrolysis Conducted by Zhang et al. [23]

The effect of temperature and comparison of pure thermal pyrolysis and catalytic pyrolysis with reactant to catalyst ratio of 3 is investigated by Zhang et al. [23] as below:

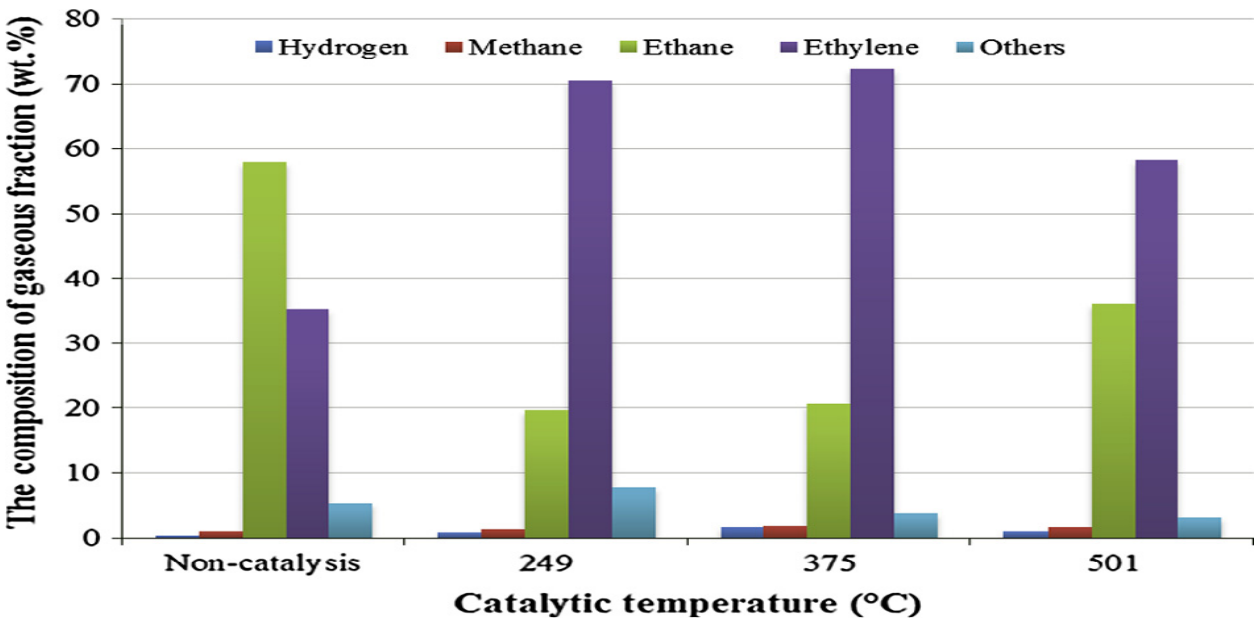


Figure 2.8: Composition Analysis in Zhang et al. Work. [23]

Chapter 3

Thermal and Catalytic Pyrolysis of Plastics: Mechanism and Literature Review

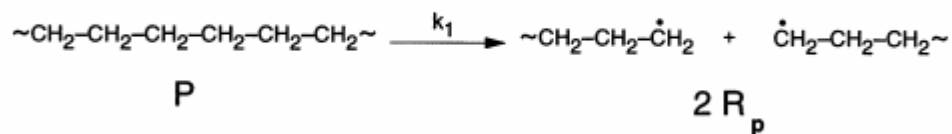
3.1 Pyrolysis of Commonly Used Plastics.

Different plastics undergo different reaction mechanisms in the pyrolysis process. When polystyrene, PS, and Poly (methyl methacrylate), PMMA, undergo the thermal pyrolysis process, a high yield of their monomers is obtained. However, the mechanism of thermal pyrolysis of polyolefins is known as thermal scission which gives waxes and oils, gaseous products, and solid residue with a broad range of carbon numbers. Low and high-density polyethylene and polypropylene are examples of polyolefins. [25]

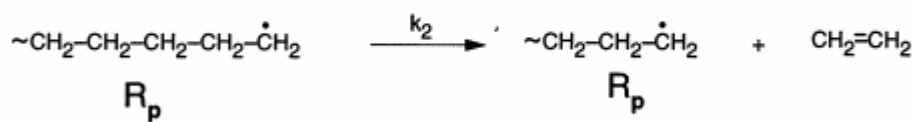
3.2 Random Scission mechanism

This mechanism consists of the initiation step, propagation, β -scission, intra- and inter-molecular hydrogen transfer, and termination. [26]

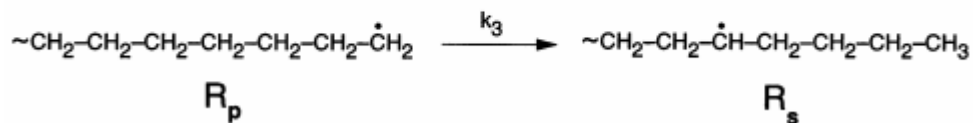
initiation:

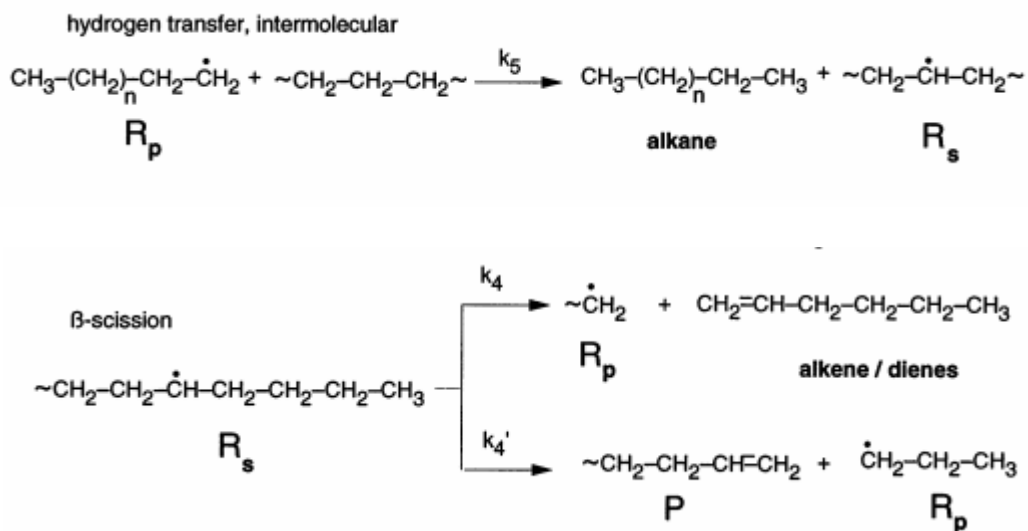


propagation:



hydrogen transfer, intramolecular





At high temperatures up to 650 °C and moderate residence time, secondary reactions may follow scission reactions and result in an increase in high aromatic yield [25].

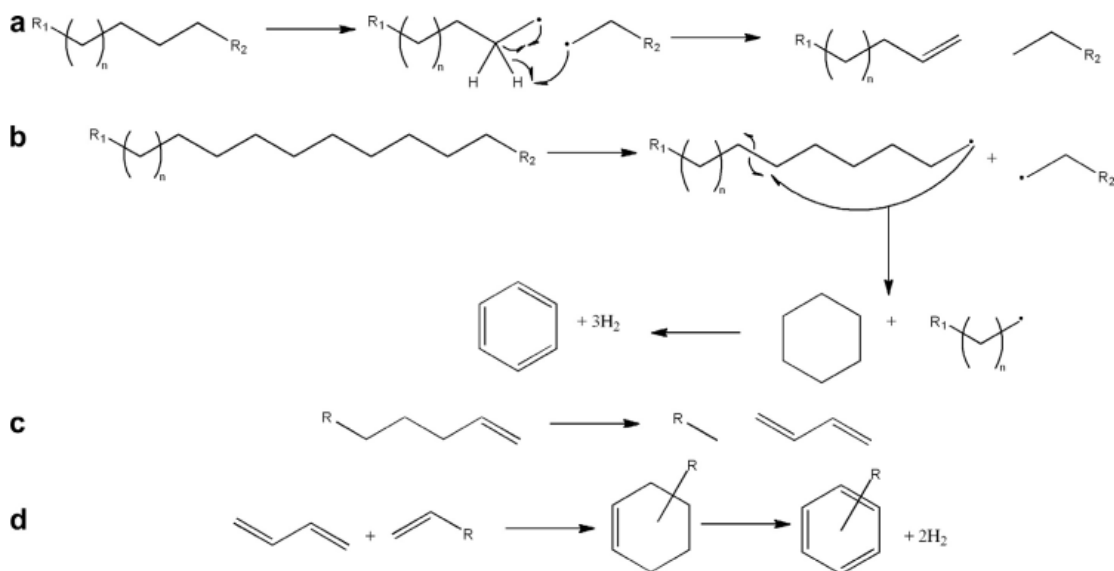


Figure 3.1: "(a) alkane and alkene formation; (b) cyclo-alkane and aromatic formation; (c) diene formation; and (d) aromatics formation through Diels–Alder reaction." [27].

3.3 Thermal Pyrolysis Review

Mastral et al. [28] pyrolyzed and gasified HDPE in a continuous fluidized bed and investigated temperature and residence time effect. The product yield of their experiment is as below:

Table 3.1: Product Yield of Pyrolysis and Gasification of HDPE Done by Mastral et al. [28]

Product yields (wt.% of feed) for pyrolysis and gasification of HDPE											
Temperature (°C)	640		680		730		780		850		
Process	Pyrolysis	Gasification	Pyrolysis	Gasification	Pyrolysis	Gasification	Pyrolysis	Gasification	Pyrolysis	Gasification	
H ₂	0.09	0.23	0.60	0.80	0.60	1.41	0.60	1.30	1.50	2.30	
O ₂	0.00	3.40	0.00	1.00	0.00	0.60	0.00	0.50	0.00	0.90	
CO	0.00	6.65	0.00	11.00	0.00	14.60	0.00	16.00	0.00	20.00	
CO ₂	0.00	11.10	0.00	14.30	0.00	11.30	0.00	7.00	0.00	6.70	
CH ₄	2.20	2.91	4.80	5.60	7.80	6.40	9.70	9.40	15.30	14.70	
C ₂ H ₄	7.60	13.25	17.00	20.00	25.30	24.60	37.00	32.00	40.50	34.10	
C ₂ H ₆	2.10	1.67	3.40	3.10	4.80	3.10	3.80	2.70	2.50	2.30	
C ₃	8.00	8.84	17.40	13.20	23.70	17.50	20.00	11.80	5.40	3.20	
C ₄	9.50	9.00	17.00	12.00	17.00	13.90	13.00	7.70	4.80	2.70	
Oxygenated	0.00	14.35	0.00	15.80	0.00	0.55	0.00	0.00	0.00	0.00	
Aromatic	1.50	2.28	4.86	8.13	12.62	14.55	21.71	26.08	29.73	31.22	
C ₅ -C ₈	14.90	4.43	31.10	6.40	13.14	7.30	5.33	1.04	5.60	0.24	
C ₉ -C ₁₂	7.70	8.70	4.10	3.80	1.90	2.30	0.70	0.05	0.00	0.00	
C ₁₃ -C ₁₉	14.40	10.30	5.90	5.07	1.70	0.74	0.00	0.00	0.00	0.00	
C ₁₉ -C ₃₂	23.00	5.25	2.80	1.55	1.10	0.03	0.00	0.00	0.00	0.00	
C ₃₃ -C ₆₀	11.00	3.40	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00	

Increasing temperature from 640 to 680 °C favors the yield of C5-C8 hydrocarbons. Increasing the temperature further causes a reduction in C5-C8 hydrocarbons and an increase in aromatic compounds which is the indicator of secondary reactions. [28]

Effect of residence time:

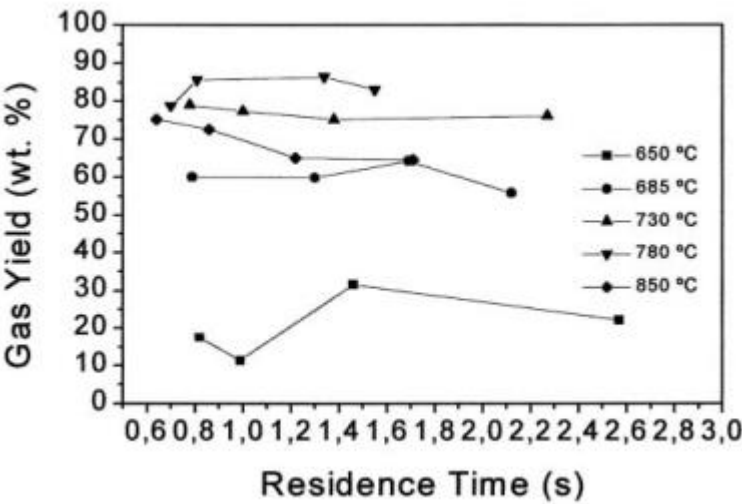


Figure 3.2: Effect of Residence Time for Different Temperatures on Gas Yield Done by Mastral et al. [28]

Residence time may slightly enhance the gas yield but a further increase in the residence time results in gas yield which is again the result of secondary reactions. The effect of residence time on gas yield is much more obvious at low temperatures (650 °C). [29]

Berrueco et al. [30] pyrolyzed HDPE in a fluidized bed continuously and the results are as follows:

Table 3.2: Product Distribution of HDPE Pyrolysis Done by Berrueco et al. [30]

residence time (s):	temperature (°C)																		
	650			685				730				780				850			
	0.8	1.0	1.5	0.8	1.3	1.7	2.1	0.8	1.0	1.4	2.3	0.7	0.8	1.3	1.6	0.6	0.9	1.2	1.7
% gas	20.3	21.1	31.5	66.6	60.4	67.9	59.3	80.4	79.3	80.8	86.5	84.7	90.4	86.6	86.3	88.6	83.8	84.6	87.8
% wax + oil	79.7	78.9	68.5	33.4	39.6	32.1	40.7	19.6	20.7	19.2	13.5	15.3	9.6	13.4	13.7	11.4	16.2	15.4	12.2
total olefins	79.7	78.9	68.5	33.1	38.7	29.7	37.7	13.5	18.7	17.4	8.6	4.7	2.9	2.1	2.6	1.9	3.4	2.5	0.9
C ₅ –C ₈	3.3	20.5	12.4	8.9	25.9	15.5	28.8	7.8	8.0	6.7	4.4	3.4	2.2	2.1	2.6	1.9	3.4	2.5	0.9
C ₉ –C ₁₂	6.7	14.8	7.7	6.5	4.1	4.7	4.6	3.0	4.2	3.7	2.2	0.6	0.7	0.0	0.0	0.0	0.0	0.0	0.0
C ₁₃ –C ₁₈	17.7	18.3	14.4	10.7	5.9	7.9	4.3	2.2	4.6	4.0	1.7	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₁₉ –C ₃₂	23.1	16.2	23.1	6.6	2.8	1.5	0.0	0.6	2.0	3.0	0.3	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₃₃ –C ₆₀	28.8	9.1	11.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
total aromatics	0.0	0.0	0.0	0.3	0.9	2.4	3.0	2.4	2.0	1.8	4.9	10.6	6.7	11.5	11.1	9.5	12.8	12.9	11.3
benzene	0.0	0.0	0.0	0.3	0.8	2.3	2.4	1.2	0.9	1.3	2.3	1.8	0.6	1.9	3.7	1.2	3.1	3.5	4.0
toluene	0.0	0.0	0.0	0.0	0.0	0.1	0.6	0.5	0.5	0.3	1.3	1.7	2.1	2.2	2.0	0.6	1.1	1.7	1.3
xylene/ethylbenzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	0.3	0.3	0.4	0.2	0.1	0.8	0.0	0.1
styrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.1	0.3	1.7	1.2	1.2	0.7	0.8	0.7	1.2	1.0
indene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.3	0.8	0.1	0.9	0.8	0.9	0.1	0.6	0.3
naphthalene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.0	0.3	3.6	1.5	3.9	2.8	4.2	5.0	4.8	4.2
upnaphthalene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.0	0.2	0.8	0.9	1.0	1.0	1.6	1.9	1.0	0.4

This is in agreement with the works already reviewed in [30].

Williams and Williams [31,32] pyrolyzed LDPE in a batch fluidized bed. From the result of their work, one concludes that thermal pyrolysis of plastics yields mostly wax at temperatures near 500 °C.

Table 3.3: Product Yield of Thermal Pyrolysis of LDPE Done by Paul T. Williams and Elizabeth A. Williams [31,32]

Product	Temperature (°C)				
	500	550	600	650	700
Gas	10.8	21.4	24.2	40.1	71.4
Oil	43.9	43.2	51.0	47.8	24.6
Wax	45.3	35.4	24.8	12.1	4.0
Oil + Wax	89.2	78.6	75.8	59.9	28.6

From this review it can be observed that thermal pyrolysis needs high temperature since at low temperatures, wax is the major product. Also, the yield contains a broad range of hydrocarbons which is not desirable for one who seeks to obtain high-value hydrocarbons with consuming minimum energy. Hence catalytic pyrolysis will be studied.

In conclusion, Thermal pyrolysis at low temperatures results in a high yield of wax with a broad range of hydrocarbons. Temperatures in the range of 650-800 °C with moderate residence time favor secondary reactions and result in a high yield of aromatic compounds.

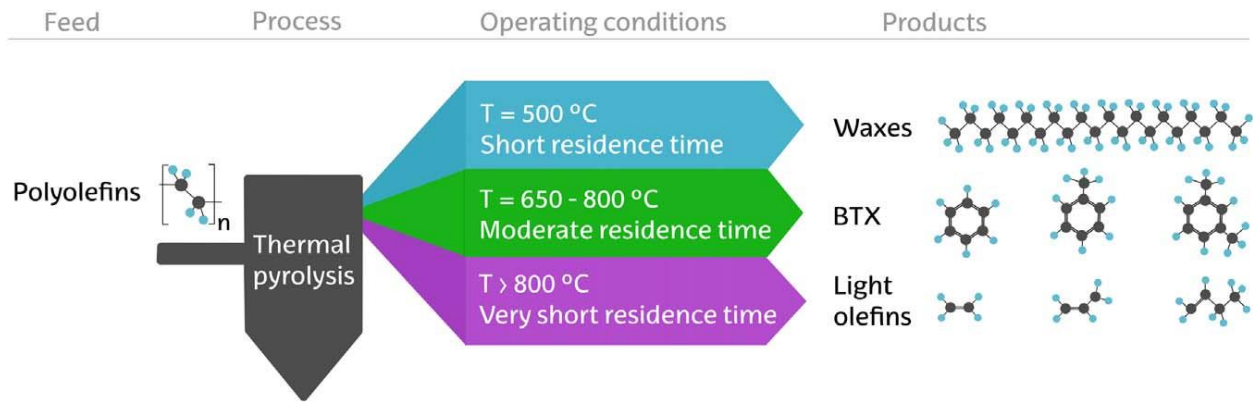


Figure 3.3: Conditions for Thermal Cracking. [25]

3.4 Catalytic Pyrolysis Mechanism

As discussed earlier, thermal pyrolysis occurs by a random scission mechanism where in the initiation step radicals are formed. However, in catalytic pyrolysis, where the catalyst is usually acidic, the initiation step is occurred either by abstracting a hydride (Lewis acid) from a polymer or by donating a proton to the polymer where a carbonium ion is formed, therefore this mechanism is known as carbonium ion mechanism.

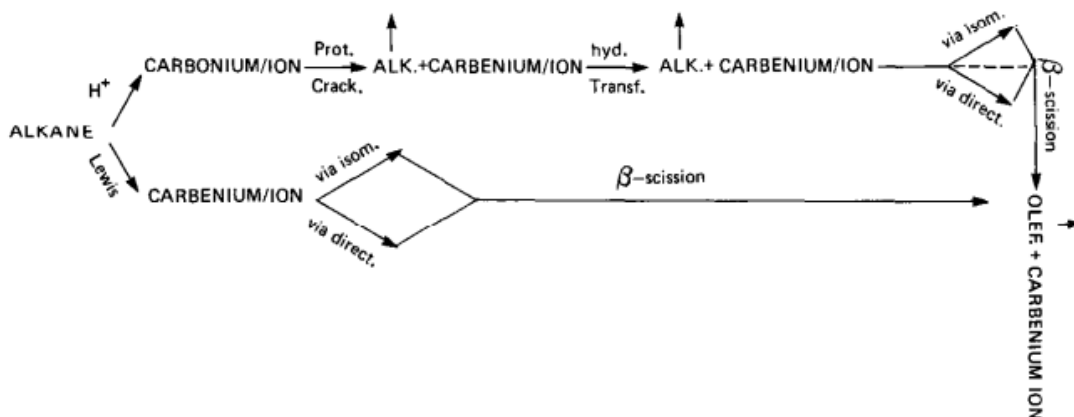


Figure 3.4: Carbonium Ion Mechanism [35].

In a catalyst with a small pore size, the bimolecular reactions are hindered and lighter hydrocarbons are able to diffuse through, hence the smaller the pore size, the lighter the products of catalytic pyrolysis. [33,34,35,36,37].

3.5 Catalytic Pyrolysis Review

Mastral et al. [37] pyrolyzed HDPE over HZSM-5 zeolite and compared the results with thermal pyrolysis of the same plastic.

Table 3.4: Experiment Results of Pyrolysis one by Mastral et al. [37]

Experiment	B1	B2	B3	B4
HDPE/Cat	0.93	1.41	9.2	$\infty_{(\text{Thermal})}$
Number of batches	7	5	5	3
g_{BATCH} (g)	2	4	4	4
$\% \text{Zeolyte}_{\text{BED}}$	10	10	1.35	0
$Q_{\text{fluidization}}$ (ml N/s)	35	35	30	30
t_{TOTAL} (min)	76	35	56	100
Gas yield (%)	80.13	78.48	46.86	33.16
Wax yield (%)	19.87	21.52	53.14	66.84
Solid residue (%)	0.00	0.00	0.00	0.00

Gas yield is much higher in catalytic pyrolysis compared to thermal pyrolysis. By increasing the catalyst, gas yield also increases.

