AMERICAN UNIVERSITY OF BEIRUT

OXIDATIVE CRACKING OF OCTADECANE, AS A MODEL COMPOUND OF HDPE, INTO USEFUL CHEMICALS AND FUEL

by

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AN ABSTRACT OF THE THESIS OF

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Title: Oxidative Cracking of Octadecane, as a Model Compound of HDPE, into Useful Chemicals and Fuel.

Plastics are polymers that have dominated the chemical industry for over seven decades, which has led to environmental problems due to their short lifetimes and slow decomposition rates. This study explores an alternative method for utilizing plastics whereby they are transformed into smaller useful molecules, either to form fuel (gasoline, diesel) or chemical building blocks (olefins) through cracking.

This study explores the oxidative cracking of HDPE as an alternative process to thermal cracking. At first, we investigated the role of oxygen in oxidative cracking of octadecane, as a model compound to HDPE, and compared results to that of the thermal cracking process. It was found that oxygen boosts the radical chemistry by increasing the concentration of radical propagation steps ($OH^{.}$). At temperatures as low as 600°C, oxygen concentration as low as 10% showed high octadecane conversion (68 wt. %) and good area % of light olefins (43.57%). Moreover, presence of oxygen enhanced oil production. Finally, to prove concept, we performed preliminary experiments on domestic HDPE shredded bottles. Results showed that the introduction of low concentration of oxygen significantly enhanced the light olefins production.

In an attempt to develop an active and selective catalyst for the oxidative cracking of HDPE, we explored the performance of Li/MgO catalyst for the oxidative cracking of octadecane and compared results to that obtained with the H-Beta zeolite. Li/MgO showed very low activity compared to H-Beta mainly due to its low surface area and low

concentration of active sites. Basic-acidic mesoporeous catalyst systems could be potential catalyst systems for future investigation.

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CHAPTER I

INTRODUCTION

Plastics have become an important product in everyday use competing with typical used materials due to their numerous benefits and diverse applications (Feldman, 2008). According to statistics from 2018, the production of plastics has increased in volume worldwide from 1.5 million metric tons in 1950 to 335 million metric tons in 2016 as shown in Figure 1. The global increase in the demand of plastics is largely owed to the advantages that these products provide. Plastics are characterized by a series of properties such as high mechanical strength, impermeability to water and microorganisms, durability, ability to be molded or shaped under pressure and heat, and low production cost due to large-scale industries and process optimization (Rodriguez, 2019).

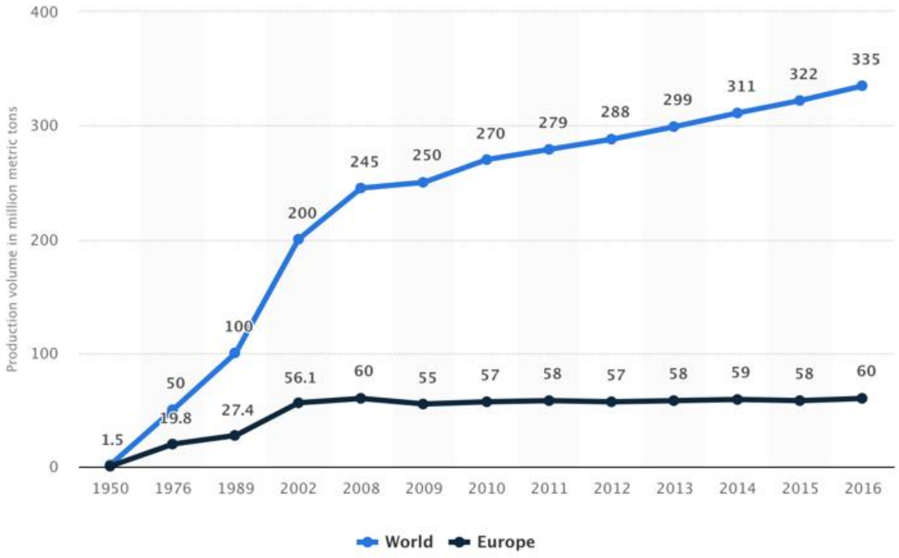


Figure 1: Plastic production in the World and Europe from 1950 to 2016 (statista, 2018)

This extensive production and use of plastics raises awareness around the enormous amounts of accumulated plastic wastes on land and plastics fragments in the oceans (Ojeda, 2013). Hence, it is proposed that thermochemical alternative processes such as pyrolysis, gasification and incineration can lead to waste minimization while maximizing energy savings.

The main objectives of this study were to understand and optimize the oxidative cracking process of Octadecane, as model compound to HDPE, for maximizing light olefins production as a new technique to get rid of accumulated HDPE waste while minimizing energy usage.