The composition of gas yield is as below:

Table 3.5: Composition of The Gas Yield of Pyrolysis of HDPE Over HZSM-5 Done by Mastral et al. [37]

Experiment	B1	B2	B3	B4
PE/Cat	0.93	1.41	9.2	∞ (Thermal)
CH ₄	0.00	0.00	0.05	0.26
C ₂ H ₆	0.00	0.00	0.13	0.29
C ₂ H ₄	0.93	0.78	0.30	0.40
C ₂ H ₂	0.00	0.00	0.00	0.09
C ₃ H ₈	0.35	0.26	0.25	0.24
C ₃ H ₆	9.72	18.17	5.85	2.58
C ₄	44.54	23.85	8.60	4.24
C ₄ H ₁₀	0.06	0.21	0.23	0.31
<i>cis</i> -C ₄ H ₈ / <i>trans</i> -C ₄ H ₈	18.16	10.30	3.71	1.73
<i>i</i> -C ₄ H ₈	17.54	9.64	3.20	1.06
C ₄ H ₈ (1-butene)	8.84	3.84	1.68	1.07
C ₄ H ₆ (1,3-butadiene)	0.00	0.07	0.00	0.06
C ₅ –C ₇	25.64	35.99	34.08	25.72

By using HZSM-5, the product is rich with light hydrocarbons selectively compared to thermal process. [37]

Hernandez et al. [38], pyrolyzed HDPE thermally and catalytically over HZSM-5 and HUSY. The results are as below:

Table 3.6: Product Yield of Thermal and Catalytic Pyrolysis of HDPE Done by M del Remedio Hernandez et al [38]

	Thermal pyrolysis				HZSM-5 pyrolysis				HUSY pyrolysis			
<i>T</i> (°C)	500	600	700	800	500	600	700	800	500	600	700	800
Gases	15.2	32.4	57.8	66.3	88.3	82.6	90.9	87.2	83.4	79.3	86.9	90.2
Liquids	40.9	37.6	24.0	13.6	4.3	4.4	8.8	6.8	9.7	12.6	11.6	9.8
Waxes	7.4	5.4	6.7	5.8	5.0	6.7	2.5	1.8	1.0	0.1	0.6	0.4
Solid residue ^a	36.5	24.6	11.5	14.3	5.6	8.5	3.1	9.4	10.9	7.9	4.3	4.8

C1-C7 yield of thermal and 2 catalytic processes:

Table 3.7: C1-C7 Yield of Thermal and Catalytic Pyrolysis of HDPE Done by M del Remedio Hernandez et al [38]

Compounds	Thermal				HZSM-5				HUSY			
	500 °C	600 °C	700 °C	800 °C	500 °C	600 °C	700 °C	800 °C	500 °C	600 °C	700 °C	800 °C
Paraffins												
C ₁	0.26	0.51	4.18	4.76	0.17	0.53	4.44	11.01	0.72	0.83	1.83	4.88
C ₂	0.50	0.65	2.91	2.99	0.21	0.39	1.57	2.27	0.38	0.44	0.93	1.73
C ₃	0.34	0.48	0.70	0.74	5.86	5.51	5.12	2.19	0.85	0.85	1.19	1.19
C ₄	0.21	0.28	0.26	0.28	6.58	6.18	5.10	1.49	5.94	5.70	6.37	4.88
C ₅	0.17	0.22	0.15	0.12	4.06	3.66	3.00	0.66	7.16	6.69	7.04	4.85
C ₆	0.26	0.56	1.80	2.05	0.19	0.15	0.05	1.78	0.99	0.99	1.28	0.71
C ₇	0.13	0.38	0.65	0.76	0.14	0.16	0.23	0.16	0.00	0.43	0.33	0.20
Olefins												
C ₂	0.56	1.50	12.48	16.46	2.99	4.64	9.52	15.14	0.87	0.97	2.03	5.63
C ₃	1.62	5.65	7.62	10.49	19.46	21.66	25.99	20.50	7.60	7.89	11.04	13.98
C ₄	2.36	6.88	9.04	10.86	25.67	23.02	22.61	15.05	13.06	13.41	16.31	17.77
C ₅	0.50	0.86	1.86	2.28	10.30	6.39	4.67	2.91	6.31	6.23	6.78	5.65
C ₆	1.05	1.54	2.79	2.81	0.49	0.30	0.25	0.38	1.49	1.45	1.25	1.03
C ₇	0.66	0.79	1.45	1.49	0.00	0.00	0.00	0.00	0.19	0.16	0.14	0.11

It is concluded that HZSM-5 favors the yield of gas and light olefinic compounds at low temperatures compared to the HUSY catalyst and thermal process. [38]

Mertinkat et al. [39] pyrolyzed PE thermally and two different used FCC catalysts. The results are as below:

Table 3.8: Results of Thermal and Catalytic Pyrolysis Over 2 Used FCC Catalysts Done by J. Mertinkat et al. [39]

Fluidized bed Input material	Cat 2 ^c PE	Cat 2 PE	Sand ^d PE
Temperature (°C)	450	515	515
Residence time (s)	12	10	1–2
Gases			
Hydrogen	0.1	0.1	^a
Methane	0.8	2.1	0.2
Ethane	0.7	1.6	0.3
Ethene	0.9	1.5	0.4
Propane	4.9	7.5	0.4
Propene	9.2	12.4	0.5
Methylpropane	12.5	8.3	^b
Butane	2.4	2.6	0.2
Butenes	9.8	12.9	0.4
Other C ₄ -compounds	7.0	2.8	^a
Σ Gas	48.3	51.8	2.4
Oils			
Methylbutanes	3.8	2.3	^b
Methylbutenes	3.5	4.8	^b
Pentene	1.3	2.1	0.4
Methylpentenes	1.2	2.6	^b
Hexane	0.3	0.3	0.2
Hexenes	0.4	1.0	0.9
Other C ₅ -aliphatics	0.5	0.6	0.3
Other C ₆ -aliphatics	1.1	0.7	0.1
C ₇ -aliphatics	2.5	3.9	1.0
C ₈ -aliphatics	1.3	2.1	0.9
C ₉ -aliphatics	1.3	1.8	0.6
C ₁₀ -aliphatics	0.6	0.5	0.9
C _{11–20} -aliphatics	7.1	4.8	4.8
Aromatics	8.8	8.9	^a
Other waxes	0.5	0.7	87.3
Σ Oil	37.6	39.0	97.4
Soot/Coke	14.1	9.2	0.2

Each two FCC catalysts increased the yield of light gaseous product compared to thermal pyrolysis. [39]

Lin et al. [40] pyrolyzed a mixture of PE, PP, and PS which was a post-consumer waste plastic in Taiwan. The catalysts used were FCC, silicate, HUSY, HZSM-5, and SAHA. Results are as below when the temperature was set at 390 °C:

Table 3.9: Product Yield and Distribution of Catalytic Pyrolysis of PE/PP/PS Done by Hung-Ta Lin [40]

	Catalyst type				
	FCC-R1	Silicalite	HUSY	ZSM-5	SAHA
<i>Yield (wt.% feed)</i>					
Gaseous	82.4	13.5	85.6	88.3	84.1
Liquid ^a	3.8	1.4	3.3	3.4	3.6
Residue ^b	11.7	85.1	8.6	6.4	10.5
Involatile residue	9.3	83.2	4.1	4.9	8.4
Coke	2.4	1.9	4.5	1.5	2.1
HCl	2.1	1.4	2.5	1.9	1.8
Mass balance (%)	97.8	98.3	96.5	97.4	95.7
<i>Distribution of gaseous products (wt.% feed)</i>					
Light gases (C ₁ –C ₄)	24.0	6.8	35.7	52.7	30.2
Gasoline (C ₅ –C ₉)	54.8	6.2	48.4	34.5	52.4
Styrene	0.7	0.1	0.5	0.6	0.8
BTX ^c	1.6	0.4	1.0	0.5	0.7

This is observable that HZSM-5 selectively yields gas and light hydrocarbons (C1-C4) in much more quantity compared to other catalysts. [40]

Y.-H. Lin et al [41] pyrolyzed HDPE over MCM-41, SAHA, and ZSM-5 at 360 °C. The results are as below:

Table 3.10: Product Yield and Distribution of Catalytic Pyrolysis of HDPE Done by Y.-H. Lin et al [41]

Degradation results	Catalyst type		
	MCM-41	SAHA	ZSM-5
<i>Yield (wt% feed)</i>			
Gaseous	87.88	85.50	94.21
Liquid ^a	3.04	2.37	1.26
Residue ^b	9.08	12.13	4.53
Involatile residue	6.91	9.62	2.82
Coke	2.17	2.51	1.71
Mass balance (%)	92.83	90.21	95.48
<i>Distribution of gaseous products (wt% feed)</i>			
Hydrocarbon gases (ΣC ₁ –C ₄)	26.43	31.25	64.14
Gasoline (ΣC ₅ –C ₉)	61.37	54.22	28.06
BTX ^c	0.08	0.13	2.01

Which is in agreement with previous review and ZSM-5 yielded the most amount of light hydrocarbons. [41]

Y.-H. Lin and M.-H. Yang [42] pyrolyzed mixture HDPE and LDPE over HUSY, HZSM-5, HMOR SAHA and MCM-41. Results at 360°C, are as below:

Table 3.11: Product Yield and Distribution of Catalytic Pyrolysis of HDPE/LDPE Mixture Done by Y.-H. Lin and M.-H. Yang [42]

Degradation results	Catalyst type				
	HUSY	HZSM-5	HMOR	SAHA	MCM-41
Yield (wt% feed)					
Gaseous	89.4	92.5	87.9	85.3	85.8
Liquid ^a	3.7	3.2	4.7	4.9	6.4
Residue ^b	6.9	4.3	7.4	9.7	7.8
Involatile residue	3.4	2.9	4.7	7.4	5.6
Coke	3.5	1.4	2.7	2.3	2.2
Distribution of gaseous products (wt% feed)					
Hydrocarbon gases (ΣC_1-C_4)	35.2	64.2	55.9	23.4	26.7
Gasoline (ΣC_5-C_9)	54.2	26.2	30.8	61.6	58.2
BTX ^c	1.4	2.1	1.2	0.3	0.9

Olefin Products:

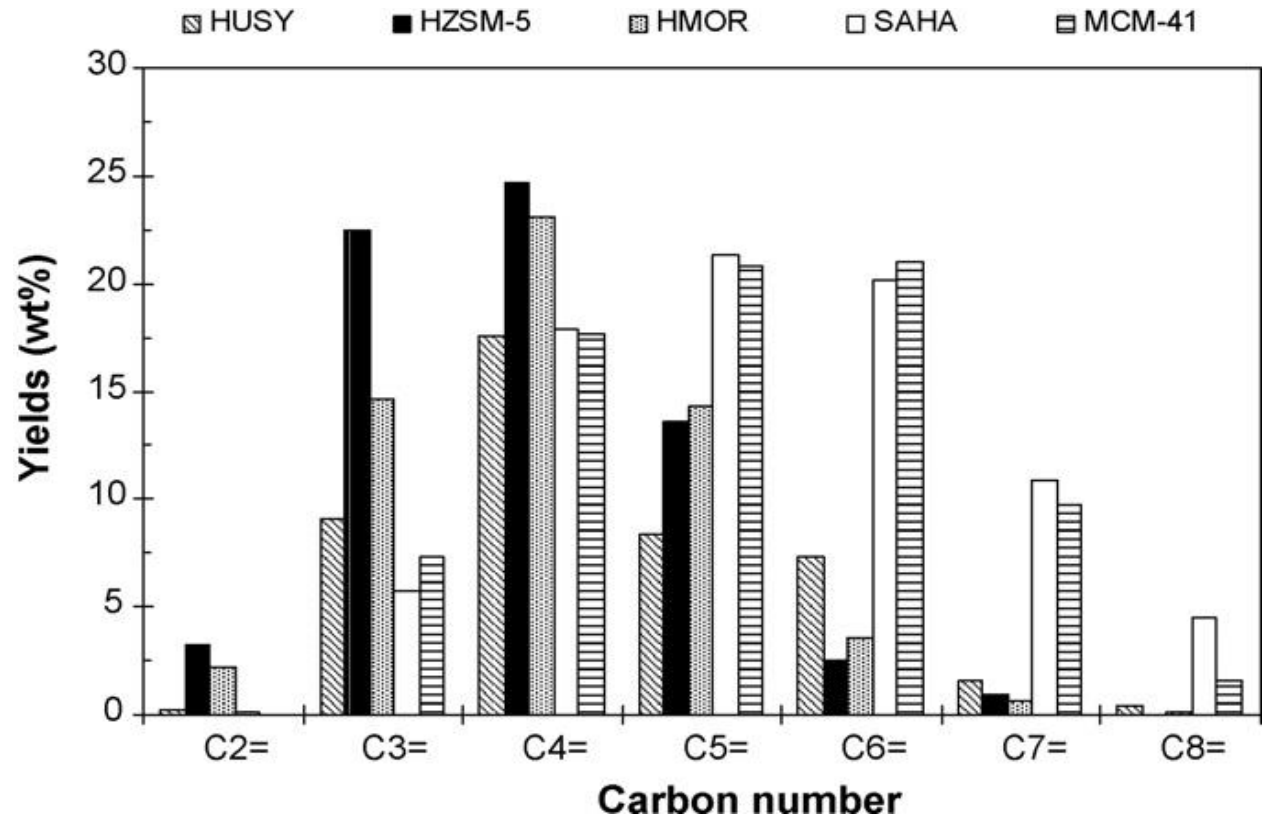


Figure 3.5: Olefin Products of Pyrolysis of HDPE/LDPE Mixture Over Various Catalysts Done by Y.-H. Lin and M.-H. Yang [42]

Paraffin Products:

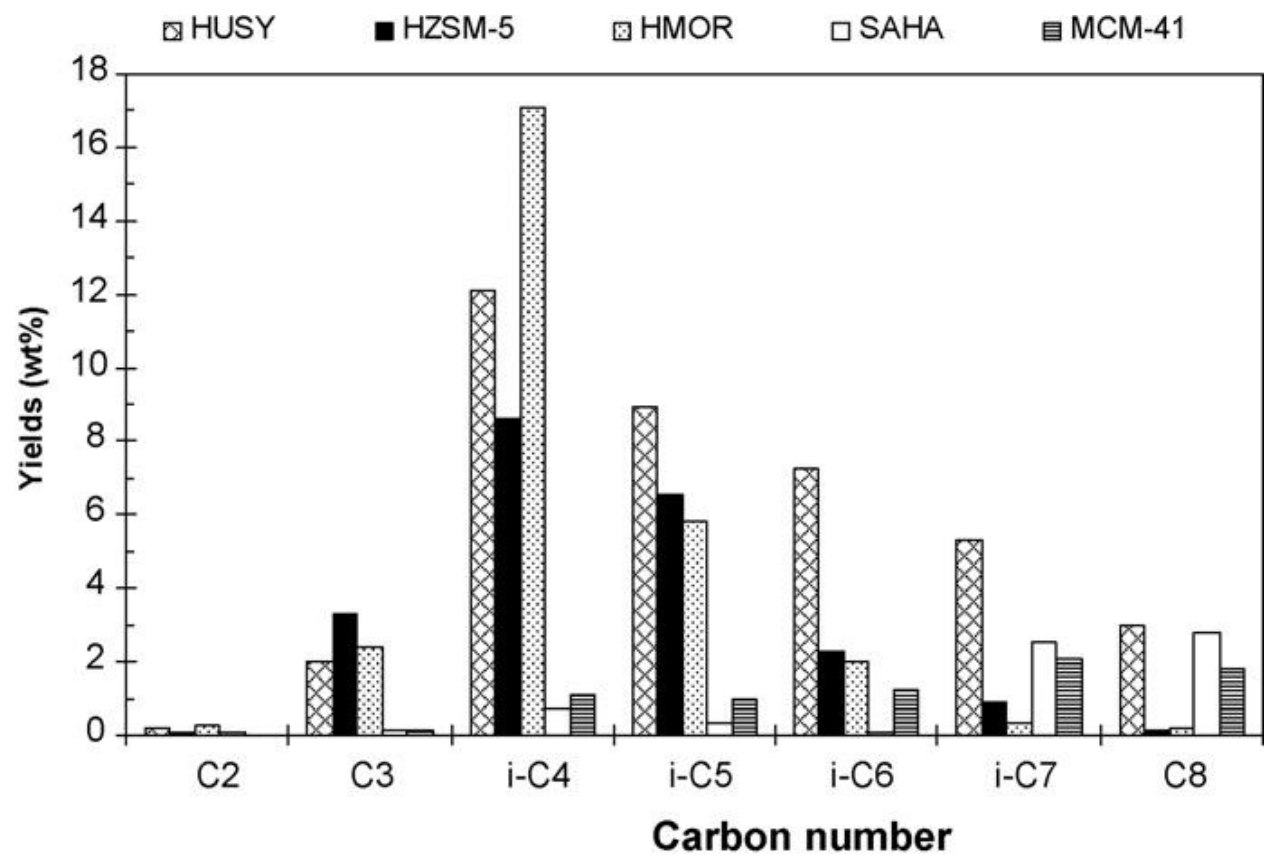


Figure 3.6: Paraffin Products of Pyrolysis of HDPE/LDPE Mixture Over Various Catalysts Done by Y.-H. Lin and M.-H. Yang [42]

It is concluded that in addition to the higher yield of gaseous products obtained when using HZSM-5, higher olefin yields among which propylene has the most share. [42]

Ali et al. [43] pyrolyzed HDPE over HUSY, HZSM-5, and ASA and used FCC, and compared the results. At 360 °C results are as below (left-hand side are paraffin yields and the right-hand side is olefin yields):

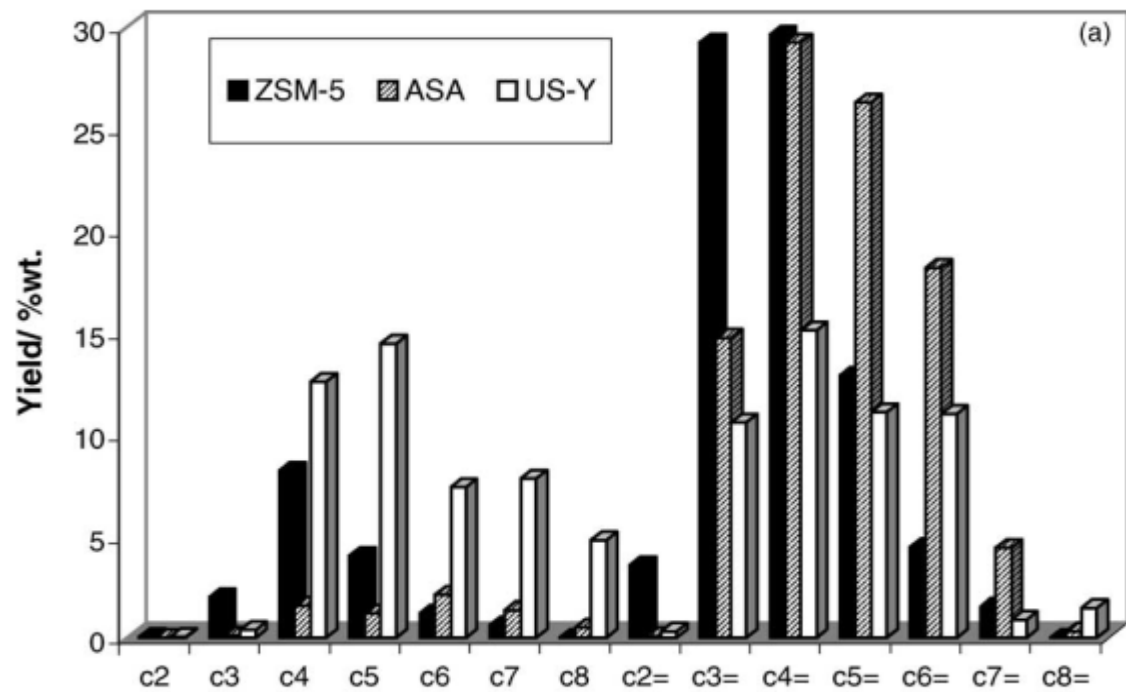


Figure 3.7: The Product Yield of Pyrolysis of HDPE Over ZSM-5, ASA, and USY done by Ali et al. [43]

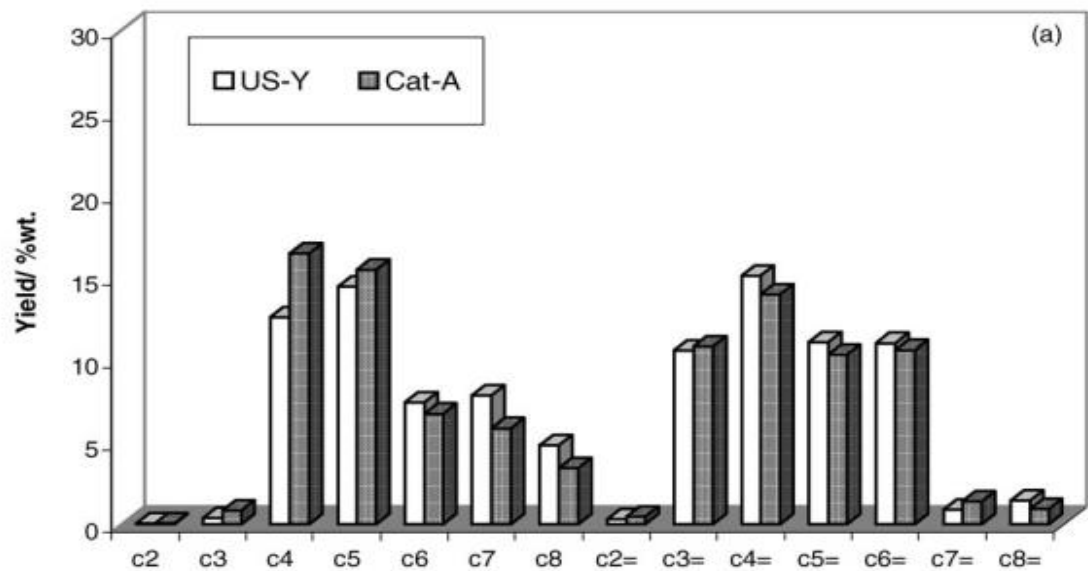


Figure 3.8: The Product Yield of Pyrolysis of HDPE Over Used FCC and USY Done by Ali et al. [43]

In conclusion FCC gives product with broader range of hydrocarbons compared to HZSM-5. [43]

Grieken et al [45] pyrolyzed LDPE. The results are as below:

Gas Yield:

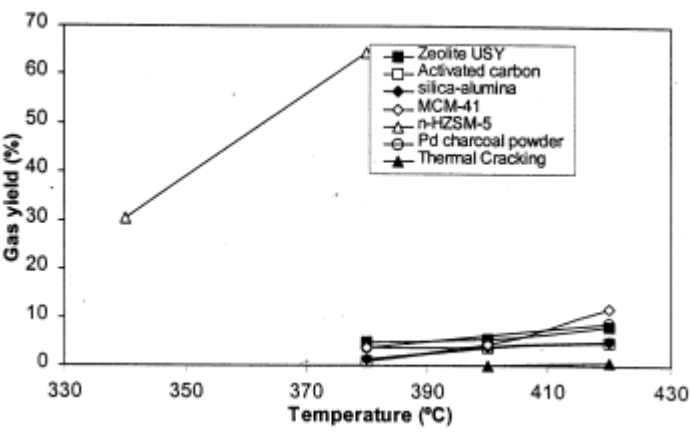


Figure 3.9: Temperature Vs Gas Yield of Pyrolysis of LDPE [45]

Liquid Yield:

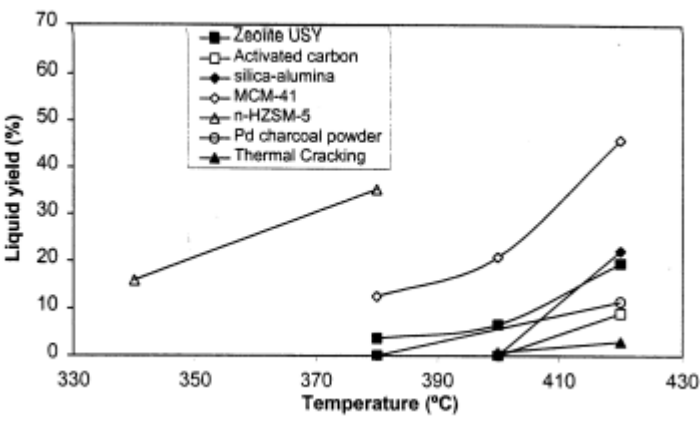


Figure 3.10: Temperature Vs Liquid Yield of Pyrolysis of LDPE [45]

Solid Yield:

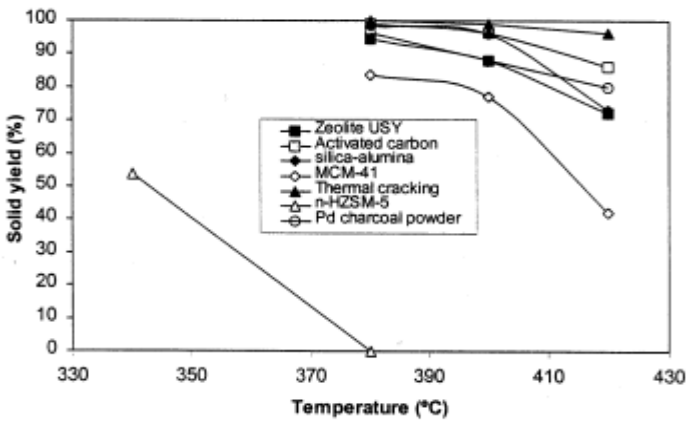
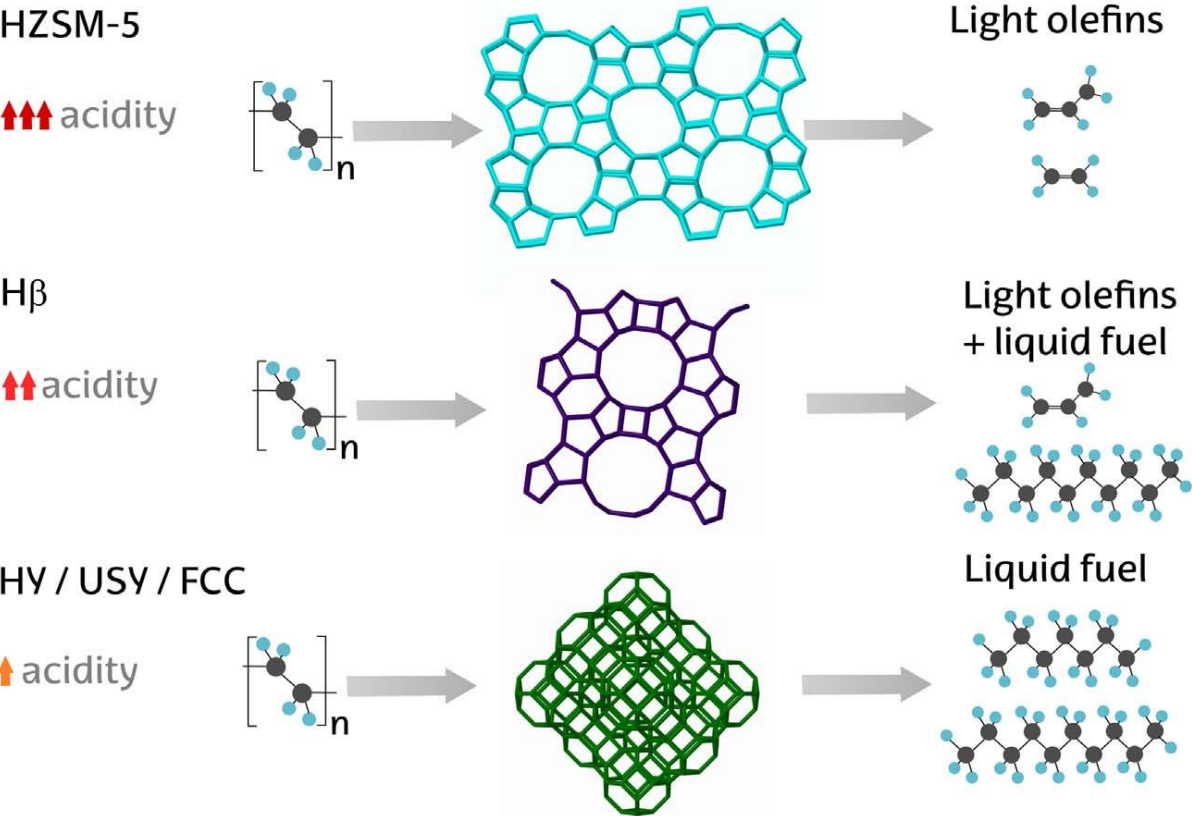


Figure 3.11: Temperature Vs Solid Yield of Pyrolysis of LDPE [45]

This study shows that HZSM-5 yields high gaseous products and low solid products at low temperatures compared to other catalysts and thermal pyrolysis. [45]

In conclusion, HZSM-5 gives lighter hydrocarbons compared to other catalysts that have been reviewed in this thesis. The reason for that is the small pore size and high acidity of HZSM-5. [25]

Zeolites



Mesoporous catalysts

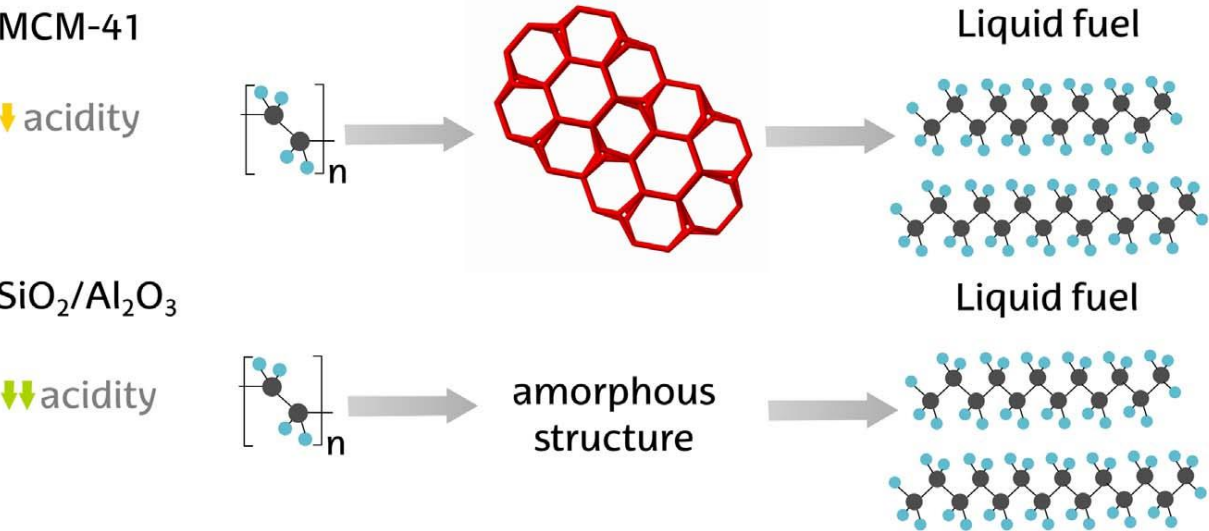


Figure 3.12: The Main Products in Catalytic Pyrolysis [25]

Chapter 4

Simulation Results & Discussion

4a. Microwave Reactor Geometry and Results

4a.1 Incentives for Simulation of Microwave

The pyrolysis process which be simulated in proceeding section is simulated in a steady-state study and since the reaction is endothermic, the power of the microwave must be manipulated in order to maintain the temperature at a desired value which needs a control scheme which is beyond the scope of this project. Hence the transient study of microwave heating is simulated which is necessary for preparing the reactor for pyrolysis reaction.

4a.2 Governing Equations

Maxwell's equations:

$$\begin{aligned}\nabla \times \vec{H} &= \vec{J} + \frac{\partial \vec{D}}{\partial t} \\ \nabla \times \vec{E} &= -\mu \frac{\partial \vec{H}}{\partial t} \\ \nabla \cdot \vec{B} &= 0 \\ \nabla \cdot \vec{D} &= \rho_e,\end{aligned}$$

where

E and H are the electric field and magnetic field intensity, respectively; D is the electric field flux intensity; B is the magnetic field flux intensity; J is the conduction current; μ is the permeability; and ρ_e is the free charge density.

Power loss:

$$Q_e = \frac{1}{2} \omega \epsilon_0 \epsilon'' |\vec{E}|^2.$$

Temperature of microwave receptor:

$$\rho C_p \frac{\partial T}{\partial t} - k \nabla^2 T = Q = Q_e.$$

4a.3 Dimensions of Reactor

A 500 mL volume is considered as a microwave reactor. Since this reactor is a fluidized bed reactor, a length to diameter ratio of 2 is chosen for proper mixing. [47]

$$V = 500 \text{ mL} = 0.5 \text{ L} = 0.5 * 10^{-3} \text{ m}^3$$

The volume of a tubular reactor:

$$V = \frac{\pi D^2}{4} L; \quad \frac{L}{D} = 2; \quad V = \frac{\pi D^3}{2}; \quad D = \sqrt[3]{\frac{2V}{\pi}}$$

$$D = \sqrt[3]{\frac{2 * 0.5 * 10^{-3} \text{ m}^3}{3.14}} = 0.068 \cong 0.07 \text{ m} \quad D = 7 \text{ cm}$$

Hence:

$$L = 2 * D = 2 * 7 \text{ cm} = 14 \text{ cm}$$

The reactor is placed in a waveguide which is filled with air to conduct microwave irradiations.

4a.4 Geometry

Waveguide with 10 cm width and tube thickness of 5 cm was assumed and randomly altered to ultimately give a satisfactory temperature. The geometry is sketched in COMSOL as shown below:

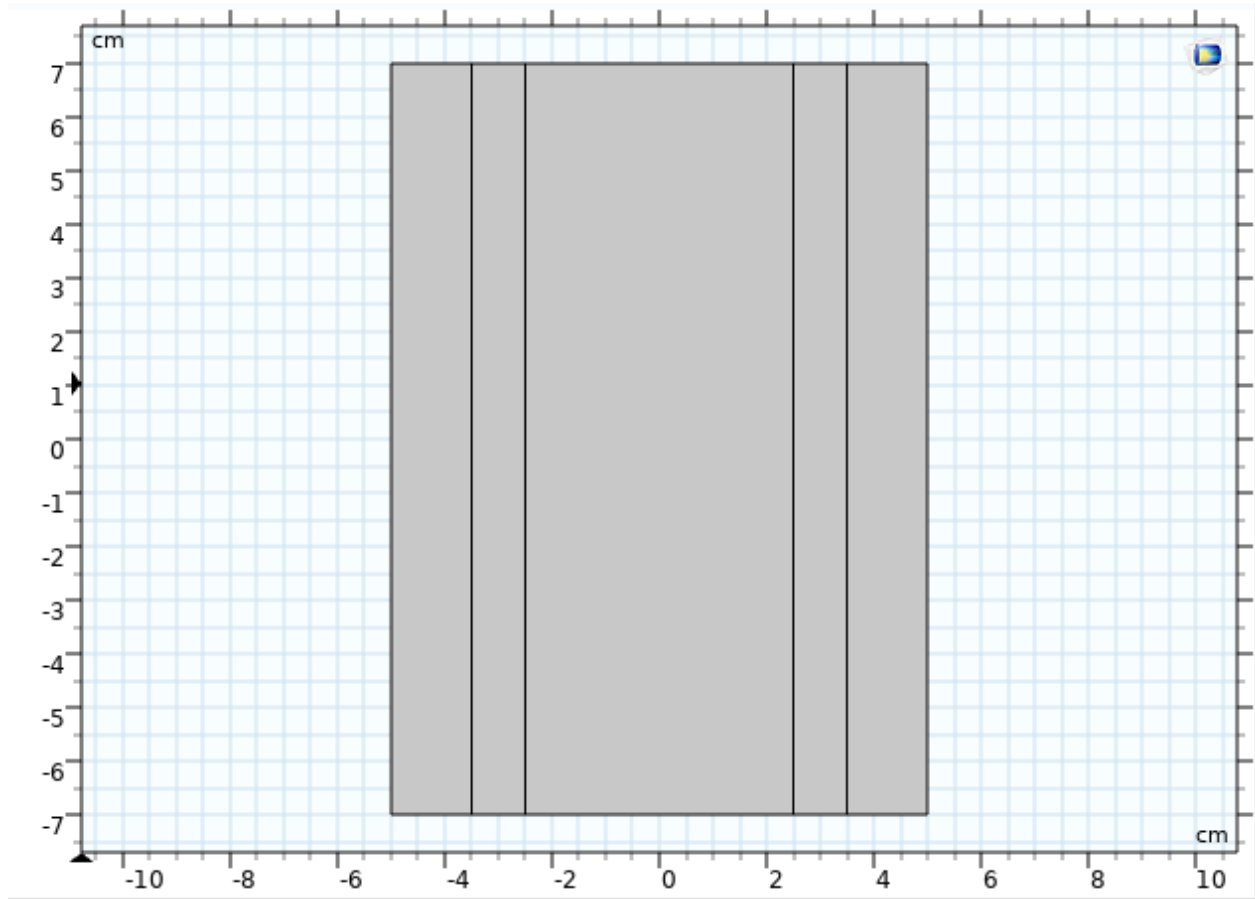


Figure 4a.1: Geometry of Microwave Heater.

Waveguide material was air, the wall of reactor was silicon carbide and the inside of reactor was filled with nitrogen gas.

4a.5 Boundary Conditions

The First Excitation Port:

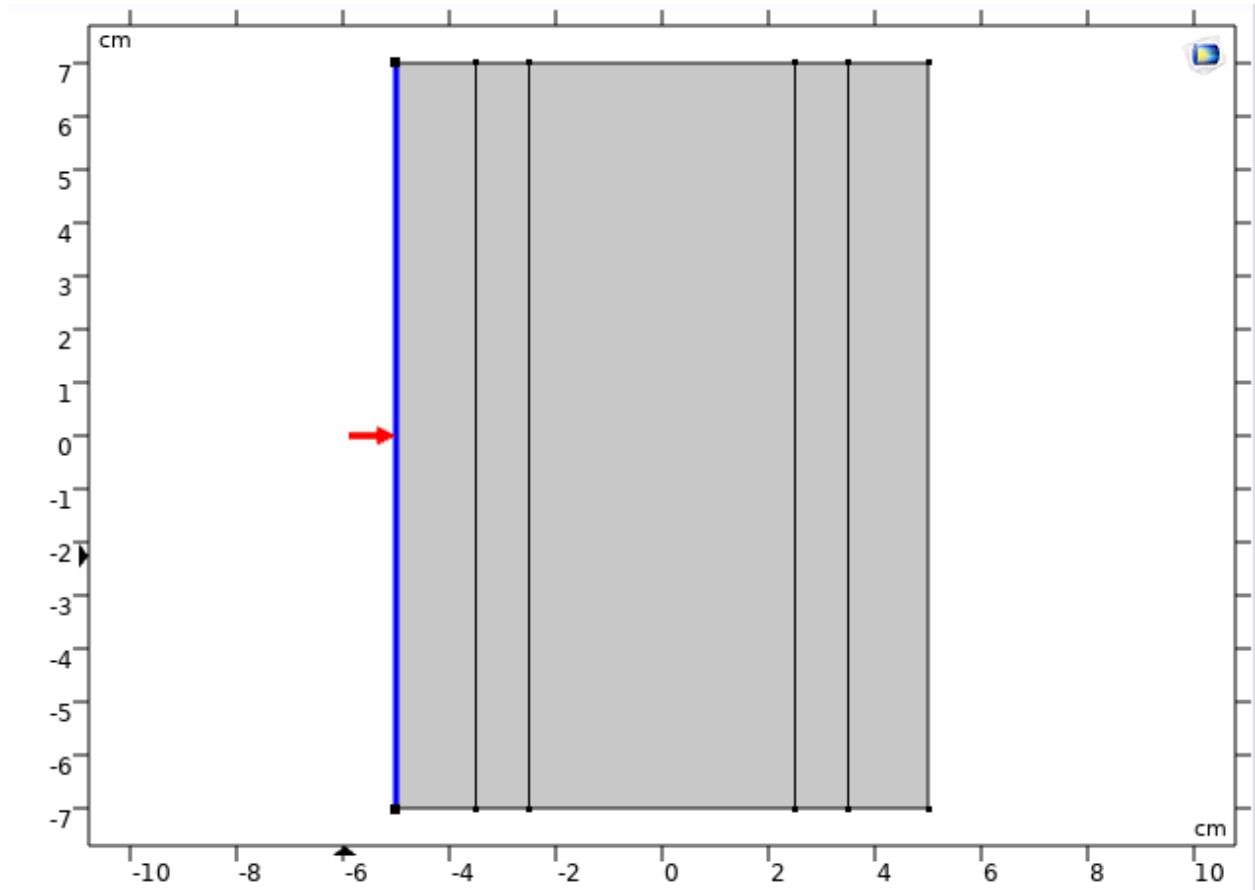


Figure 4a.2: Microwave Generator (Excitation port) with 800 W Power from Left-Hand-Side.

The second excitation port:

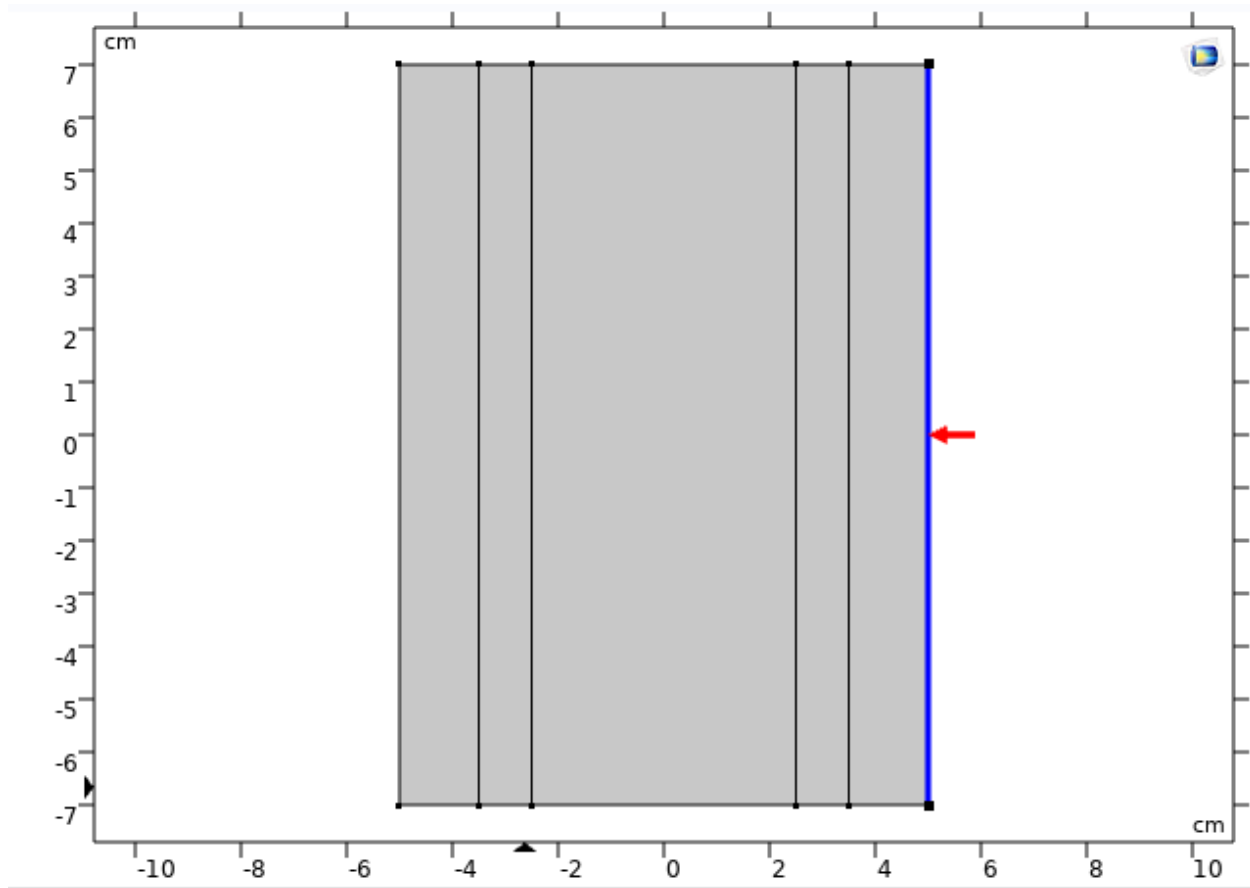


Figure 4a.3: Microwave Generator (Excitation port) with 800 W Power from Right-Hand-Side.

Both excitation ports were rectangular with the mode of transverse electric (TE) with input power of 800 W with number of modes of 3.

The simulation was run for 150 s. The temperature surface is shown at the end of the simulation time in the below figures.

Perfect electric conductor boundaries:

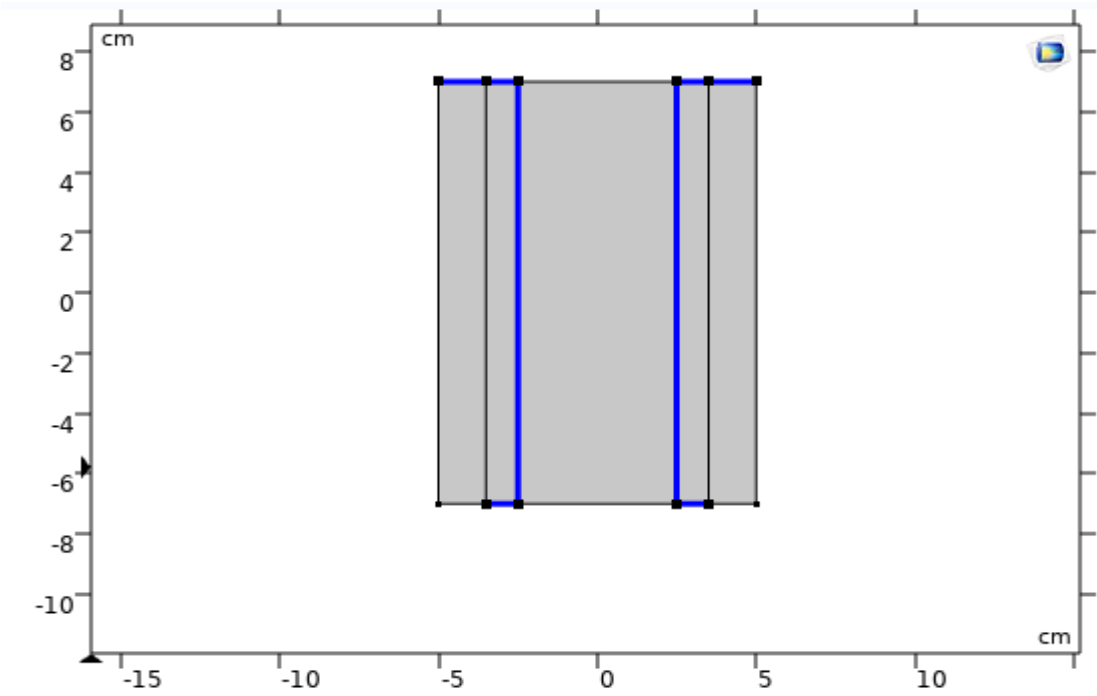


Figure 4a.4: Perfect Electric Conductor Boundaries.

Thermal insulation boundaries:

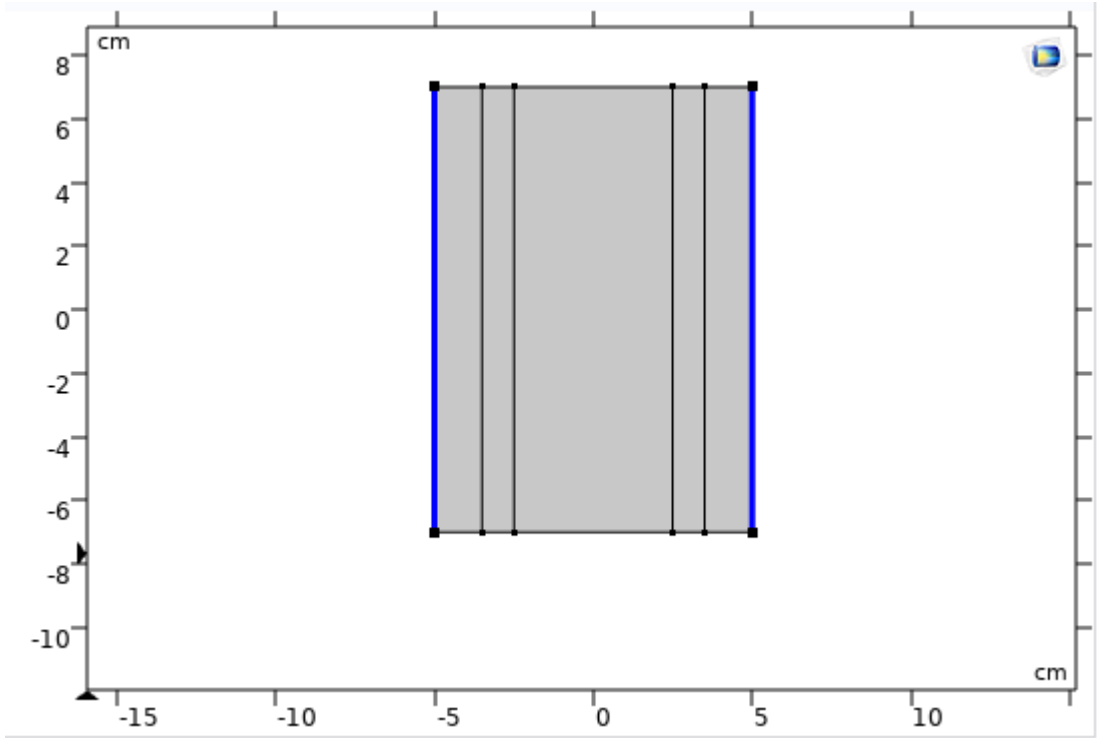


Figure 4a.5: Thermal Insulation Boundaries.

Heat flux boundaries

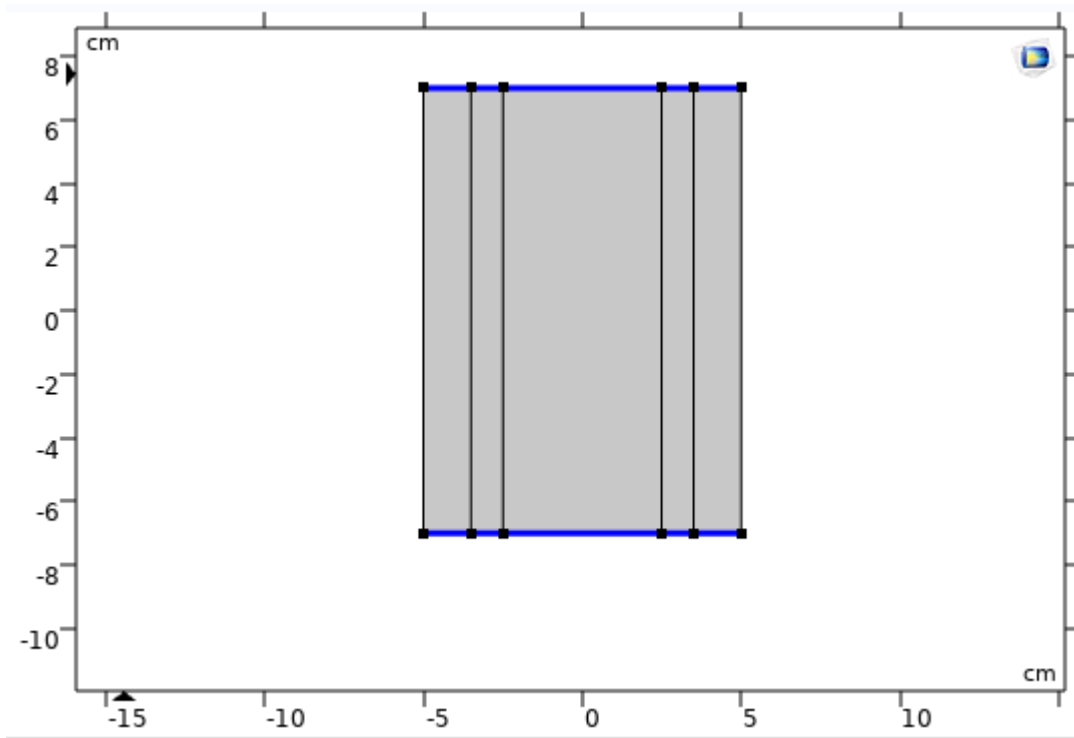


Figure 4a.6: Heat Flux Boundaries

Which is natural convection with atmosphere with heat transfer coefficient of $5 \text{ W}/(\text{m}^2 \cdot ^\circ\text{C})$

Initially the electric field is zero and the temperature is 20°C , when the microwave generators start working, the electric field will be formed and temperature will increase. Transient study was carried out for 150 s.