This thesis is organized as follows Chapter 2 is dedicated to literature review by introducing plastic waste production along with the pyrolysis and cracking processes, parameters affecting HDPE pyrolysis and the types of acidic and oxidic non-redox catalysts used in previous studies. Then, research objectives and methodology applied in this thesis are highlighted in Chapters 2 and 3. The reader is guided afterwards to the setup preparation adopted in cracking experiments in Chapter 4, where the test runs and results of thermal and oxidative cracking at different conditions are displayed. In Chapter 5, a full description of the catalyst preparation and characterization techniques is given, following which catalytic oxidative cracking test runs and results are shown. Chapter 6 shows the preliminary results of oxidative cracking of shredded HDPE waste bottles. Finally, the conclusion section summarizes achieved research outcomes and recommendations for further research.

CHAPTER II

LITERATURE REVIEW

A. Waste production in Lebanon

Despite the prevalence of environmental crises worldwide, Lebanon scores as one of the top countries in hazardous waste treatment problems. On 15 July 2015, “Naameh Landfill ’’, which is one of the largest and most heavily relied on landfills in Lebanon was forcefully shut down which gave rise to the ongoing trash crisis in Lebanon.

According to Sweep Net (2014), the MSW generation per Capita in Lebanon was estimated to be around 1.05 kg/day, varying between 0.8 kg per day in rural areas and 1.2 kg per day in urban areas. In 2015, the total generation of MSW was 6455 tons per day with 49 % of which was generated by Beirut and Mount- Lebanon, of which 24% was attributed to Greater Beirut alone. This aggravated the Lebanese waste crisis and made recycling a necessity.

The composition of these municipal solid wastes mainly consisted of organic materials, followed by paper and plastics as shown in Figure 2 (Sweep Net, 2014). Therefore, organic wastes need to be separated from inorganic wastes (plastics, papers…) before performing any waste treatment approach since organic wastes are highly biodegradable as opposed to inorganic wastes. Plastic wastes take many years to breakdown; for example, HDPE plastic bottles take more than 450 years to decompose into their chemical components.

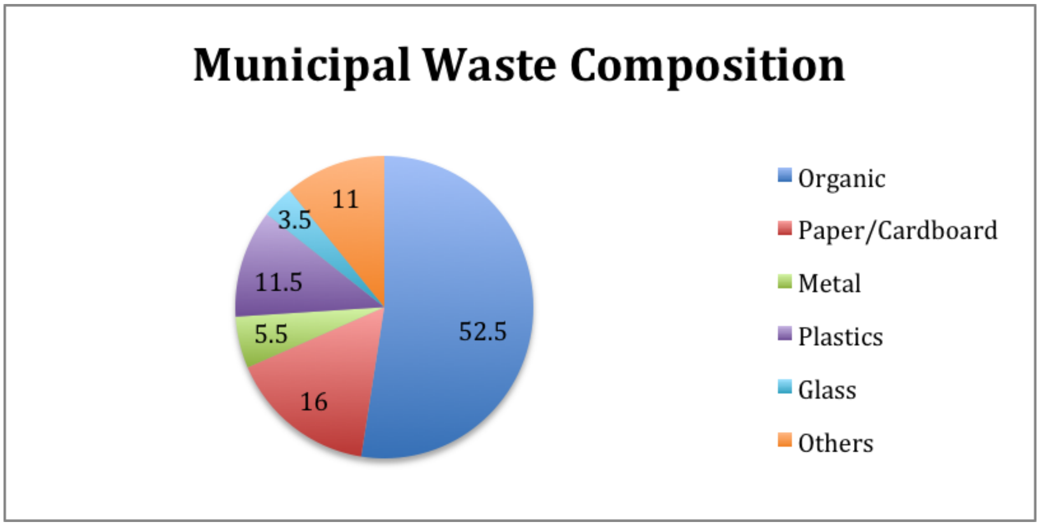


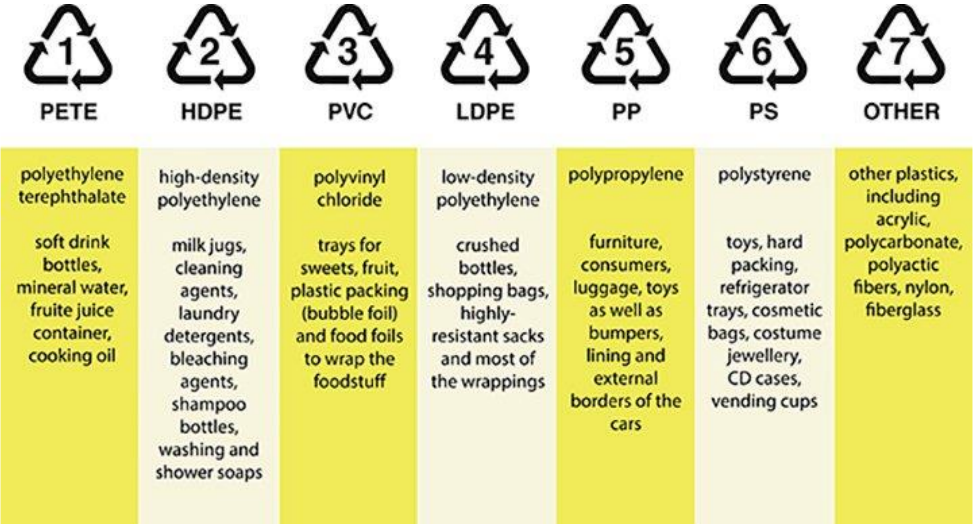
Figure 2: Solid waste compositions in Lebanon (Sweep Net, 2014)

As a consequence, there is a very strong and irreversible movement around the globe to eliminate municipal plastic wastes. Taking advantage of these petroleum-based plastics by applying new techniques may prove to be a useful approach. Incineration, for instance, has shown to be a useful method to produce energy from plastic bottles, but it is not environmentally friendly as it releases large amounts of pollutants and particulate matter when plastics are burnt.