4a.6 Results and Comparison

As stated before, the microwave reactor was simulated with a transient study. As a results of the electric field formation, the microwave receptor, Silicon Carbide, heated by microwave irradiation and the heating of reactor wall results in heating the air in waveguide and nitrogen gas inside the tube. The temperature of waveguide is not of interest and is not shown. The temperature surface at 0 s and 150 s are as below:

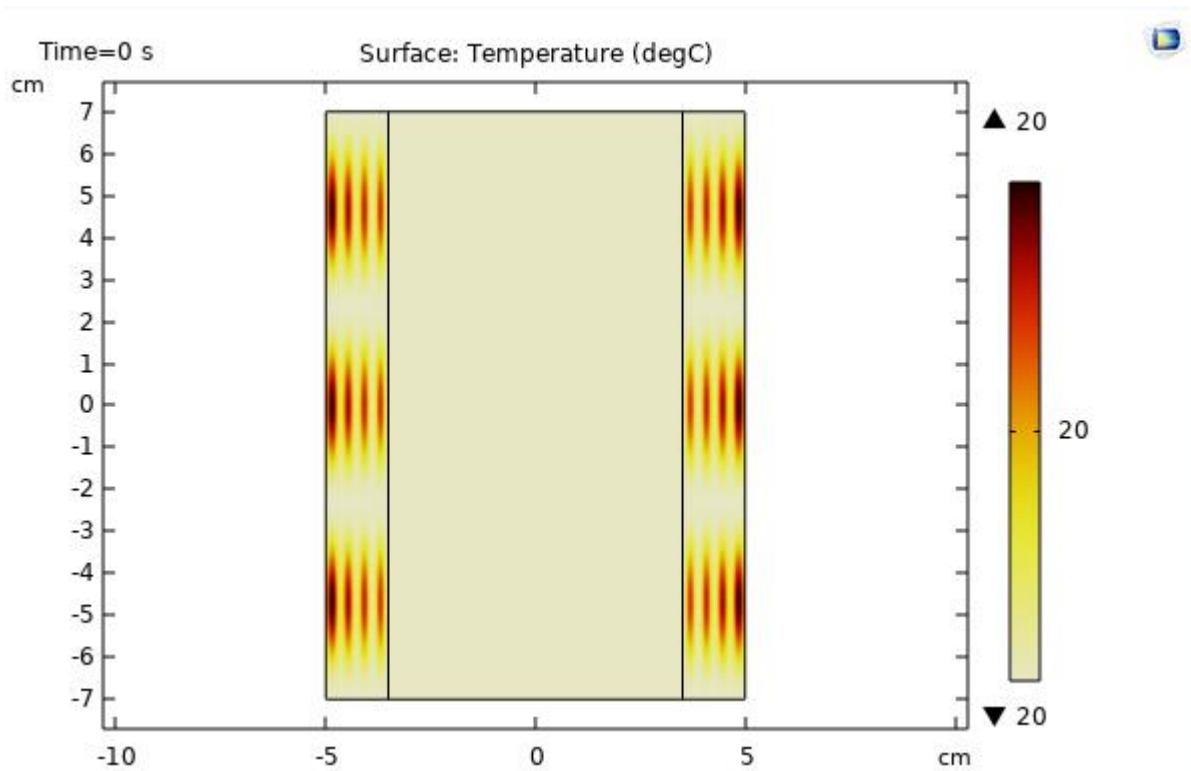


Figure 4a.7: Temperature Surface of Microwave Reactor at Initial Time

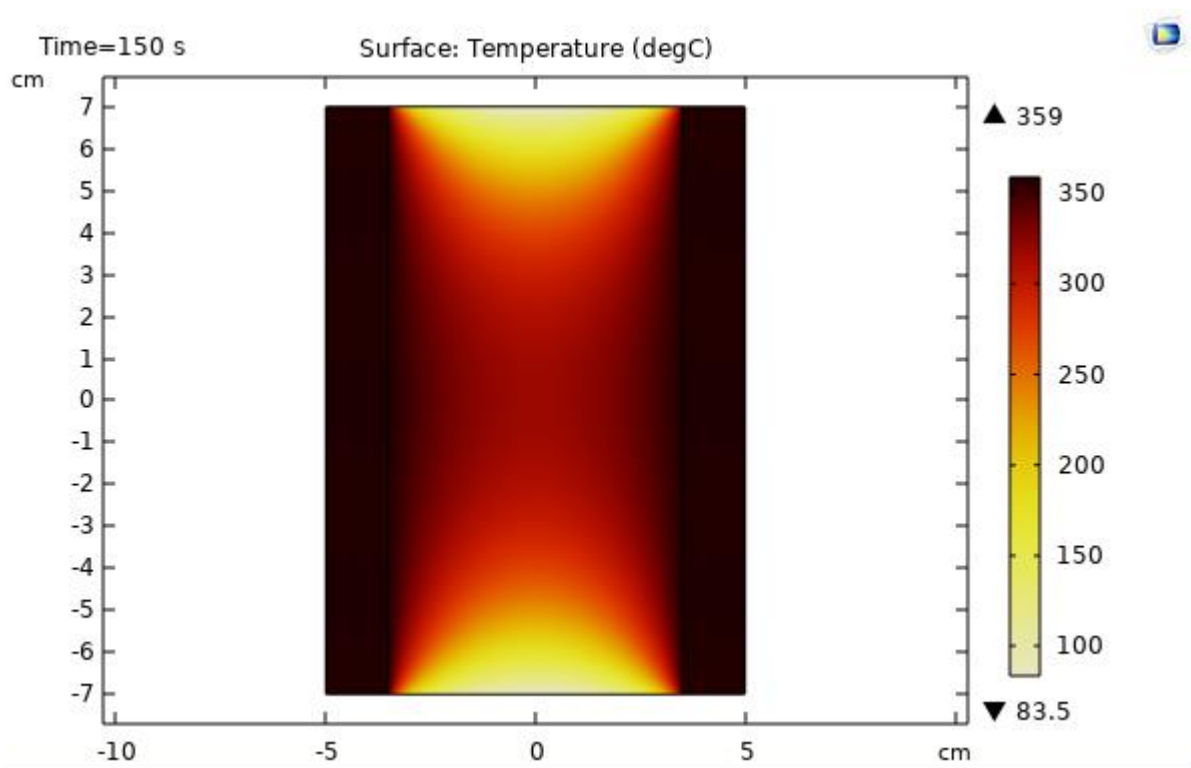


Figure 4a.8: Temperature Surface of Microwave Reactor after 150 s.

By altering the power input, or increasing the heating time, higher temperatures are achieved.

A simulation study for heating oleic acid passing through a porous silicon carbide heated by microwave was carried out by Ma et al [15] in COMSOL. The results are:

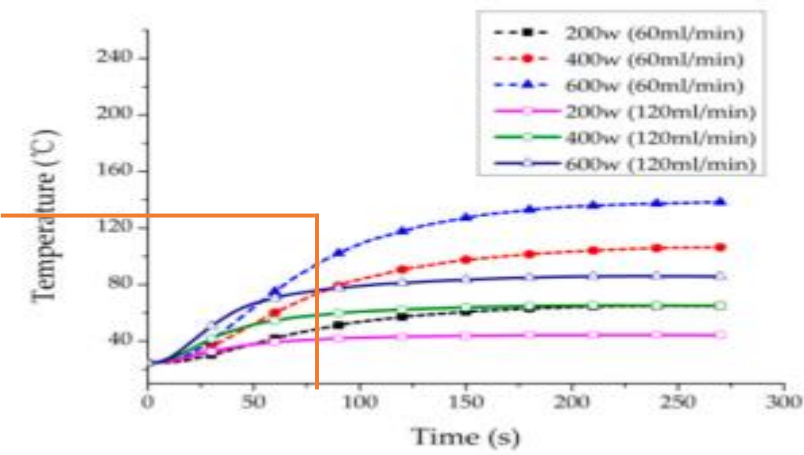


Figure 4a.9: Results of Simulation Study of Microwave Heating Conducted by Ma et al [15].

By taking into account that Ma et al [15] used 1 microwave generator and convective heat flux out of the reactor is present, the results are in good agreement.

4b. Reaction Pathway and Kinetics

4b.1 Reaction Pathway

A plastic mixture of 62 wt. % PE (37 % HDPE, 25% LDPE) 33 wt. % PP and 5 wt. % PS. undergoes catalytic cracking on HZSM-5. The plastic mixture is a post-consumer plastic waste which was acquired from a hospital waste collection center in north Taiwan [46]. The experiment was carried out by Huang et al. [46]. The proposed reaction pathway is as below:

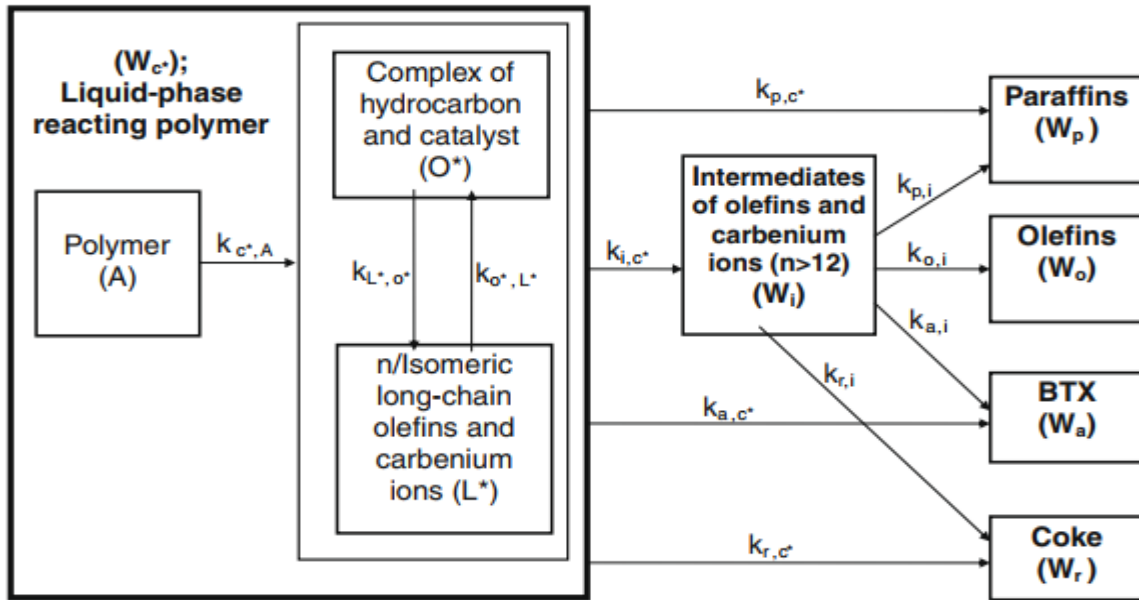


Figure 4b.1: Results of Simulation Study of Microwave Heating Conducted by Ma et al [15].

Note: In the above figure W is used as Concentration, in this thesis C is used for concentration.

Assumptions:

- 1) The rate formation of polymer-catalyst complex is very fast
- 2) The polymer entering the reactor is melted immediately

4b.2 Symbols & Reaction Kinetics

The table below shows the symbols of species chosen in this simulation study:

Table 4b.1: Symbols of Species Involved in Pyrolysis Reaction

Symbol	Species
A	Plastic Mixture
I	Intermediate
O	Olefins
P	Paraffins
BTX	Aromatics: Benzene, Toluene & Xylene
C	Coke

Since the pyrolysis is catalytic, the reaction mechanism is carbonium ion mechanism, which was discussed in Chapter 3. Kinetics parameters of pyrolysis of the plastic mixture over HZSM-5 as catalyst at 360°C were experimentally obtained by Huang et al., and are as below [46]:

Table 4b.2: Rate Constants of Pyrolysis Reaction

Rate Constant	Value (1/min)	Corresponding Reaction
k_{ic}	2.286	$A \rightarrow I$
k_{rc}	0.015	$A \rightarrow C$
k_{pc}	0.0012	$A \rightarrow P$
k_{ac}	0.00006	$A \rightarrow BTX$
k_{oi}	0.252	$I \rightarrow O$
k_{ri}	0.007	$I \rightarrow C$
k_{pi}	0.092	$I \rightarrow P$
k_{ai}	0.0014	$I \rightarrow BTX$

Differential equations associated with this pyrolysis reaction are:

$$\frac{dC(A)}{dt} = -\exp(-C(C)) * (k_{ic} + k_{pc} + k_{ac} + k_{rc}) * C(A)$$

$$\frac{dC(I)}{dt} = \exp(-C(C)) * [k_{ic} * C(A) - (k_{oi} + k_{pi} + k_{ai} + k_{ri}) * C(I)]$$

$$\frac{dC(O)}{dt} = \exp(-C(C)) * k_{oi} * C(I)$$

$$\frac{dC(P)}{dt} = \exp(-C(C)) * [k_{pi} * C(I) + k_{pc} * C(A)]$$

$$\frac{dC(BTX)}{dt} = \exp(-C(C)) * [k_{ai} * C(I) + k_{ac} * C(A)]$$

$$\frac{dC(C)}{dt} = \exp(-C(C)) * [k_{ri} * C(I) + k_{rc} * C(A)]$$

The exponential term corresponds to catalyst deactivation due to coke formation during the reaction.

In MATLAB, the dependent variables of a system of equations must be numbered, hence the number of each symbol is chosen as below:

Table 4b.3: Number of Each Symbol in MATLAB

Symbol	Number
A	1
I	2
O	3
P	4
BTX	5
C	6

Initial condition: Every species has a zero concentration except the waste plastic mixture which is 5 mol/m³. In MATLAB the above 6 equations were solved by ODE45 solver in the interval of 0-20 s. This interval is the reaction time if batch reactor is used. In continuous operation, this interval is interpreted as the mean residence time of the reactor.

4b.3 MATLAB Script & Results

```
%1:polymer 2:Intermediate 3: olefin 4: paraffine 5:BTX 6:coke
function Fluidized_Bed_Catalytic_Pyrolysis_HZSM-5
clear
close all
clc
Cpolymer0=5;
CIntermediate0=0;
Colefin0=0;
Cparaffin0=0;
CBTX0=0;
Ccoke0=0;
IC=[Cpolymer0 CIntermediate0 Colefin0 Cparaffin0 CBTX0 Ccoke0];
Interval=[0 20];
[t,c]=ode45(@myode,Interval,IC);
plot(t,c)
xlabel('Residence Time-min')
ylabel('Concentration-mol/m^3')
legend('c_A','c_I','c_O','c_P','c_BT','c_C')

function dc=myode(t,c)
% All the reaction rates are determined for T=360°C
kic=2.286;
krc=0.015;
kpc=0.0012;
kac=0.00006;
koi=0.252;
kri=0.007;
kpi=0.092;
kai=0.0014;

dc=zeros(6,1);
dc(1)=-exp(-c(6))*(kic+kpc+kac+krc)*c(1);
dc(2)=exp(-c(6))*[kic*c(1)-(koi+kpi+kai+kri)*c(2)];
dc(3)=exp(-c(6))*koi*c(2);
dc(4)=exp(-c(6))*[kpi*c(2)+kpc*c(1)];
dc(5)=exp(-c(6))*[kai*c(2)+kac*c(1)];
dc(6)=exp(-c(6))*[kri*c(2)+krc*c(1)];
```

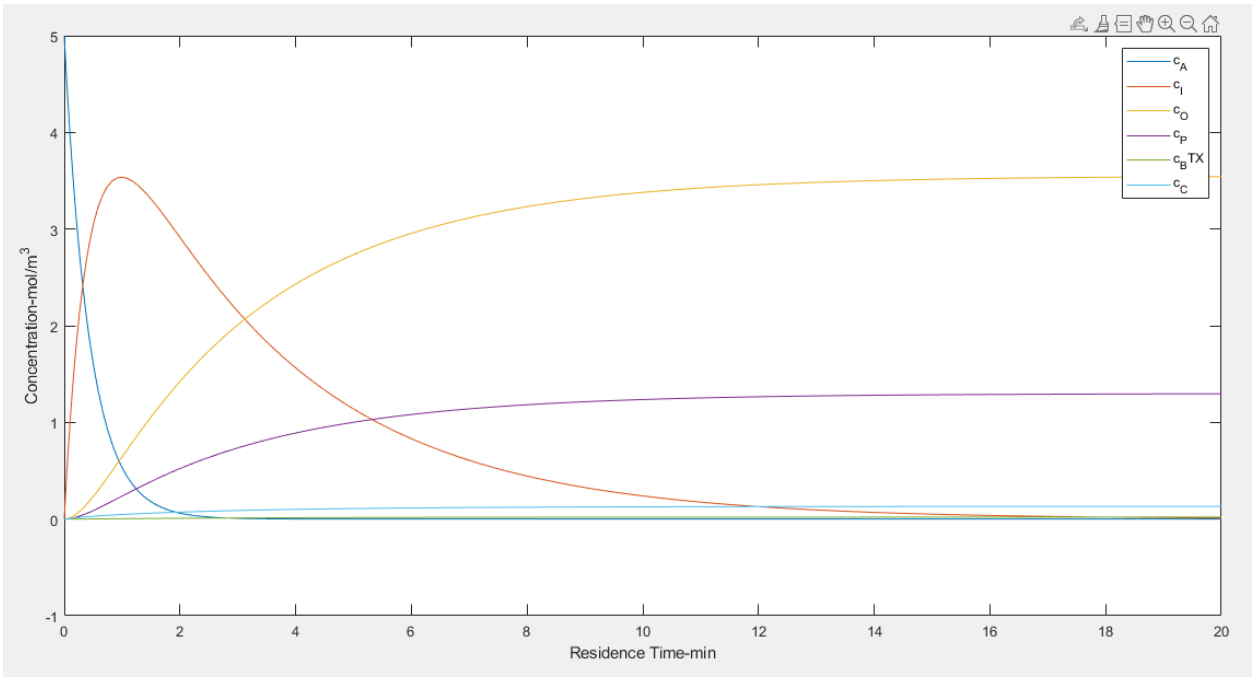


Figure 4b.2: Concentration (mol/m³) Vs Mean Residence Time (min) at 360°C.

From the above figure, it is observed that plastic mixture, A, is consumed over time and intermediates, I, is formed and then converted to olefins, O, paraffins, P, Aromatics, BTX and coke, C. As can be seen, the major products consist of olefins and then paraffins. BTX and coke content of product is relatively insignificant.

4b.4 Comparison with Experimental Results

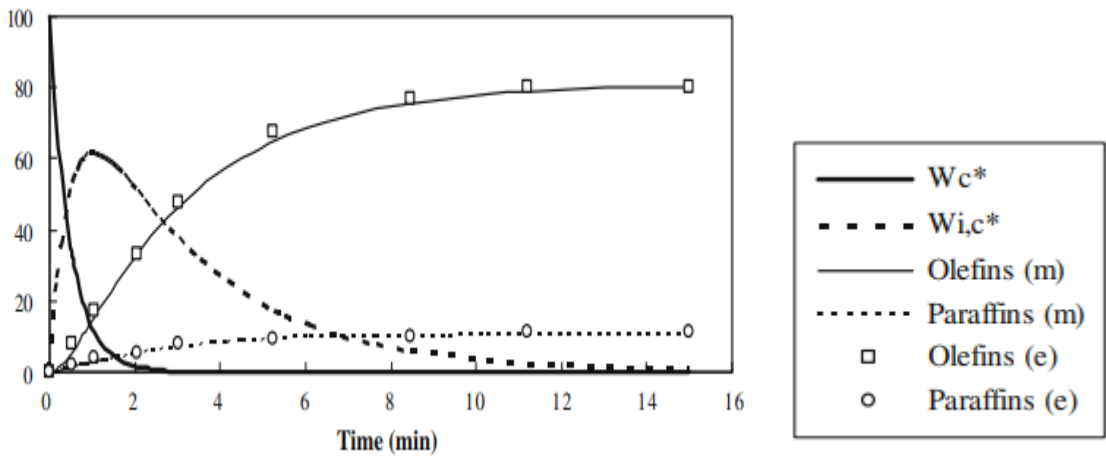


Figure 4b.3: Concentration (mol/m³) Vs Mean Residence Time (min) at 360°C (Experimental)

Where y axis is concentration.

The MATLAB output is in agreement with experimental results.

At 360°C, the main product distribution of the plastic mixture pyrolysis over HZSM-5 is as below:

Table 4b.4: Yield of Main Products and Gaseous Product Distribution of Pyrolysis of the Plastic Mixture at 360°C (Experimental Results) [46]

Yield (wt.% of Feed)	Value
Gas	93.1
Liquid	3.3
Coke	1.2
Non-Volatile Residue (Wax)	2.4
Gaseous Product distribution (wt.% of Feed)	
Ligh hydrocarbon gases (C1-C4)	65.8
Gasoline (C5-C9)	25.5
BTX	1.8

Using HZSM-5 as catalyst, results in over 50% of C3-C4 olefins, and over 15% C3-C5 paraffins. [46]. In the following section the discussed reactions are simulated in a 3-D geometry and the effects of mass of catalyst, velocity of fluidizing gas and particle diameter of catalyst are investigated and discussed.

4c. Modeling the Reaction

4c.1 Basic Data & Calculations

Porosity of the catalyst is obtained as below:

$$\varepsilon = 1 - \frac{\rho_{bulk}}{\rho_{particle}}$$

Where:

$$\rho_{bulk} = \frac{W}{V} \quad W: \text{mass of catalys} \quad V: \text{volume of reactor}$$

Density of HZSM-5 is 720 kg/m³. [48]

Density of nitrogen gas is 0.8 kg/m³. [49]

Viscosity of nitrogen is 0.00001744 kg/(m*s)

Molecular weight of nitrogen: 14 kg/kmole

Permeability (Kozeny-Carman Model):

$$\kappa = \frac{D_p^2 * \varepsilon^3}{180 * (1 - \varepsilon)^2}$$

Where:

D_p : particle diameter

Reactive surface area:

$$S_e = \frac{6}{D_p}$$

The porosity at minimum fluidization:

$$\varepsilon_{mf} = \left(\frac{0.071}{\psi} \right)^{1/3} \quad \psi: \text{sphersity}$$

Usually in the absence of experimental data, ψ is assumed to be 0.6. Hence:

$$\varepsilon_{mf} = \left(\frac{0.071}{0.6} \right)^{1/3} = 0.49$$

Minimum fluidization velocity:

$$150(1 - \varepsilon_{mf})u_{mf} + 1.75 * u_{mf}^2 * D_P = \varepsilon_{mf}^3 * D_P^2$$

Terminal Velocity Assuming Spherical Particles

$$u_t = g(\rho_{particle} - \rho_{nitrogen}) * \frac{D_P^2}{18 * \mu}$$

For $D_P=100\mu m$,

$$u_{mf} = 0.00001 \frac{m}{s}$$

$$u_t = 0.22 \frac{m}{s}$$

For fluidization to occur, the velocity of fluidizing gas, nitrogen gas, must be above minimum fluidization velocity and less than terminal velocity in order to avoid the entrainment of catalyst particles.

Reynolds number for $U=0.00005 \text{ m/s}$

$$Re = \frac{\rho U D}{\mu} = \frac{0.8 \frac{kg}{m^3} * 0.00005 \frac{m}{s} * 0.07 \text{ m}}{0.00002 \frac{kg}{m * s}} = 0.14 \text{ laminar flow}$$

Mach number:

$$Ma = \frac{U}{c} = \frac{0.00005 \frac{m}{s}}{343 \frac{m}{s}} = 1.2 * 10^{-7} \frac{m}{s} \quad \text{where } c \text{ is the speed of light}$$

Hence the flow is assumed to be incompressible.

4c.2 Governing Equations

The fluid flow is laminar and passes through porous material, hence the governing equation for fluid flow is Brinkman equation:

$$\frac{\rho}{\varepsilon} \left((\mathbf{U} \cdot \nabla) \frac{\mathbf{U}}{\varepsilon} \right) + \frac{\mu}{\kappa} \mathbf{U} = \nabla \cdot \left[-p \cdot \mathbf{I} + \frac{\mu}{\varepsilon} (\nabla \mathbf{U} + (\nabla \mathbf{U})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{U}) \mathbf{I} \right]$$

Where $\mathbf{I}$ and p are identity matrix and pressure respectively.

Conservation of mass:

$$\rho \nabla \cdot \mathbf{U} = 0$$

Bold letters represent vectors. It shall be noted that Brinkman and conservation of mass equations are written in steady state form.

Transport of species:

$$\nabla \cdot \mathbf{J}_i + \mathbf{U} \cdot \nabla C_i = R_i$$

$$\mathbf{J}_i = -(D_i + D_{e-i}) \nabla C_i$$

Where D and D_e are diffusivity and effective diffusivity respectively, where:

$$D_e = \frac{4}{\varepsilon^3} * D$$

4c.3 Diffusivity Calculation for Pure Products

Diffusivity calculation is carried out assuming the only olefinic product is propylene. The only paraffinic and aromatic products are butane and toluene respectively and all the products are assumed to diffuse in pure nitrogen gas. The results are obviously not valid and for obtaining the exact values, another detailed research is required.

Diffusivity of a gas diffusing in another gas can be obtained by the Wike-Lee modification of the Hirschfelder-Bird-Spotz method [50]:

$$D_{AB} = \frac{10^{-4} * \left(1.084 - 0.249 * \sqrt{\frac{1}{M_A} + \frac{1}{M_B}} \right) * T^{\frac{3}{2}} * \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{p(r_{AB})^2 f \left(\frac{kT}{\varepsilon_{AB}} \right)}$$

Where:

T: Absolute Temperature-K

p: Absolute Pressure-Pa

M: Molecular Weight-kg/kmole

r_{AB} : Molecular Separation at collision= $(r_A+r_B)/2$ -nm

ϵ_{AB} : Energy of Molecular Attraction= $(\epsilon_A*\epsilon_B)^{1/2}$

k: Boltzmann's Constant

$f(kT/\epsilon_{AB})$: Collision Function

r and ϵ/k for nitrogen gas are 0.4 nm and 71.4 K respectively.

r and ϵ/k can be obtained using below equations:

$$r = 1.18 v^{\frac{1}{3}} \quad \frac{\epsilon}{k} = 1.21 T_b$$

Where v and T_b are molal volume at normal boiling point, and normal boiling point respectively.

To calculate the molal volume, atomic volumes of each element in a molecule must be known. For carbon and hydrogen atomic volumes are 0.0148 m^3 and 0.0037 m^3 respectively.

For propylene (C_3H_6):

$$M = 42 \frac{kg}{kmol} \quad T_b = 225.6 K$$

$$v = 3 * 0.0148 \text{ m}^3 + 6 * 0.0037 \text{ m}^3 = 0.067 \text{ m}^3$$

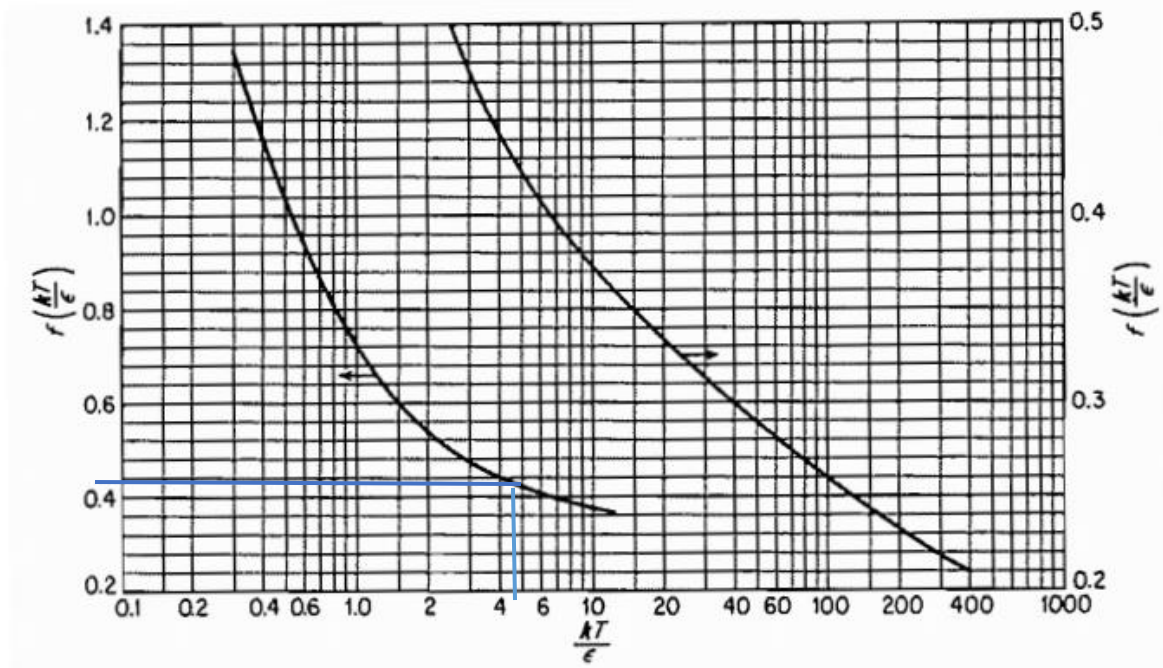
$$r = 1.18 v^{\frac{1}{3}} = 1.18 * 0.067^{\frac{1}{3}} = 0.5 \text{ nm}$$

$$\frac{\epsilon}{k} = 1.21 * 225.6 = 273 K$$

$$r_{C_3H_6--N_2} = \frac{(0.5 + 0.4) \text{ nm}}{2} = 0.45 \text{ nm}$$

$$\frac{\epsilon_{C_3H_6--N_2}}{k} = \sqrt{273 K * 71.4 K} = 140 K$$

$$\frac{kT}{\epsilon_{C_3H_6--N_2}} = \frac{(360 + 273)K}{140 K} = 4.52$$



$$f\left(\frac{kT}{\epsilon_{C_3H_6--N_2}}\right) = 0.42$$

For butane (C_4H_{10}):

$$M = 58 \frac{kg}{kmol} \quad T_b = 272 \text{ K}$$

$$v = 4 * 0.0148 \text{ m}^3 + 10 * 0.0037 \text{ m}^3 = 0.1 \text{ m}^3$$

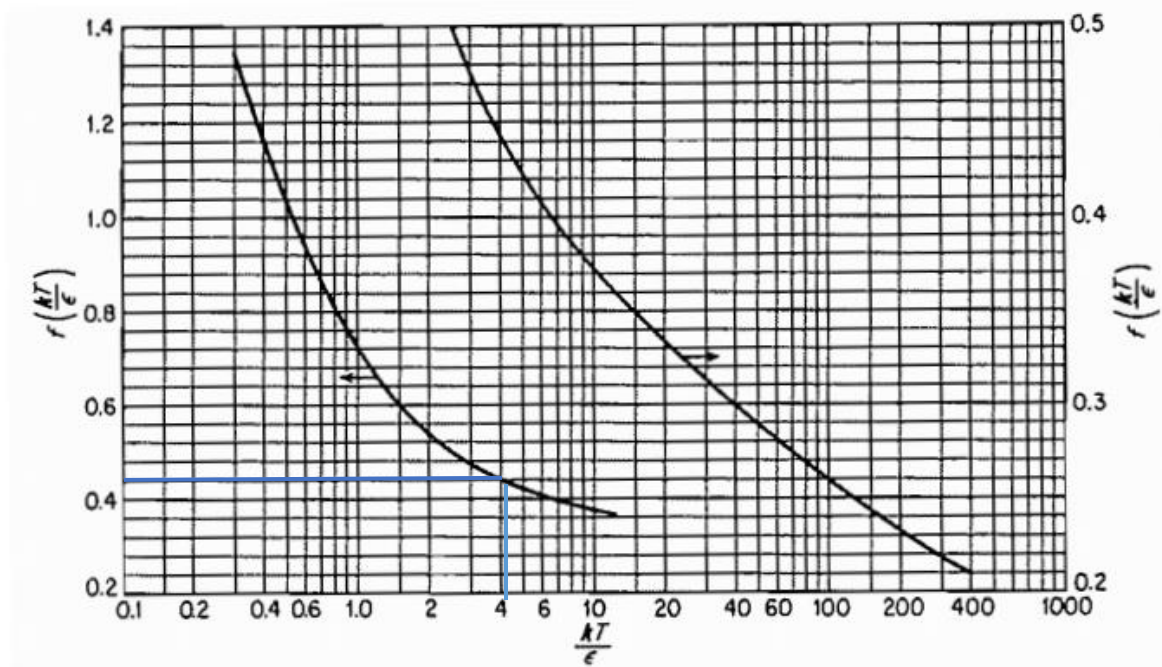
$$r = 1.18 v^{\frac{1}{3}} = 1.18 * 0.1^{\frac{1}{3}} = 0.5 \text{ nm}$$

$$\frac{\epsilon}{k} = 1.21 * 272 = 329 \text{ K}$$

$$r_{C_4H_{10}--N_2} = \frac{(0.5 + 0.4) \text{ nm}}{2} = 0.45 \text{ nm}$$

$$\frac{\epsilon_{C_4H_{10}--N_2}}{k} = \sqrt{329 \text{ K} * 71.4 \text{ K}} = 153 \text{ K}$$

$$\frac{kT}{\epsilon_{C_4H_{10}--N_2}} = \frac{(360 + 273) \text{ K}}{153 \text{ K}} = 4.1$$



$$f\left(\frac{kT}{\epsilon_{C_4H_{10}-N_2}}\right) = 0.42$$

For toluene (C_7H_8):

$$M = 92 \frac{kg}{kmol} \quad T_b = 384 K$$

$$v = 7 * 0.0148 m^3 + 8 * 0.0037 m^3 = 0.13 m^3$$

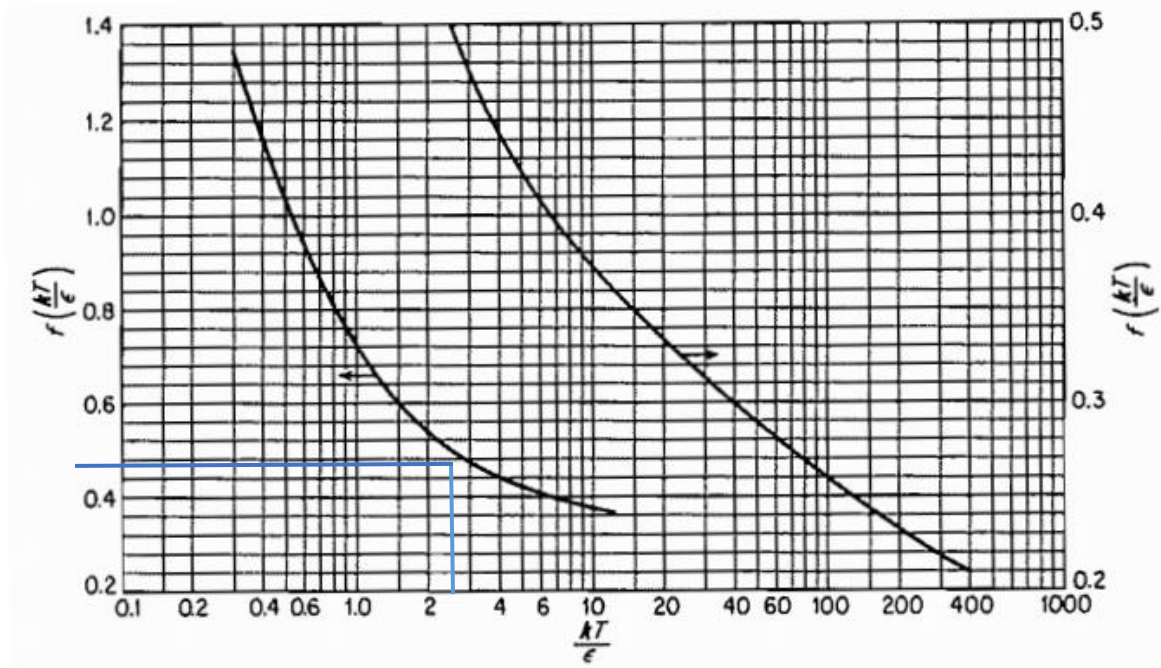
$$r = 1.18 v^{\frac{1}{3}} = 1.18 * 0.13^{\frac{1}{3}} = 0.6 nm$$

$$\frac{\epsilon}{k} = 1.21 * 384 = 465 K$$

$$r_{C_7H_8--N_2} = \frac{(0.6 + 0.4) nm}{2} = 0.5 nm$$

$$\frac{\epsilon_{C_7H_8--N_2}}{k} = \sqrt{465 K * 71.4 K} = 182 K$$

$$\frac{kT}{\epsilon_{C_7H_8--N_2}} = \frac{(360 + 273)K}{182 K} = 3.5$$



$$f\left(\frac{kT}{\epsilon_{C_4H_{10}-N_2}}\right) = 0.44$$

Finally, diffusivities can be calculated:

$$D_{C_3H_6--N_2} = \frac{10^{-4} * \left(1.084 - 0.249 * \sqrt{\left(\frac{1}{42} + \frac{1}{14}\right) \frac{kmol}{kg}}\right) * (633 K)^{\frac{3}{2}} * \sqrt{\left(\frac{1}{42} + \frac{1}{14}\right) \frac{kmol}{kg}}}{101325 Pa * (0.45 nm)^2 * 0.42}$$

$$D_{C_3H_6--N_2} = 1.2 * 10^{-5} \frac{m^2}{s}$$

$$D_{C_4H_{10}-N_2} = \frac{10^{-4} * \left(1.084 - 0.249 * \sqrt{\left(\frac{1}{58} + \frac{1}{14}\right) \frac{kmol}{kg}}\right) * (633 K)^{\frac{3}{2}} * \sqrt{\left(\frac{1}{58} + \frac{1}{14}\right) \frac{kmol}{kg}}}{101325 Pa * (0.45 nm)^2 * 0.42}$$

$$D_{C_4H_{10}-N_2} = 1.2 * 10^{-5} \frac{m^2}{s}$$

$$D_{C_7H_8--N_2} = \frac{10^{-4} * \left(1.084 - 0.249 * \sqrt{\left(\frac{1}{92} + \frac{1}{14}\right) \frac{kmol}{kg}}\right) * (633 K)^{\frac{3}{2}} * \sqrt{\left(\frac{1}{92} + \frac{1}{14}\right) \frac{kmol}{kg}}}{101325 Pa * (0.5 nm)^2 * 0.44}$$

$$D_{C_3H_6--N_2} = 1.5 * 10^{-5} \frac{m^2}{s}$$

Since nature of intermediates is difficult to determine, the diffusivity of intermediates is assumed to be the average of the three diffusivities calculated.

$$D_{I--N_2} = 1.3 * 10^{-5} \frac{m^2}{s}$$

These diffusivities were assumed for pure gaseous products with no interactions between them. Obtaining the exact value of diffusivities is very complicated and is out of the scope of this project. Therefore, the diffusivities were chosen to be the default of COMSOL when the products diffuse in nitrogen gas.

4c.3 Geometry

Geometry of reactor is the same as discussed in section (a) of this Chapter. A 2-D Axisymmetric geometry is chosen in COMSOL which ultimately gives the 3-D results.

4c.4 Boundary Conditions

Inlet flow: Nitrogen flow with velocity of U (Table 4c.1)

Outlet flow: Atmospheric pressure

Inflow: 5 mol/m³ of A

Outflow: No diffusion

4c.5 Physics

Laminar reacting flow (Brinkman Equation) with transport of diluted species were used as physics. Since the diluted species is used. Mixing time is negligible and it can be assumed that plastic mixtures are carried by the entering nitrogen gas.

4c.6 Input Data & Range of Changing Parameters

Input data:

Table 4c.1: Input Data for Simulation of Pyrolysis Reaction

Parameter	Value	Description
C_A_In-mol/m ³	5	Inlet concentration of A
W-g	1	Mass of catalyst
Dp-μm	100	Diameter of catalyst particle
U-m/s	0.00005	Inlet velocity of fluidizing gas

To investigate the effect of mass of catalyst, diameter of catalyst particle and inlet velocity of fluidizing gas on the concentration of reactants and products throughout the reactor, the parameters are changed within a range by parametric sweep option of COMSOL. The results are shown for each species.

Table 4c.2: Range of Changing Parameters

Parameter	Value Range	Description
W-g	0.1,0.25,0.5,1,5,10,15	Mass of catalyst
Dp-μm	50,100,200,300,400,500	Diameter of catalyst particle
U-m/s	0.00005, 0.0001, 0.0002,0.005,0.001	Inlet velocity of fluidizing gas

As stated in section (b), the operating temperature of reaction was 360°C.

Initially, the results of simulation with input data of Table 4c.1 are shown and discussed.

4c.7 Results

The below figure shows the concentration of waste plastic mixture, A, throughout the reactor:

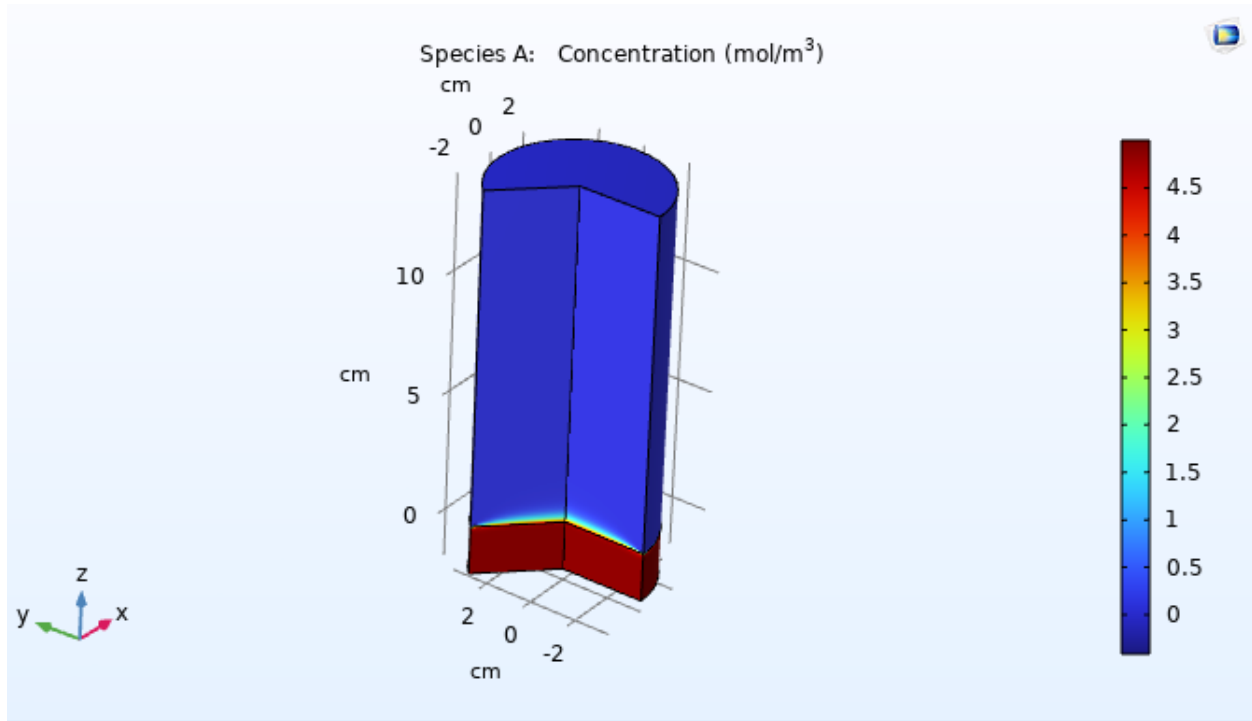


Figure 4c.1: Concentration Surface of A in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

The waste plastic mixture which contains HDPE, LDPE, PP, and PS is entered the reactor. This is observed that shortly after entering the reactor, most of the reactant converts to intermediate which is carbonium ions but as discussed before in section (b), some of the A converts to paraffins, P, aromatics, BTX and coke but not olefins, O.

The below figure shows the concentration of intermediate, I, throughout the reactor:

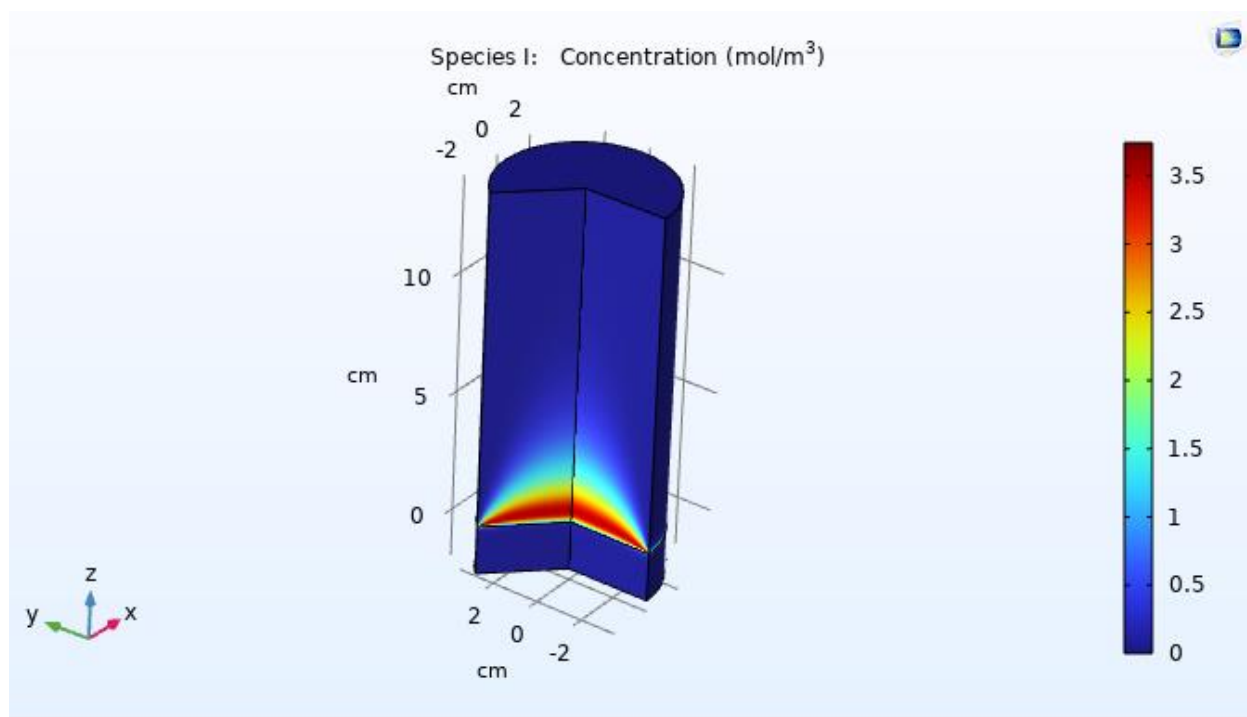


Figure 4c.2: Concentration Surface of I in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As stated before, the intermediate of catalytic pyrolysis is carbonium ion, which is the result of acidic activity of the catalyst. As it is observed from the above figure, there are no intermediates in the reactor initially as a result of entering the plastic mixture to the reactor and contacting to the catalyst surface, the intermediate, I, is produced. As the intermediate is produced, it is converted to the olefins, O, paraffins, P, aromatics, BTX and coke, by the mechanism discussed earlier.

The below figure shows the concentration of olefins, O, throughout the reactor:

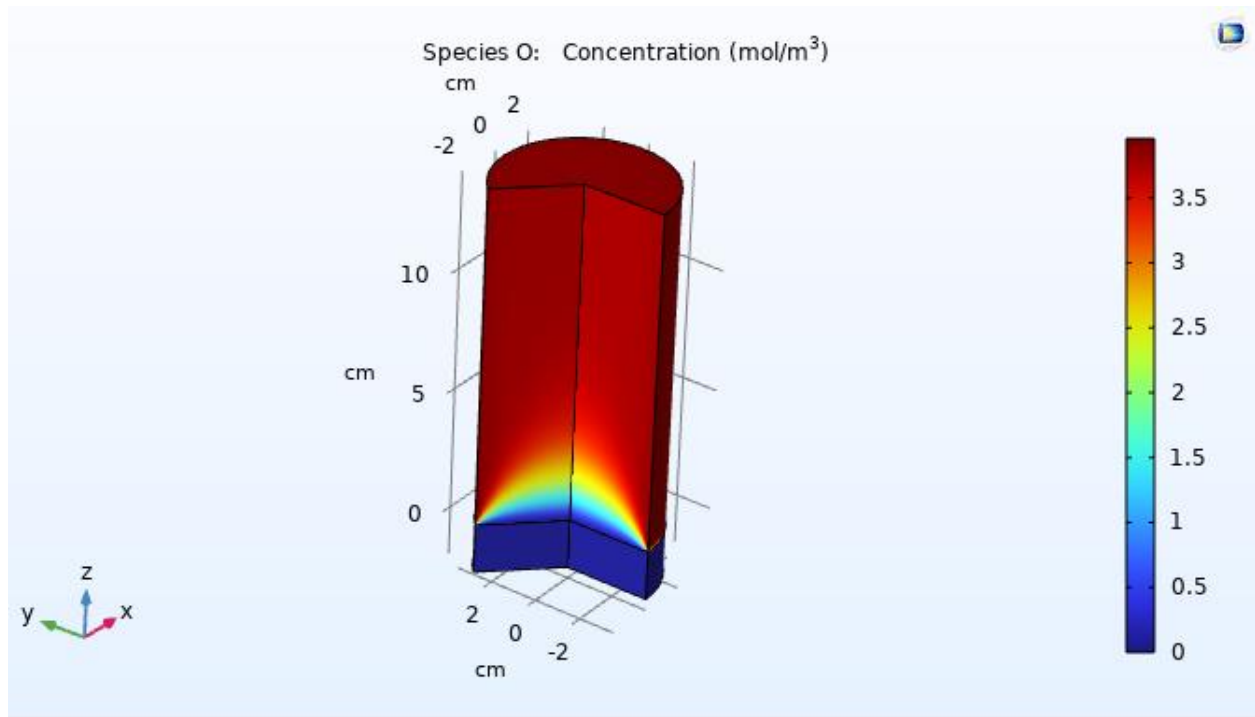


Figure 4c.3: Concentration Surface of O in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As known from section (b), the major products of simulated pyrolysis reaction are olefins which are selectively C3 and C4. The plastic mixture is not converted to olefins directly. The intermediates convert to olefins. The olefins are of special interest since they can be raw materials of polymerization plants to produce plastics again.

The below figure shows the concentration of paraffins, P, throughout the reactor:

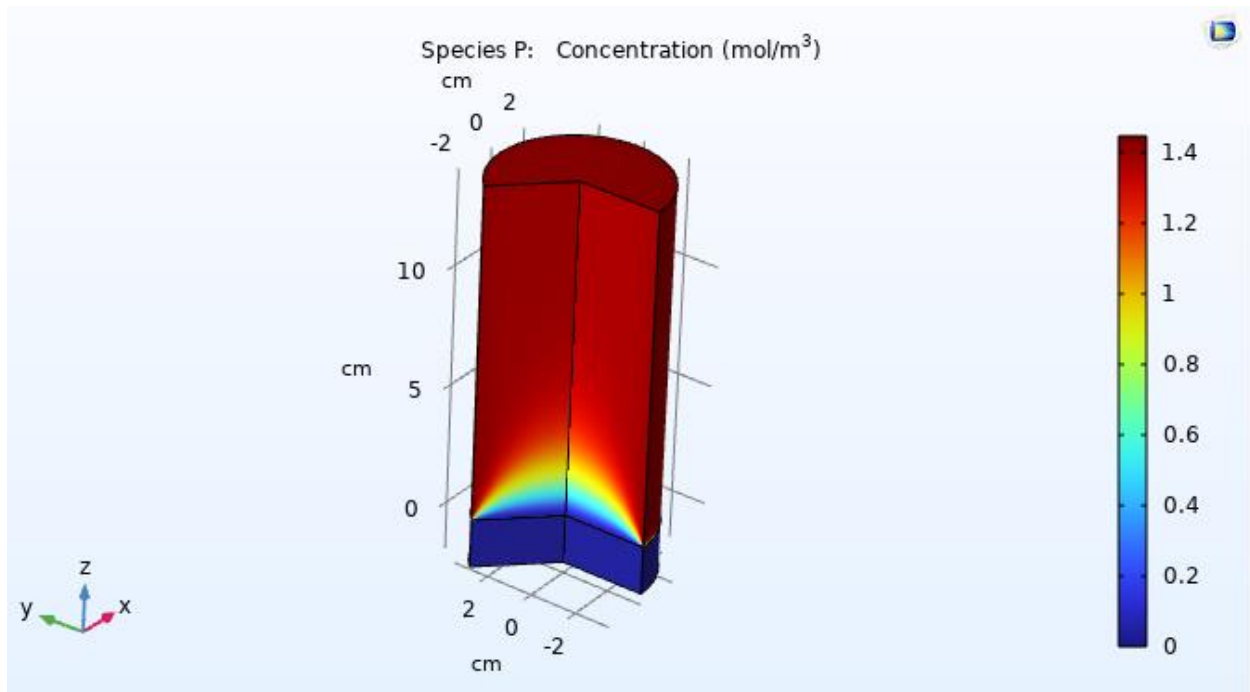


Figure 4c.4: Concentration Surface of P in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

The paraffins are the second major product of the simulated pyrolysis reaction after olefins. As discussed before, paraffins are majorly consist of C3, C4 and C5, which are good sources of fuels and petrochemical processes to produce olefins and other useful products.

The below figure shows the concentration of aromatics, BTX, throughout the reactor:

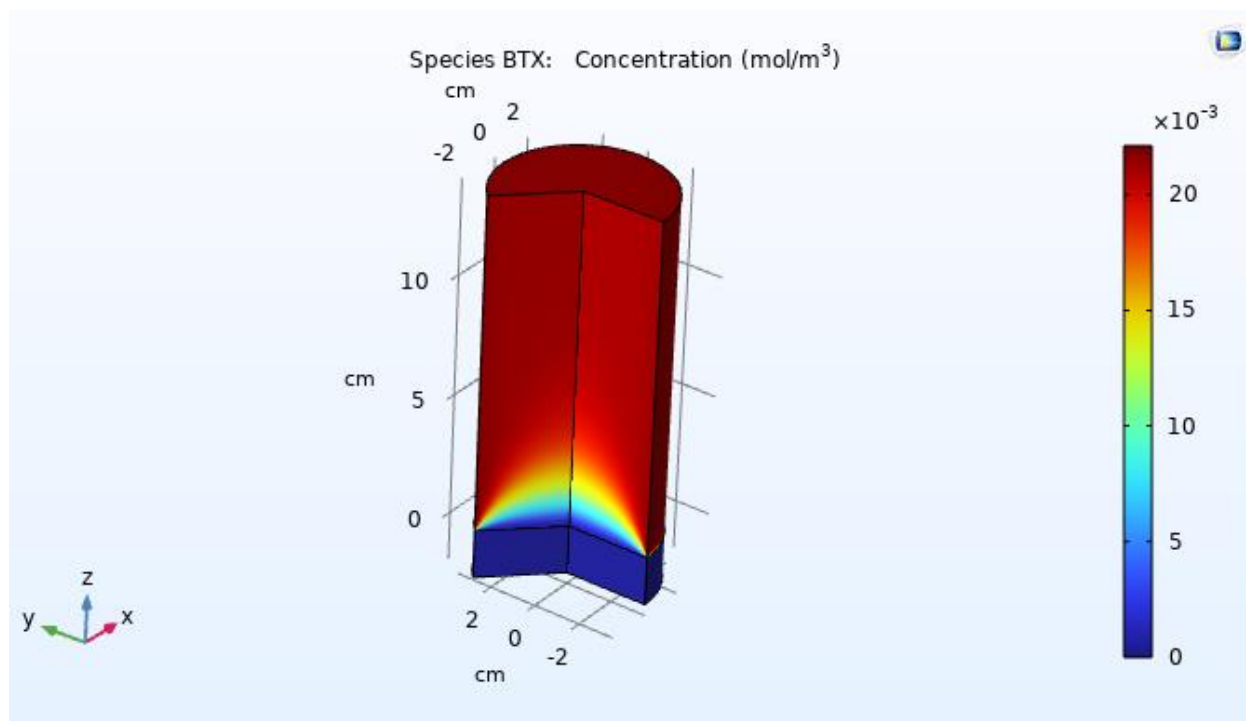


Figure 4c.5: Concentration Surface of BTX in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

The amount of aromatics produced is very little and insignificant compared to the olefins and paraffins. Both the initial plastic mixture and the intermediates convert to aromatics. Aromatics are also used in petrochemical processes. Benzene is used as a reactant in the production of styrene which is ultimately used to produce polystyrene.

The below figure shows the concentration of coke, C, throughout the reactor:

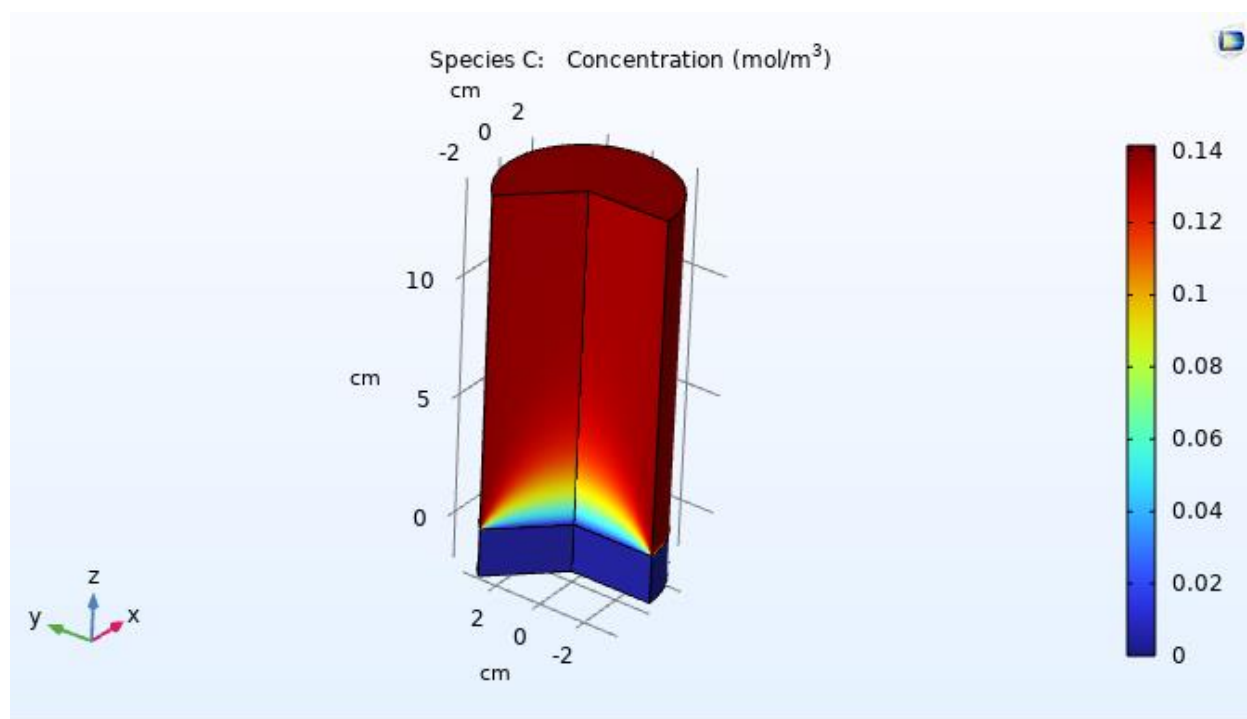


Figure 4c.6: Concentration Surface of C in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

Coke is produced in more amount than the aromatics in the simulated pyrolysis reaction but still the amount produced is insignificant compared to the olefins and paraffins which is satisfactory since coke deposition on catalyst surface causes catalyst deactivation by blocking of the pores of the catalyst. As discussed in section (b), coke deposition decreases the reaction rate exponentially, hence catalyst regeneration is necessary which is not discussed in this thesis. Both the initial plastic mixture and the intermediates convert to coke.

Overall, HZSM-5 is an excellent catalyst since it favors the formation of light hydrocarbons, especially light olefins. This is the result of small pore size of the catalyst which hinders bimolecular reactions and formation of large hydrocarbons. Having small pore size also results in low formation of coke which is desirable. Since coke is an unwanted product which cause catalyst deactivation.

The required mass of the catalyst is an important factor which affects the rate of reaction. The mass of catalyst was changed to observe the changes in reaction rate throughout the reactor.

The effect of mass of the catalyst on the rate of consumption of plastic mixture, A, is shown below:

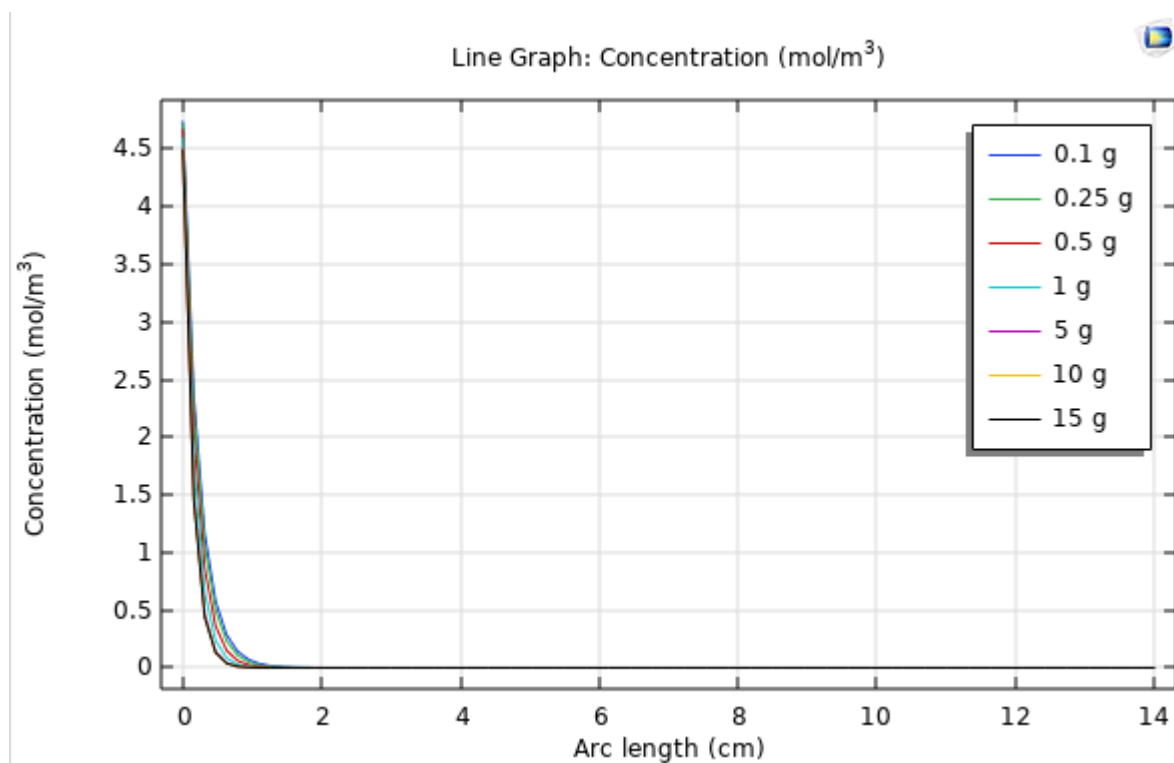


Figure 4c.7: The Effect of Mass of Catalyst on the Rate of Consumption of Plastic Mixture, A, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

It appears that the rate of consumption of plastic mixture is not much affected by altering the mass of catalyst. This was predictable based on the results obtained previously. By looking back to figure 35, it is observed that the plastic mixture readily participated in the reaction and converted to the intermediates, paraffins, aromatics and coke. Among which intermediates have the most share. It is interesting because polymeric materials are known to be hardly reactive in an inert environment and in the absence any acidic material that can act as cracking catalyst. Hence the presence of a catalyst, even in small amount, causes plastics to rapidly be converted to carbonium ions mostly are the intermediates of catalytic pyrolysis. When the lowest amount of catalyst, 0.1 g, is used, the plastic mixture is fully consumed approximately at the 1.7cm length of reactor. And when the highest amount of catalyst, 15 g, is used, the plastic mixture is fully converted approximately at the 1.3cm length of reactor.

The effect of mass of the catalyst on the rate of production & consumption of intermediates, I, is shown below:

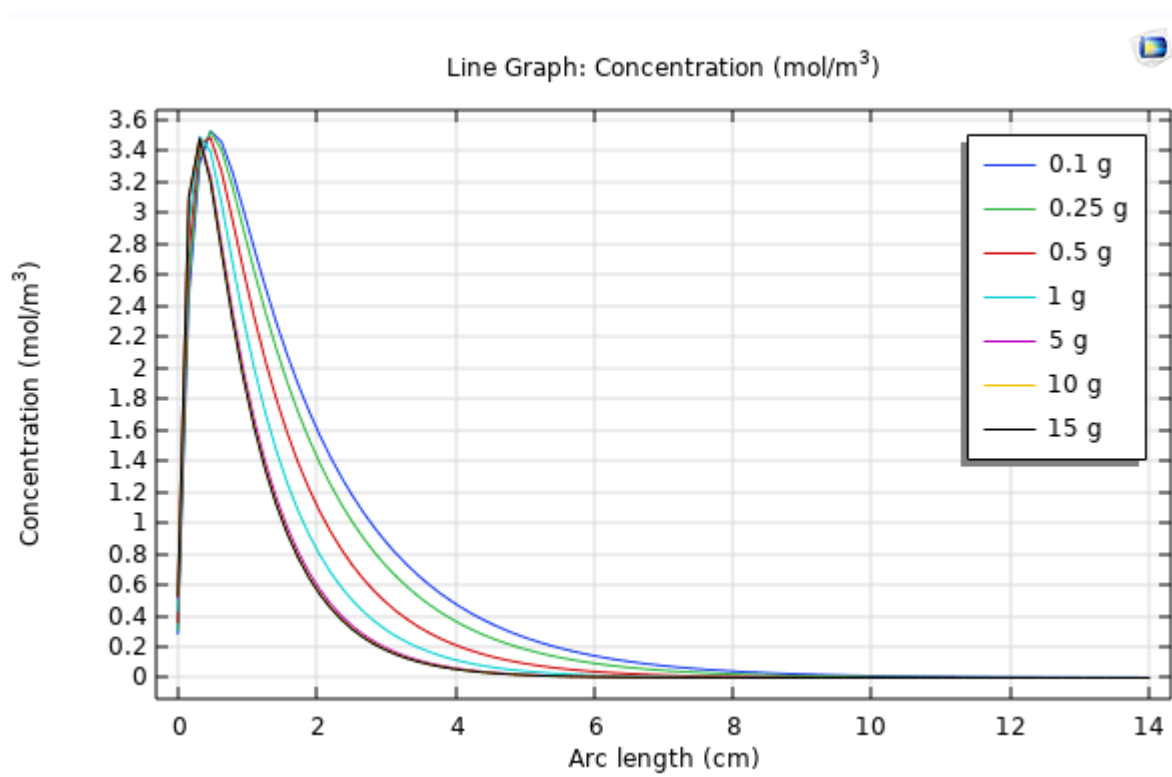


Figure 4c.8: The Effect of Mass of Catalyst on the Rate of Production & Consumption of Intermediates, I, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As it is interestingly observed, the rate of production of the intermediates is hardly affected by altering the mass of catalyst. This can be related to the results obtained for the effect of mass of catalyst on the rate of consumption of plastic mixture. As stated, the mass of catalyst does not have much effect on the rate of consumption of plastics. And this is known from kinetics of reaction that the plastic mixture is mostly converted to the intermediates and the direct conversion of plastics to paraffins, olefins, aromatics and coke is insignificant compared to the intermediates. Hence the rate of consumption of plastics is directly related to the rate of production of the intermediates. And it makes sense that both of them have similar response to the change of mass of catalyst. The production of the intermediates reaches a peak at 1.3cm length of reactor which is approximately the same length where the plastics are fully converted. Interestingly, the rate of consumption of the intermediates is much more affected by changing the mass of catalyst. The rate of consumption of the intermediates is increased by increasing the mass of catalyst from 0.1 to 5 g. Increasing the mass of catalyst further to 15 g has negligible effect on the rate of consumption of the intermediates. Since the consumption of intermediates is associated with production of products such as olefins and paraffins. It is predictable that the rate of production of all products is increased by increasing the mass of catalyst in the same manner that the rate of consumption of the intermediates increased by increasing the mass of catalyst. When the lowest amount of catalyst, 0.1 g, is used, the intermediates are fully consumed approximately at the 8cm length of reactor. And when the highest amount of catalyst, 15 g, is used, the intermediates are fully consumed approximately at the 4.2cm length of reactor.

The effect of mass of catalyst on the rate of production of olefins, O:

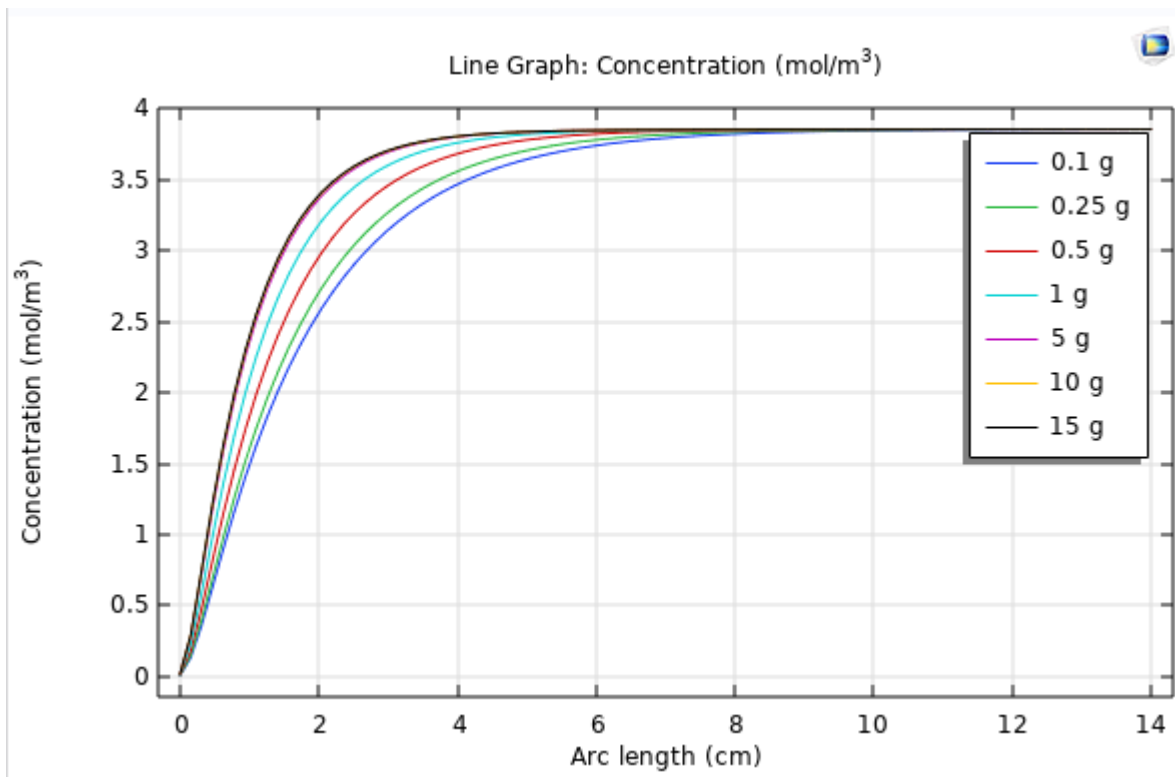


Figure 4c.9: The Effect of Mass of Catalyst on the Rate of Production of Olefins, O, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As it was predicted, the rate of production of olefins is increased by increasing the mass of catalyst from 0.1 to 5 g. Increasing the mass of catalyst to 15 g has negligible effect on the rate of production of olefins. When the lowest amount of catalyst, 0.1 g, is used, the rate of production of olefins reaches a peak approximately at the 8 cm length of reactor. And when the highest amount of catalyst, 15 g, is used, the rate of production of olefins reaches a peak approximately at the 4.2 cm length of reactor which is in correspondence with the rate of consumption of the intermediates.

The effect of mass of catalyst on the rate of production of paraffins, P:

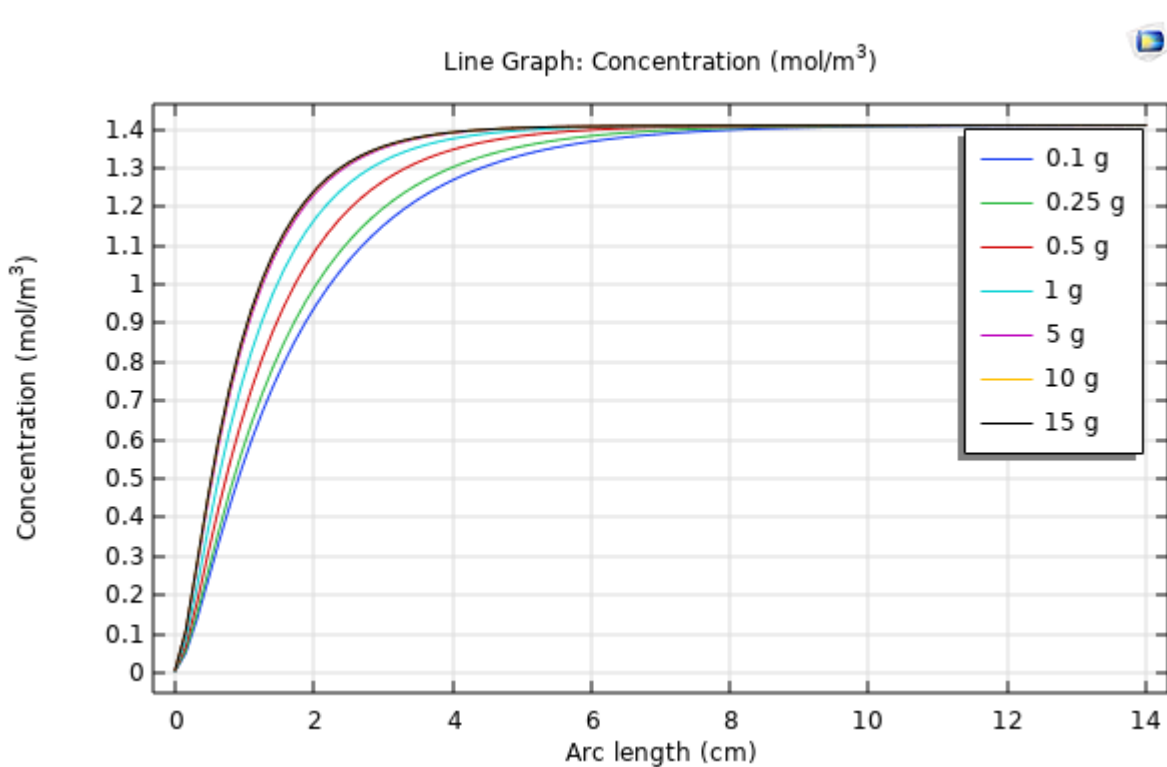


Figure 4c.10: The Effect of Mass of Catalyst on the Rate of Production of Paraffins, P, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As it was the case for olefins, the rate of production of paraffins is increased by increasing the mass of catalyst from 0.1 to 5 g. Further increase in the mass of catalyst to 15 g has negligible effect on the rate of production of paraffins. When the lowest amount of catalyst, 0.1 g, is used, the rate of production of paraffins reaches a peak approximately at the 8 cm length of reactor. And when the highest amount of catalyst, 15 g, is used, the rate of production of paraffins reaches a peak approximately at the 4.2 cm length of reactor which is in correspondence with the rate of consumption of intermediates.

The effect of mass of catalyst on the rate of production aromatics and coke will be discussed together:

The effect of mass of catalyst on the rate of production of aromatics, BTX:

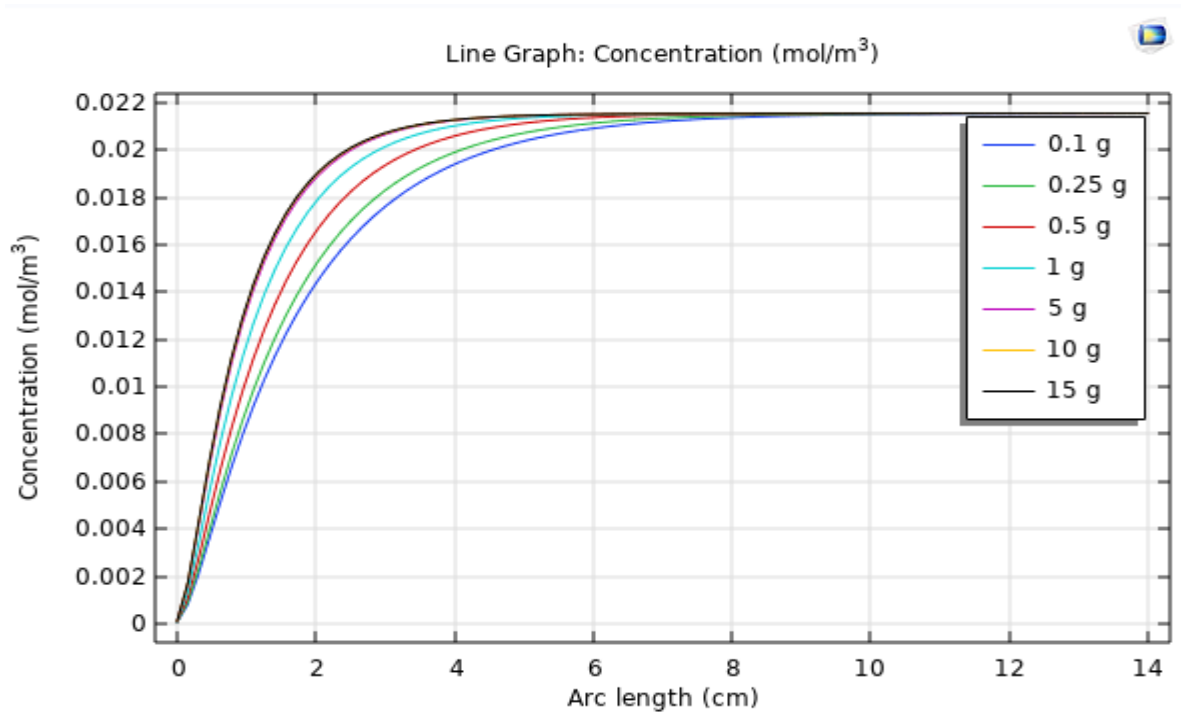


Figure 4c.11: The Effect of Mass of Catalyst on the Rate of Production of Aromatics, BTX, in Pyrolysis reaction of Waste Plastic Mixture at 360°C.

The effect of mass of catalyst on the rate of production of coke, C:

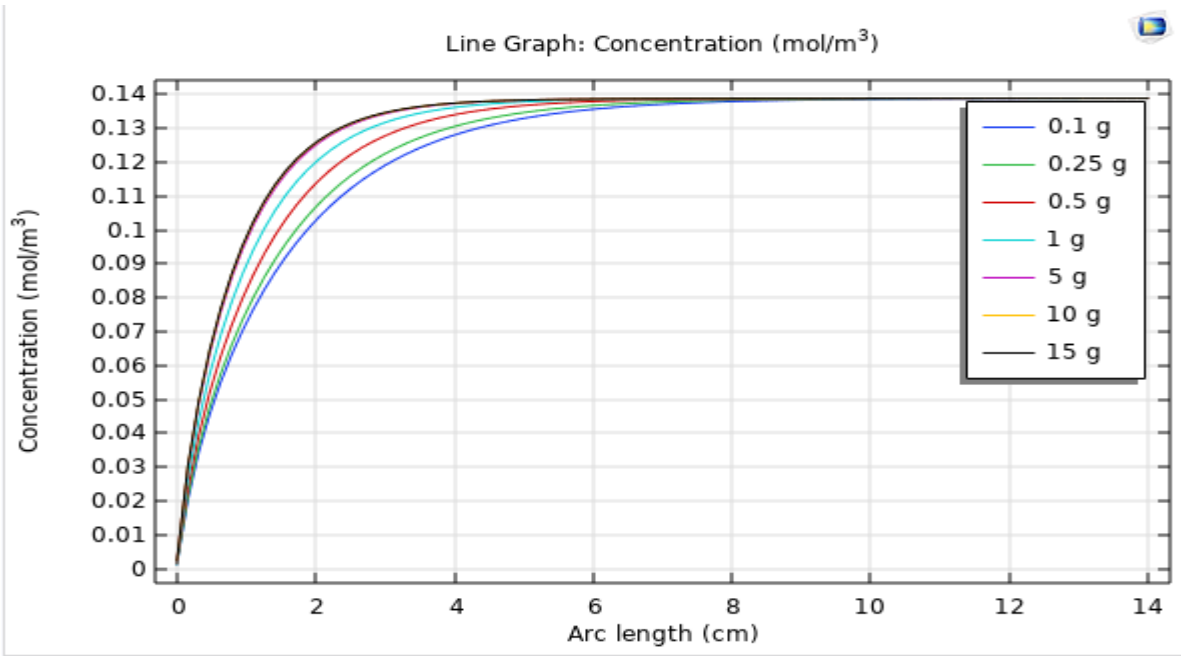


Figure 4c.12: The Effect of Mass of Catalyst on the Rate of Production of Coke, C, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

Production of aromatics and coke over HZSM-5 in pyrolysis reaction has the same trend as the production of olefins and paraffins. It should be noted that although increasing the mass of catalyst results in increasing the rate of production of the desirable products such as olefins, paraffins and aromatics, it also results in increasing the rate of production of coke which is an unwanted product. Since coke causes the deactivation of the catalysts, regeneration process is necessary and it may be concluded that with more amount of coke, the regeneration process would be more time-consuming and energy intensive which is clearly a drawback.

To investigate the effect of particle diameter of catalyst, this parameter was changed to observe the changes in the reaction rate throughout the reactor.

The effect of particle diameter of catalyst on the rate of consumption of plastic mixture, A:

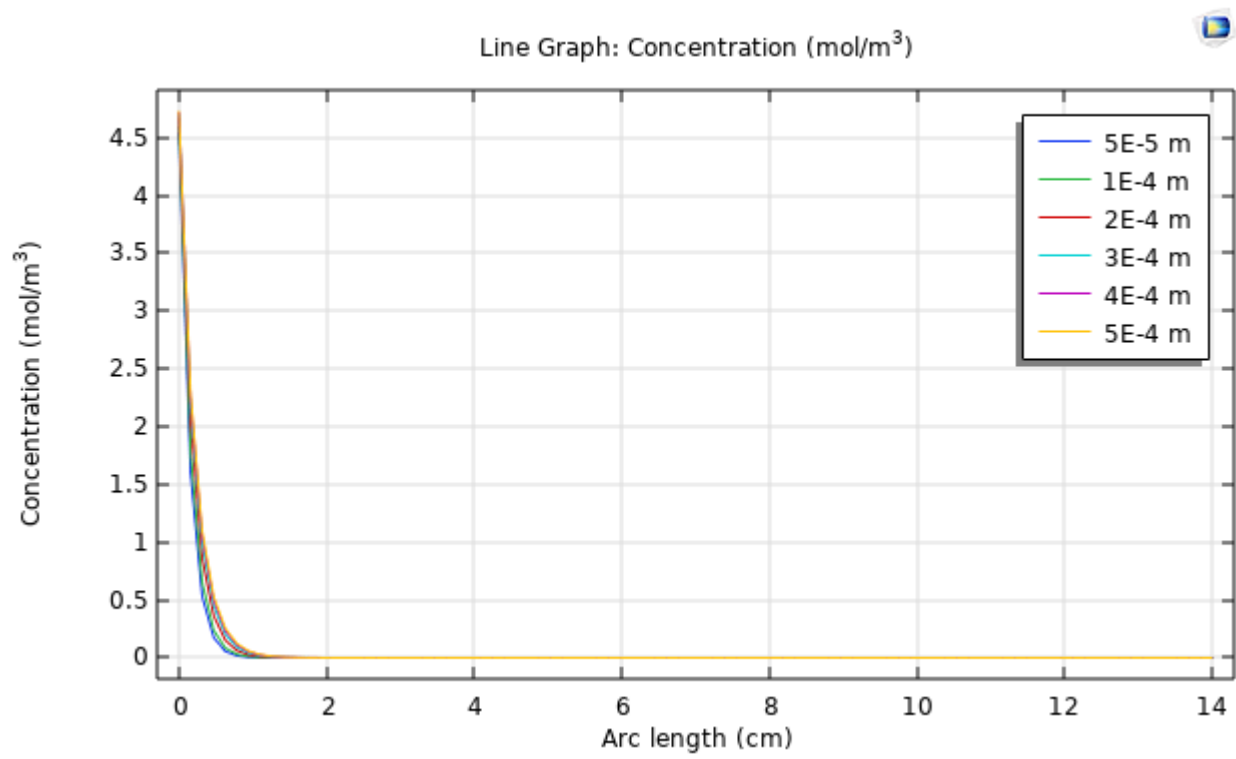


Figure 4c.13: The Effect of Particle Diameter of Catalyst on the Rate of Consumption of Plastic Mixture, A, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As it was the case for the effect of the mass of catalyst, it is observed that particle diameter of catalyst also has little effect on the rate of consumption of plastic mixture. Looking at Figure 35, plastic mixture is rapidly converted to the intermediates mostly, and minorly to paraffins, aromatics and coke. Hence the conversion of plastics occurs in the presence of catalyst even though the particle diameter is large. When the highest particle diameter, 0.5 mm is used, the plastic mixture is fully consumed approximately at the 1.7cm length of reactor. And when the smallest particle diameter, 50 μ m is used, the plastic mixture is fully consumed approximately at the 1.3cm length of reactor.

The effect of particle diameter of catalyst on the rate of production & consumption of the intermediates, I:

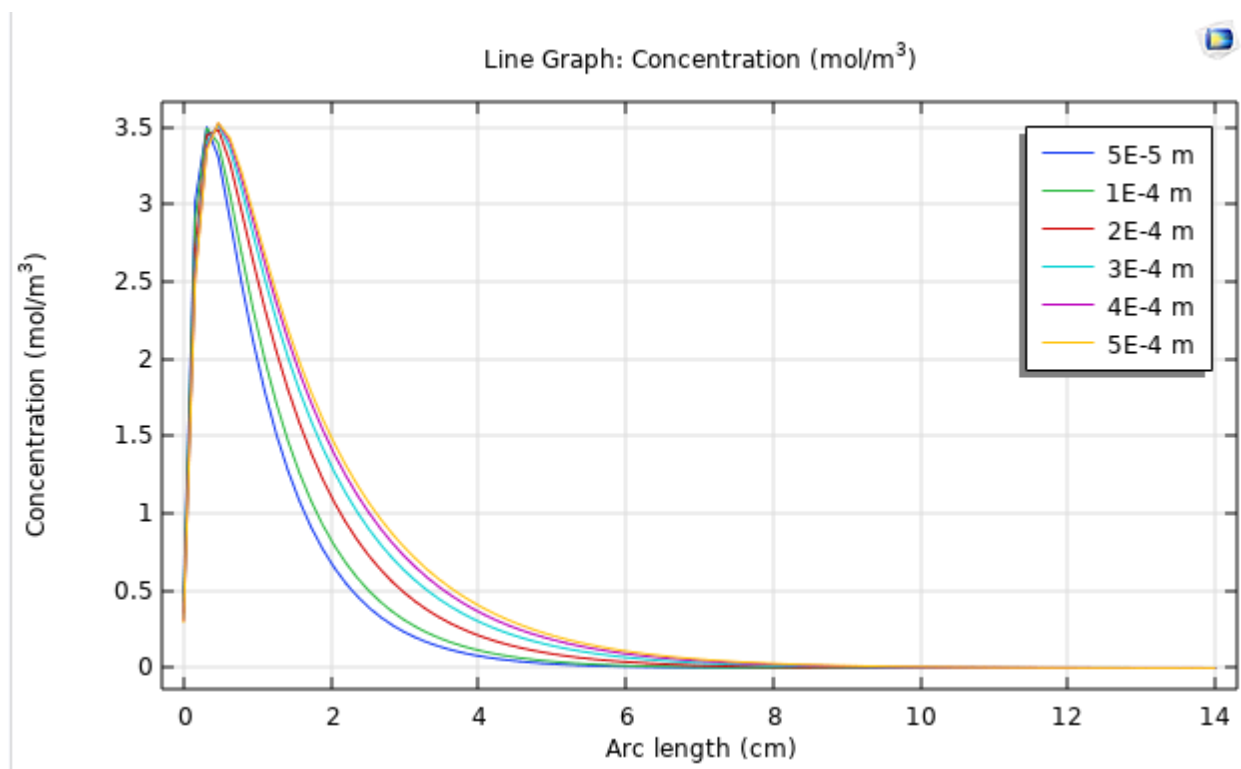


Figure 4c.14: The Effect of Particle Diameter of Catalyst on the Rate of Production & Consumption of Intermediates, I, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

It is interesting to note that the rate of production of the intermediates is hardly affected by altering the particle diameter of the catalyst. This can be related to the results obtained for the effect of particle diameter of catalyst on the rate of consumption of plastic mixture. As stated, the particle diameter of catalyst has minor effect on the rate of consumption of plastics. And this is known from kinetics of reaction that the plastic mixture is mostly converted to the intermediates and the direct conversion of plastics to paraffins, olefins, aromatics and coke is minimal compared to the intermediates. Hence the rate of consumption of plastics directly is related to the rate of production of intermediates. And it makes sense that both of them have similar response to the change of particle diameter of catalyst. The production of the intermediates reaches a peak at 1.3cm length of reactor which is approximately the same length where plastics are fully consumed. Interestingly, the rate of consumption of the intermediates is much more affected by changing the particle diameter of catalyst. The rate of consumption of the intermediates is increased by decreasing the particle diameter of catalyst from 0.5 mm to 50 μm . However, particles with diameter smaller than 50 μm are not suitable for fluidization since small particles have strong intermolecular forces which causes them to be inadequately fluidized. The consumption of the intermediates is associated with the production of products, such as olefins and paraffins. It is predictable that the rate of production of all products is increased by decreasing the particle diameter of catalyst in the same manner that the rate of consumption of the intermediates increased by decreasing the particle diameter of catalyst. The production of the intermediates reaches a peak approximately at the 1.3cm length of reactor, which is approximately the same length where plastics are fully consumed. When the largest particle diameter, 0.5 mm is used, the intermediates are fully consumed approximately at the

8cm length of reactor. And when the smallest particle diameter, 50 μm is used, the plastic mixture is fully consumed approximately at the 4.2cm length of reactor.

The effect of particle diameter of catalyst on the rate of production of olefins, O:

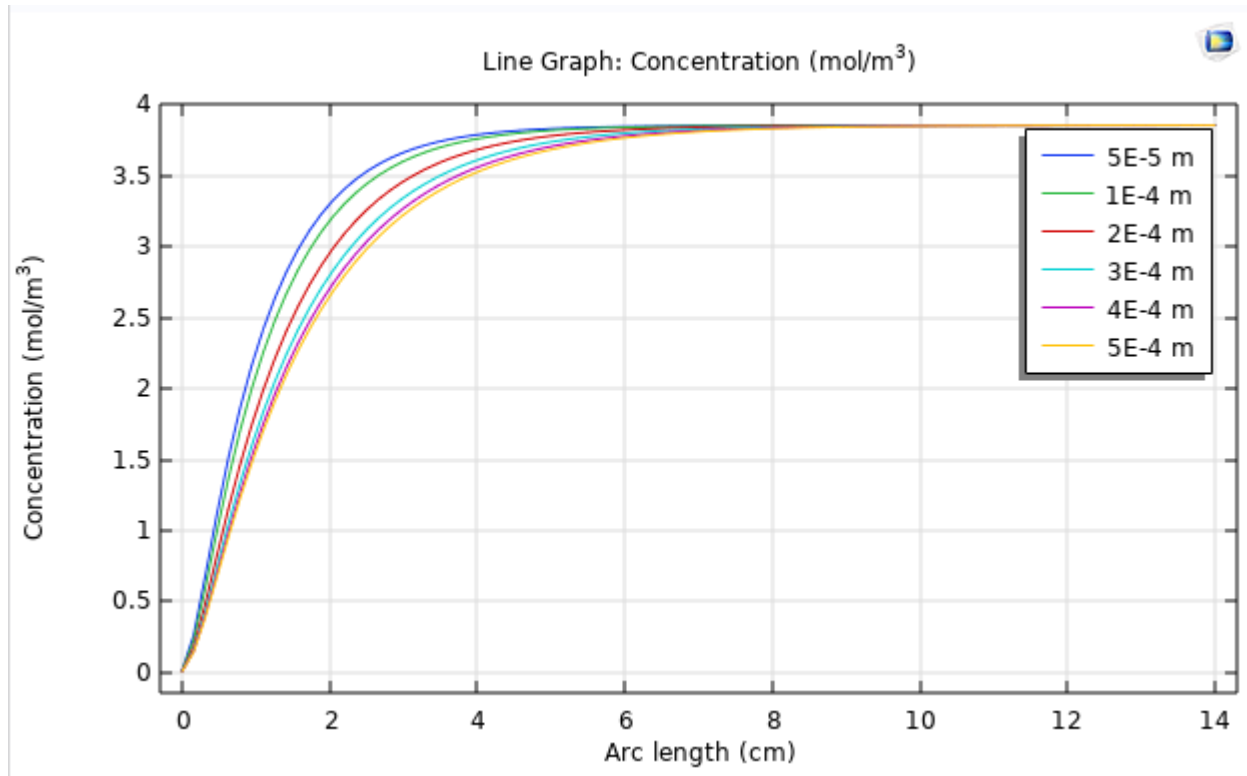


Figure 4c.15: The Effect of Particle Diameter of Catalyst on the Rate of Production of Olefins, O, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As it was predicted, the rate of production of olefins is increased by decreasing the particle diameter of catalyst from 0.5mm to 50 μm . When the largest particle diameter of catalyst, 0.5mm, is used, the rate of production of olefins reaches a peak approximately at the 8cm length of reactor. And when the smallest particle diameter of catalyst, 50 μm , is used, the rate of production of olefins reaches a peak approximately at the 4.2 cm length of reactor which corresponds to the rate of consumption of intermediates.

The effect of particle diameter of catalyst on the rate of production of paraffins, P:

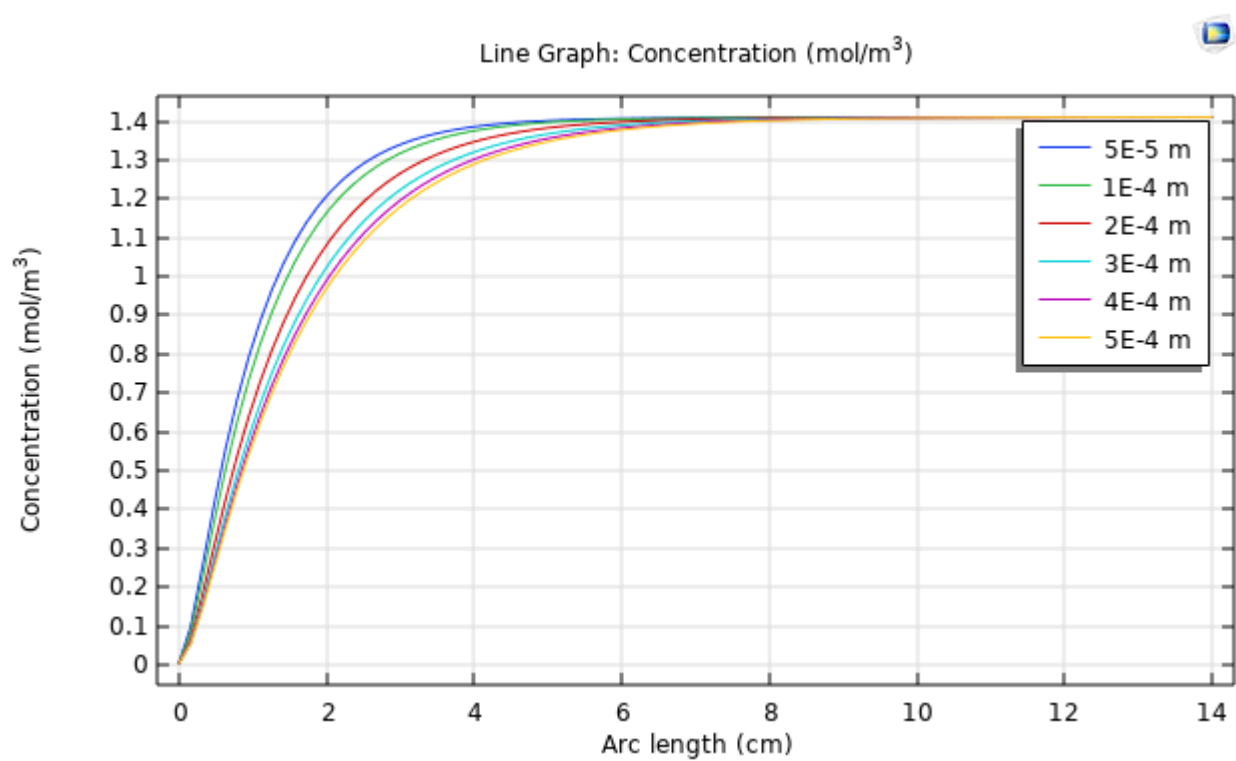


Figure 4c.16: The Effect of Particle Diameter of Catalyst on the Rate of Production of Paraffins, P, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As it was the case for olefins, the rate of production of paraffins is increased by decreasing the particle diameter of catalyst from 0.5mm to 50 μm . Using the largest particle diameter of catalyst, 0.5mm, the rate of production of paraffins reaches a peak approximately at the 8cm length of reactor. And when the smallest particle diameter of catalyst, 50 μm , is used, the rate of production of paraffins reaches a peak approximately at the 4.2 cm length of reactor corresponding to the rate of consumption of intermediates.

The effect of particle diameter of catalyst on the rate of production of aromatics and coke will be discussed together.

The effect of particle diameter of catalyst on the rate of production of aromatics, BTX:

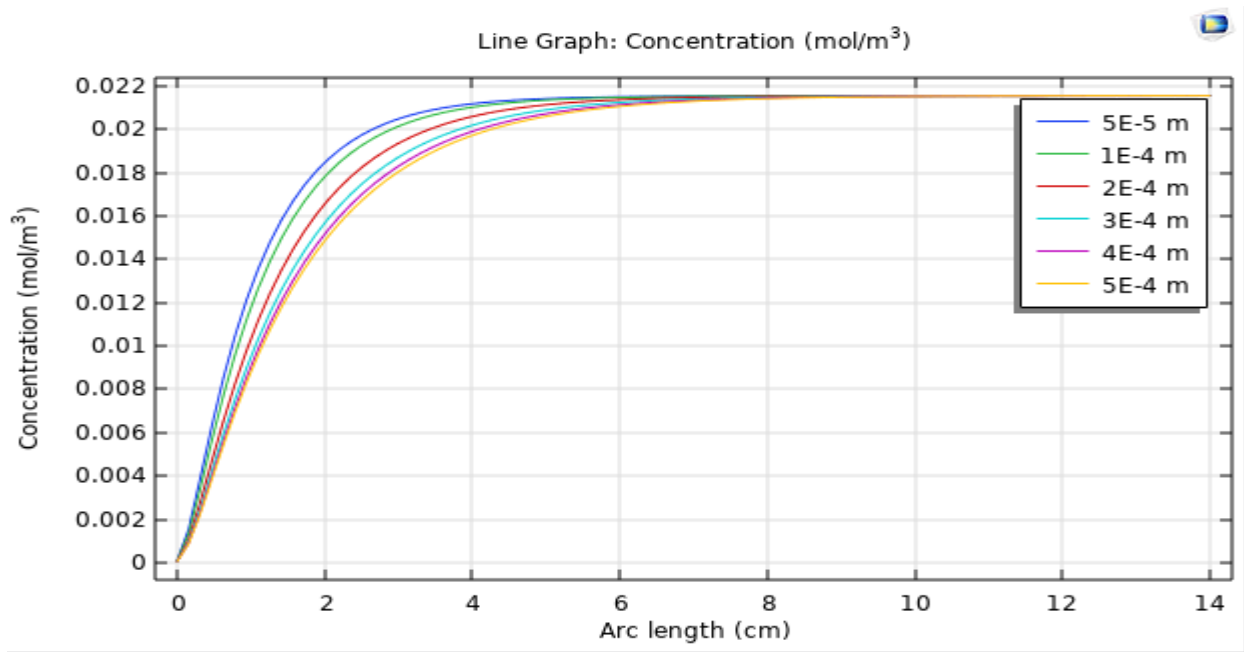


Figure 4c.17: The Effect of Particle Diameter of Catalyst on the Rate of Production of Aromatics, BTX, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

The effect of particle diameter of catalyst on the rate of production of coke, C:

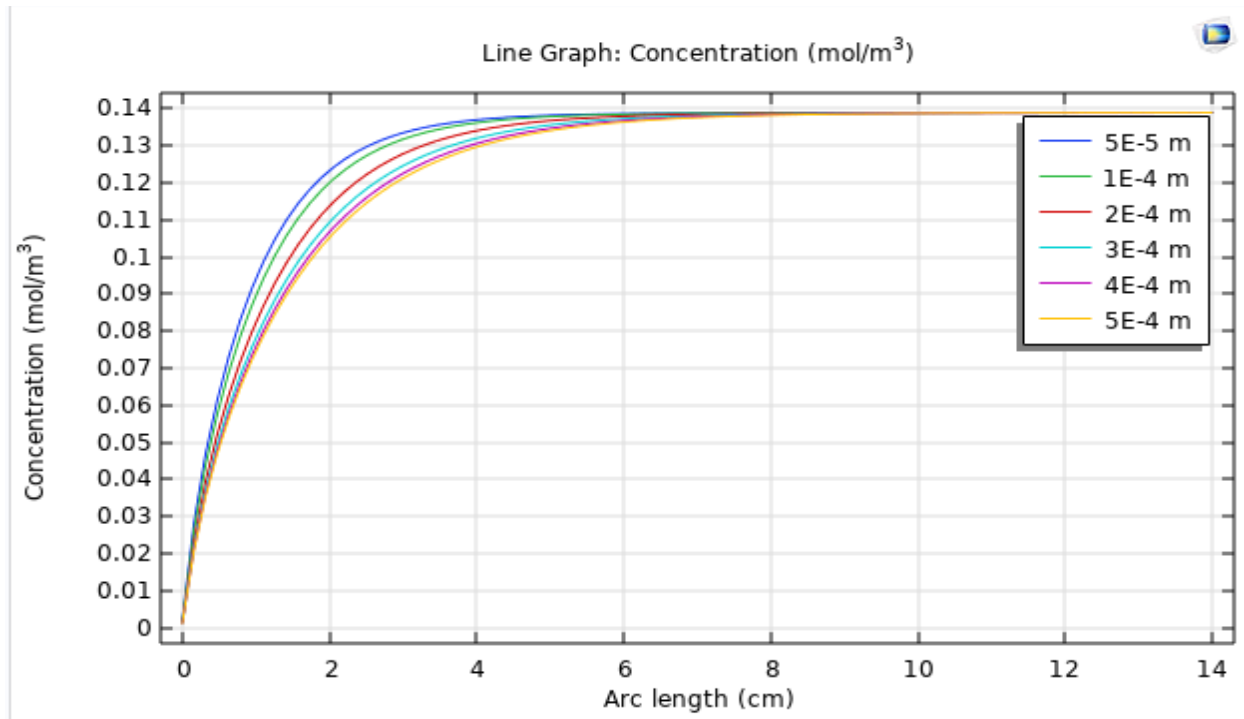


Figure 4c.18: The Effect of Particle Diameter of Catalyst on the Rate of Production of coke, C, in pyrolysis reaction of waste plastic mixture at 360°C.

Production of aromatics and coke over HZSM-5 in pyrolysis reaction has the same trend as the production of olefins and paraffins. It should be noted that although decreasing the particle diameter of catalyst results in increasing the rate of production of desirable products such as olefins, paraffins and aromatics, it also results in increasing the rate of production of coke which is an unwanted product. Since coke causes the deactivation of catalysts, regeneration process is necessary and it may be concluded that with more amount of coke, the regeneration process would be more time-consuming and energy intensive which is clearly a drawback.

To investigate the effect of inlet velocity of fluidizing gas, this parameter was changed to observe the changes in reaction rate throughout the reactor.

The effect of inlet velocity of fluidizing gas on the rate of consumption of plastic mixture, A:

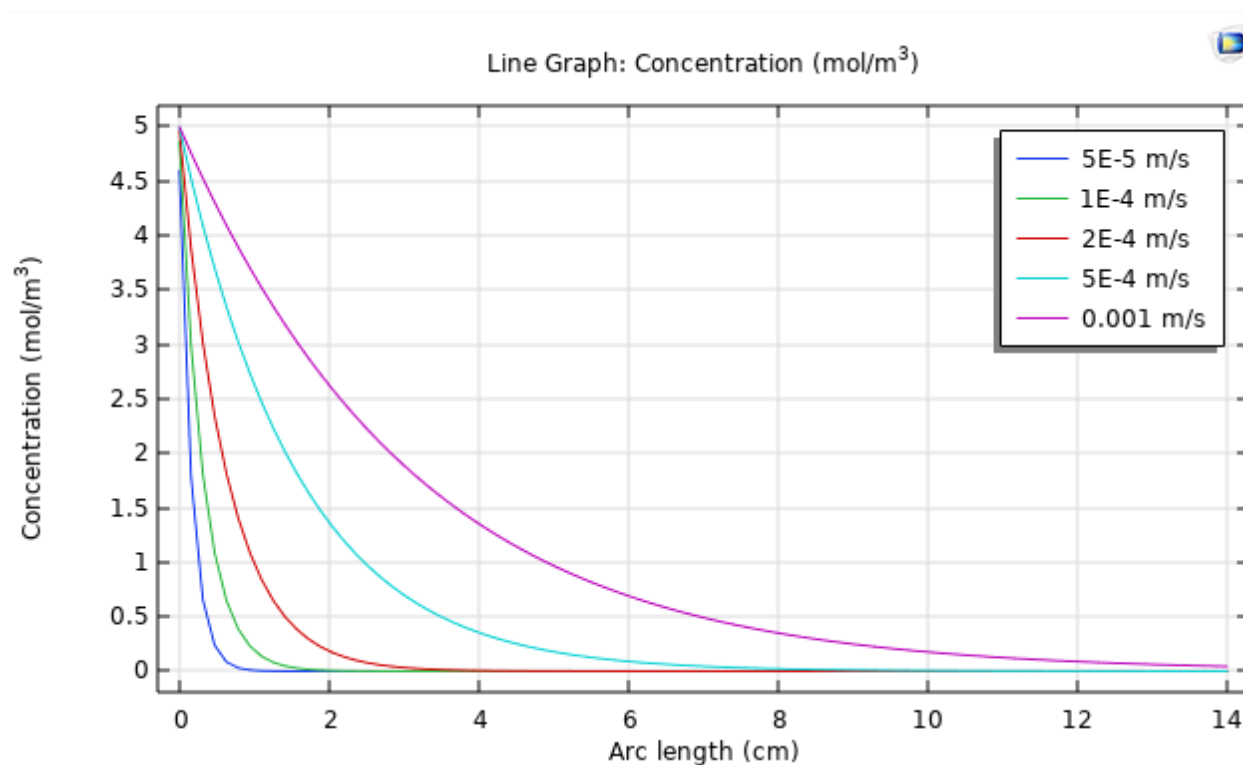


Figure 4c.19: The Effect of Inlet Velocity of Fluidizing Gas on the Rate of Consumption of Plastic Mixture, A, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

As it can be easily concluded, increasing the gas velocity, results in decreasing the reacted concentration of plastics. The same is true for production and consumption of the intermediates and production of olefins, paraffins, aromatics and coke.

The effect of inlet velocity of fluidizing gas on the rate of production & consumption of intermediates, I:

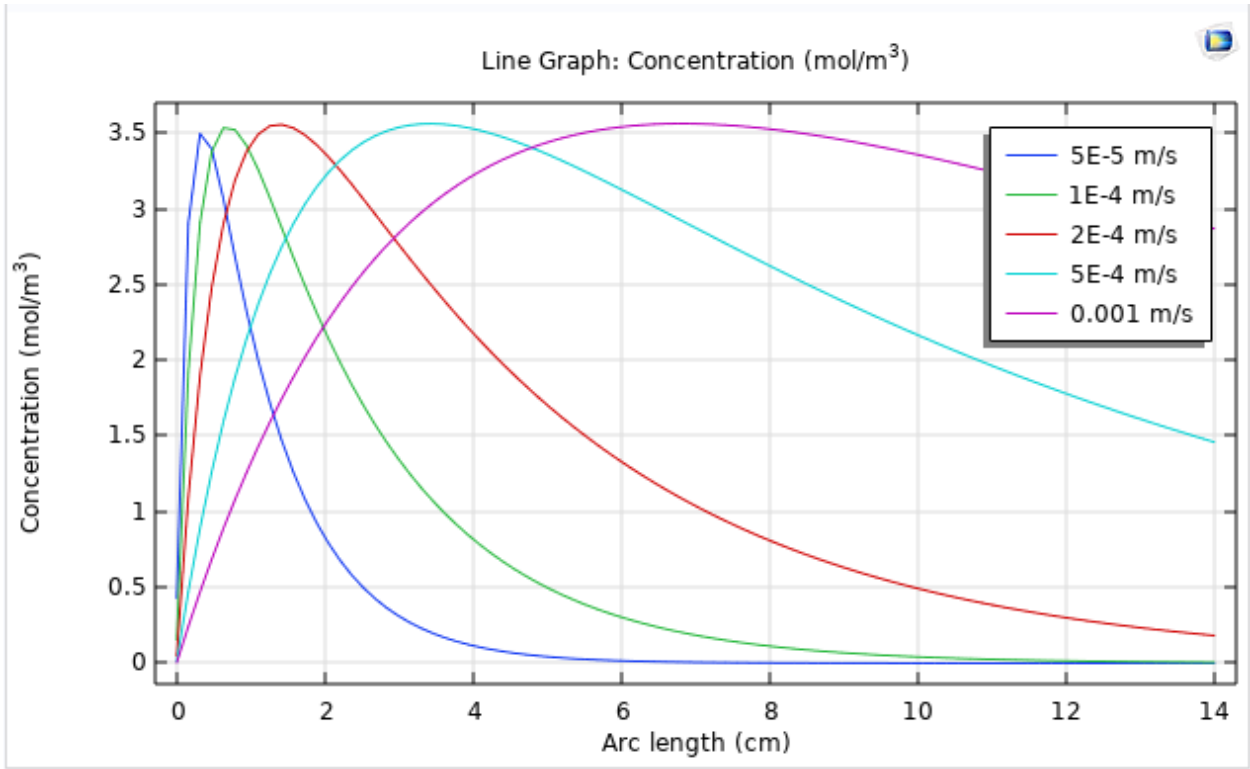


Figure 4c.20: The Effect of Inlet Velocity of Fluidizing Gas on the Rate of Production & Consumption of intermediates, I, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

Increasing the inlet velocity of fluidizing gas from 0.0001 m/s, results in incomplete conversion of the intermediates in the simulated tubular reactor with the length of 14 cm.

The effect of inlet velocity of fluidizing gas on the rate of production of olefins, O:

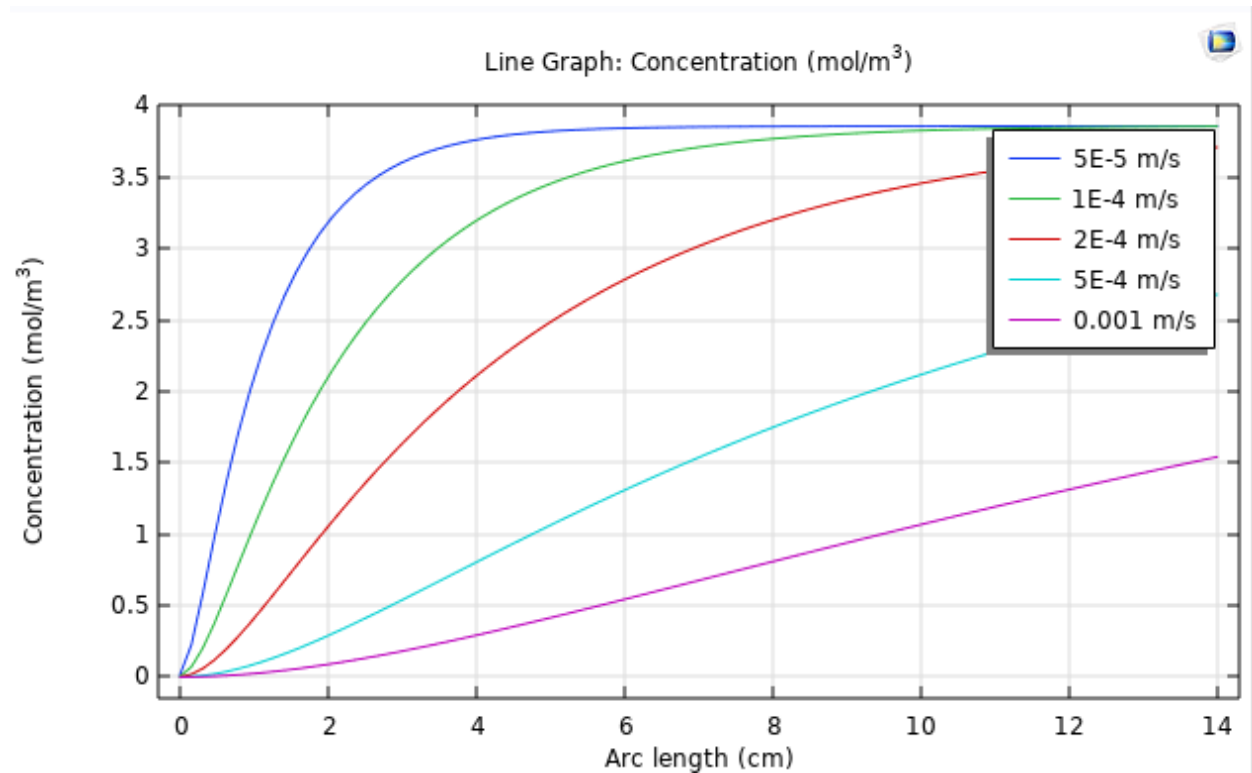


Figure 4c.21: The Effect of Inlet Velocity of Fluidizing Gas on the Rate of Production of Olefins, O, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

Increasing the inlet velocity of fluidizing gas from 0.0001 m/s, resulted in the olefins not to reach the expected peak in the simulated tubular reactor within the length of 14 cm.

The effect of inlet velocity of fluidizing gas on the rate of production of paraffins, P:

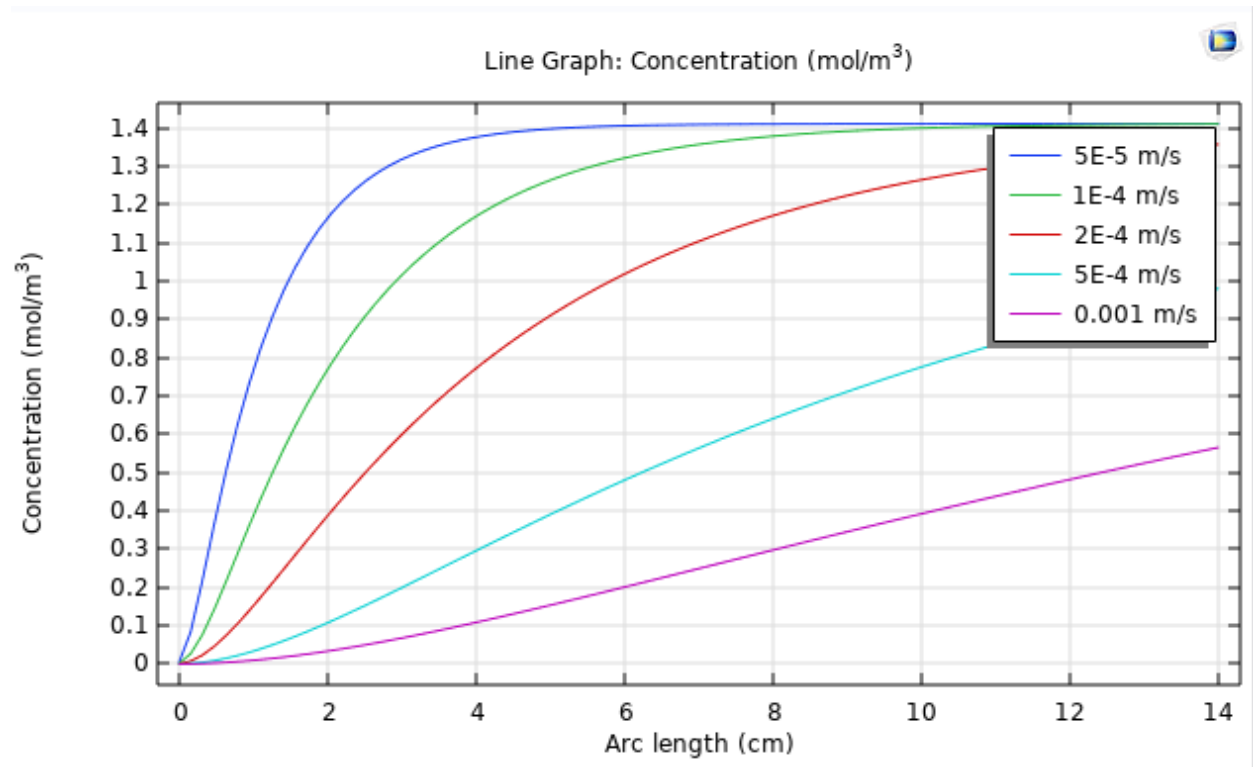


Figure 4c.22: The Effect of Inlet Velocity of Fluidizing Gas on the Rate of Production of Paraffins, P, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

Increasing the inlet velocity of fluidizing gas from 0.0001 m/s, resulted in the paraffins not to reach the expected peak in the simulated tubular reactor within the length of 14 cm.

The effect of inlet velocity of fluidizing gas on the rate of production of aromatics, BTX:

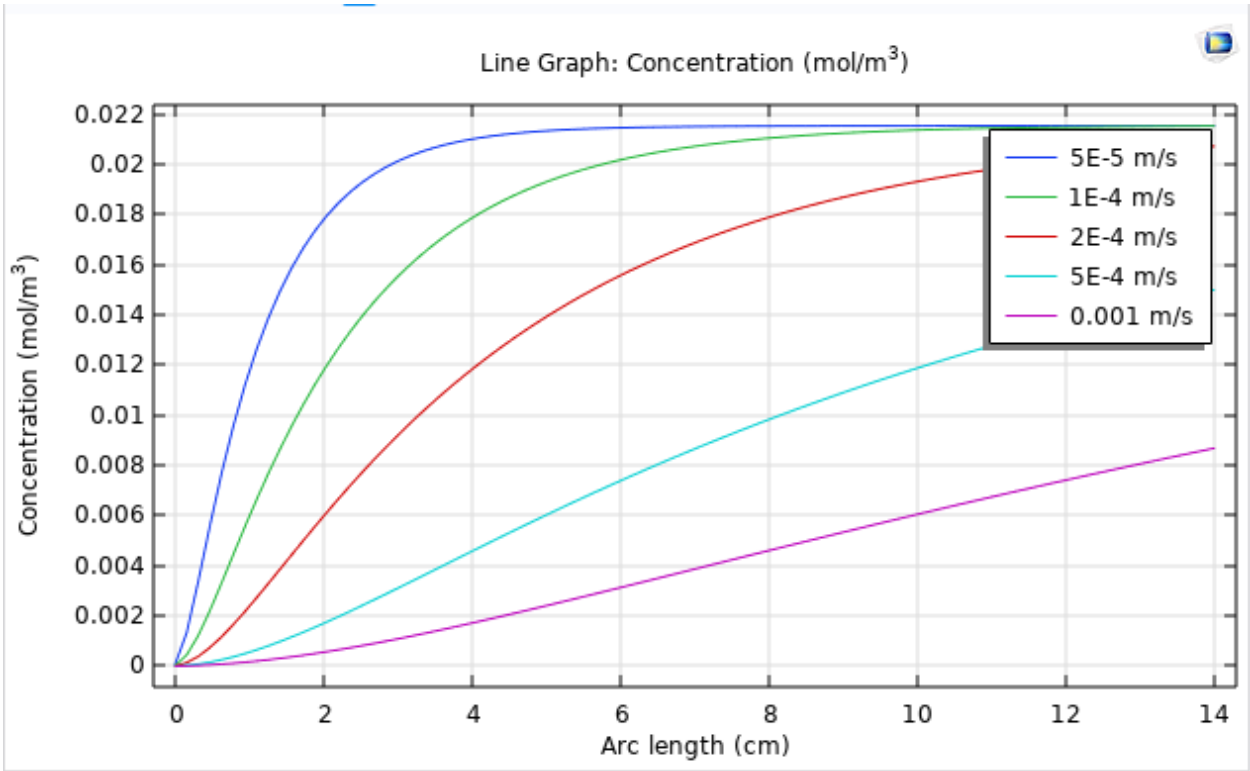


Figure 4c.23: The Effect of Inlet Velocity of Fluidizing Gas on the Rate of Production of Aromatics, BTX, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

Increasing the inlet velocity of fluidizing gas from 0.0001 m/s, resulted in the aromatics not to reach the expected peak in the simulated tubular reactor within the length of 14 cm.

The effect of inlet velocity of fluidizing gas on the rate of production of coke, C:

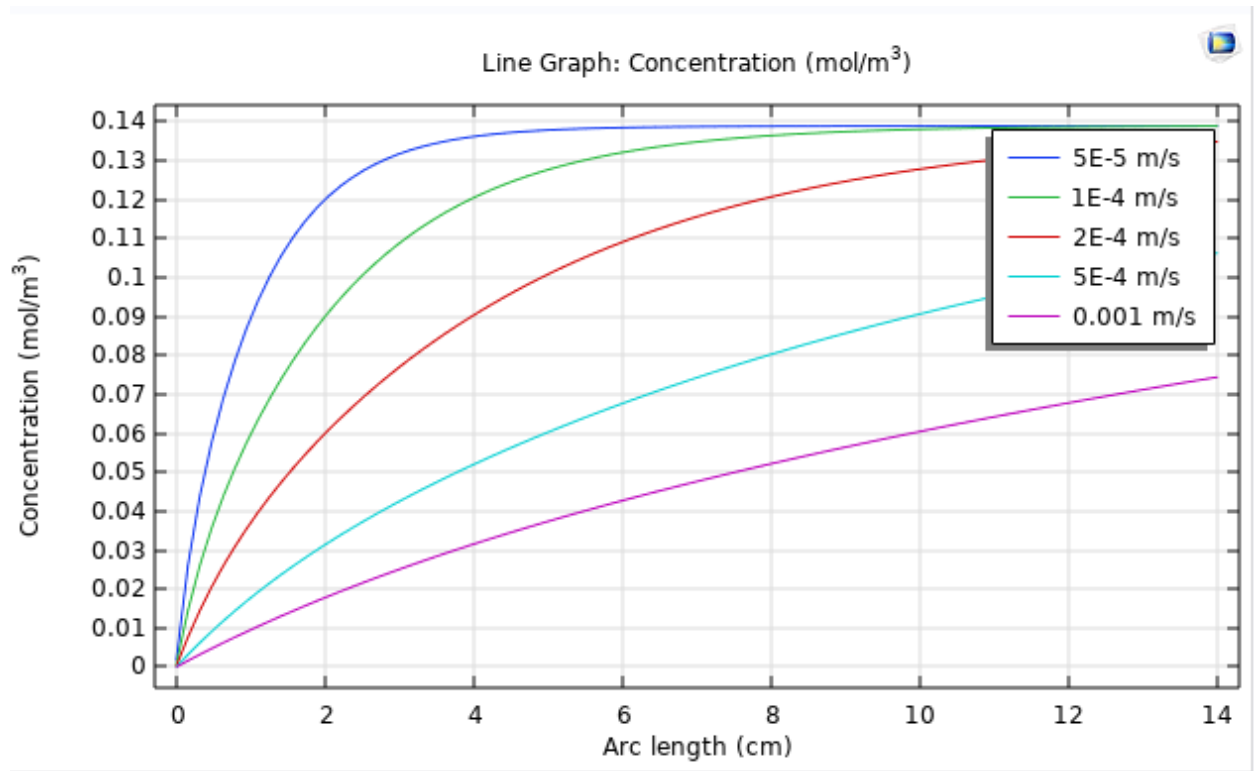


Figure 4c.24: The Effect of Inlet Velocity of Fluidizing Gas on the Rate of Production of Coke, C, in Pyrolysis Reaction of Waste Plastic Mixture at 360°C.

Increasing the inlet velocity of fluidizing gas from 0.0001 m/s, resulted in the aromatics not to reach the expected peak in the simulated tubular reactor within the length of 14 cm. which is desirable but this also decreased the production of the olefins, paraffins, aromatics and the unconverted intermediates in the reactor.

Chapter 5

Conclusion and Recommendation for Future Work

5.1 conclusion

Waste plastics cause serious environmental challenges due to low biodegradability. The methods of eliminating waste plastics are incineration which recovers the energy content of plastics but results in unacceptable emissions. The mechanical recycling is limited since only pure plastics can be recycled and the products are of low quality. Feedstock recycling or tertiary recycling reduces the disadvantages of the incineration and mechanical recycling and results in the production of valuable fuels and chemicals. Among the feedstock recycling methods, pyrolysis is a promising method in which feedstock, i.e., waste plastics are heated in the absence of oxygen. Pyrolysis is divided into two categories, thermal and catalytic pyrolysis. In the thermal pyrolysis, the reaction mechanism is called random scission which requires high amount of energy for obtaining the light hydrocarbons, nevertheless the major product would be heavy waxes. High residence time results in secondary reactions to proceed and yield of aromatics will increase. Also, thermal pyrolysis results in a broad range of hydrocarbons in the product stream. To overcome the challenges associated with thermal pyrolysis, catalytic pyrolysis may be employed. In the catalytic pyrolysis the mechanism of reaction is called carbonium ion mechanism. The operating temperature of the catalytic pyrolysis is lower than thermal pyrolysis. Also, the product range is narrower. The catalysts used in the catalytic pyrolysis are typically zeolites or amorphous aluminosilicates which are acidic. Zeolites are porous. The smaller the pore size and the more acidic the catalyst is the lighter the resultant hydrocarbons are and yield of olefinic products is favored. HZSM-5 has high acidity and small pore size which favors the production of light olefins and hinders coke formation. Since pyrolysis requires heating, microwave heating was also studied. Rapid heating offers an interesting advantage over conventional heating methods. Since plastics are transparent to microwave irradiation, a microwave reactor with tubular microwave cavity with a wall made of a microwave receptor material such as silicon carbide was assumed to be an excellent reactor for pyrolysis. The features associated with the microwaves were studied. Research works on thermal and catalytic pyrolysis as well as microwave-assisted pyrolysis were reviewed in this thesis. A microwave reactor with silicon carbide as the material of reactor wall was simulated in COMSOL. The simulation results showed reaching temperatures around 350°C in 150 s. The reaction pathway of catalytic pyrolysis of post-consumer hospital waste plastics mixture which consisted wt.37 % HDPE, wt.25 % LDPE, wt. 33 % and wt.5% PS was developed based on the experimental research done by Huang et al. The differential equations representing the kinetics of the pyrolysis reactions of the mixture over HZSM-5 as catalyst were solved using MATLAB and results were plotted. Olefins were the major product with hydrocarbons mainly in the range of C3-C5 followed by paraffins with C4 as the major hydrocarbons. Aromatics and coke yields were insignificant compared to the olefins and paraffins. The reactions were modeled in 3-D geometry. Assuming a fixed 5 mol/m³ initial concentration of reactants, the effects of mass of catalyst, particle diameter of catalyst and inlet velocity of fluidizing gas were investigated. The mass and particle diameter of catalyst have little effect on the consumption of the plastics mixture and the production of the intermediates but does affect the consumption of the intermediates and the production of olefins, paraffins, aromatics and coke significantly. Increasing the mass of

catalyst over 5 g has negligible effect on the reaction rate. Decreasing the particle diameter of catalyst generally results in increasing the reaction rate but particle diameter smaller than 50 μm is not suitable for fluidization because of the enhanced intermolecular forces of particles. Increasing the inlet velocity of fluidizing gas may result in incomplete intermediate consumption and low yield of products.

5.2 Recommendation for Future Work

1. Developing a control scheme to maintain the microwave reactor temperature at a desired value by manipulating the input power.
2. Conducting research on regeneration process and optimization of the process by minimizing the energy consumption and utilizing the lost energy.
3. Scaling up the catalytic process since the majority of research works done so far are conducted in laboratory scale.

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