Therefore, a new practice known as recycling has been introduced as an alternative to landfilling and incineration. Recycling is divided into many categories: primary recycling, secondary mechanical recycling and tertiary recycling (Miskolczi et al., 2004). Tertiary recycling, also known as chemical or thermal recycling, includes a diversity of techniques such as pyrolysis, hydrolysis, hydrogenation, methanolysis and gasification. Currently, the most appealing method is pyrolysis, or cracking, since its scope extends to mixed and contaminated plastics (Almeida & Marques, 2016).

B. Type of plastics

Plastics can be classified in different ways according to their chemical structure, synthesis process, density and many other properties. Based on their chemical structure and applications, they are divided into seven groups: polyethylene terephthalate, high density polyethylene, polyvinyl chloride, low density polyethylene, polypropylene, polystyrene and others. Each type has a specific code that is used on various products as shown in Figure 3.



1 PETE	2 HDPE	3 PVC	4 LDPE	5 PP	6 PS	7 OTHER
polyethylene terephthalate	high-density polyethylene	polyvinyl chloride	low-density polyethylene	polypropylene	polystyrene	other plastics, including acrylic, polycarbonate, polyactic fibers, nylon, fiberglass
soft drink bottles, mineral water, fruite juice container, cooking oil	milk jugs, cleaning agents, laundry detergents, bleaching agents, shampoo bottles, washing and shower soaps	trays for sweets, fruit, plastic packing (bubble foil) and food foils to wrap the foodstuff	crushed bottles, shopping bags, highly-resistant sacks and most of the wrappings	furniture, consumers, luggage, toys as well as bumpers, lining and external borders of the cars	toys, hard packing, refrigerator trays, cosmetic bags, costume jewellery, CD cases, vending cups	

Figure 3: Symbols of the seven types of various plastic products (Seaman, 2012)

The most common polymers found in solid wastes are polyethylene, polypropylene, and polystyrene, since they are an accessible source of chemicals and fuel derivatives, which explains the large number of studies done on these polymers (Gao, 2010).

C. Pyrolysis Processes

1. Types of pyrolysis

Pyrolysis is defined as the thermal decomposition of molecules at elevated temperatures in an inert atmosphere in order to produce valuable products.

The yield of pyrolysis is determined by many experimental parameters such as temperature, heating rate, and residence time of volatile materials. Based on these parameters, cracking can be categorized into two different types: fast pyrolysis and slow pyrolysis.

a. Fast pyrolysis

In this type of cracking, high heating rate and low residence time of volatiles are the essential components. In fast cracking, the volatile materials produced are removed from the reactor to permit the formation of liquid products. The gaseous products then condense and prevent the further cracking of the liquid products into simpler gaseous components. The residence time in fast pyrolysis varies milliseconds to seconds (Martínez et al, 2013).

b. Slow pyrolysis

In this type of cracking, the heating rate is low and the residence time is long. The long residence time causes the formation of coke, which negatively affects the yield of the pyrolysis and enhances the production of gas due to the secondary reactions (Buekens, 2006).

Improvements in conventional thermal cracking are continuous as part of the development of new technologies such as the use of new additives and different type of catalysts.

2. *Factors affecting pyrolysis process*

The pyrolysis of polymers is influenced by a number of process parameters such as temperature, reaction time, carrier gas, type of feedstock, and composition. The most important factors are discussed below.

a. Temperature

Temperature is a fundamental parameter in the cracking of high-density polyethylene since it is an endothermic reaction that requires energy in order to occur. Many researchers have studied the effect of temperature on HDPE cracking and they have found that the best temperature interval for liquid fuel production is between 450 and 550 °C depending on the type of reactor used. It is interesting to note that the data concerning the determination of liquid, wax, and gas fractions and optimum conditions is dependent on the experimental setup and analytical methodology adopted.

Al-Salem (2019) carried out thermal pyrolysis of high-density polyethylene between temperatures 500 and 800 °C in the presence of nitrogen as a carrier gas to produce liquid fuel, gas and solid char. They found that the main products were HC gases, condensate, and an insignificant yield of solid char.

The maximum oil yield was obtained at 550°C with 70 wt.%. The yield of oil decreased at higher temperatures to produce more gaseous product due to the rapid generation of gaseous materials at fast pyrolysis combined with the secondary cracking reaction of polyolefin.

The derived pyrolytic oil was then evaluated in terms of gasoline range hydrocarbon (C_8-C_{12}), and it was found that gasoline percentage increases with temperature to a maximum of 800°C as shown in Figure 4.

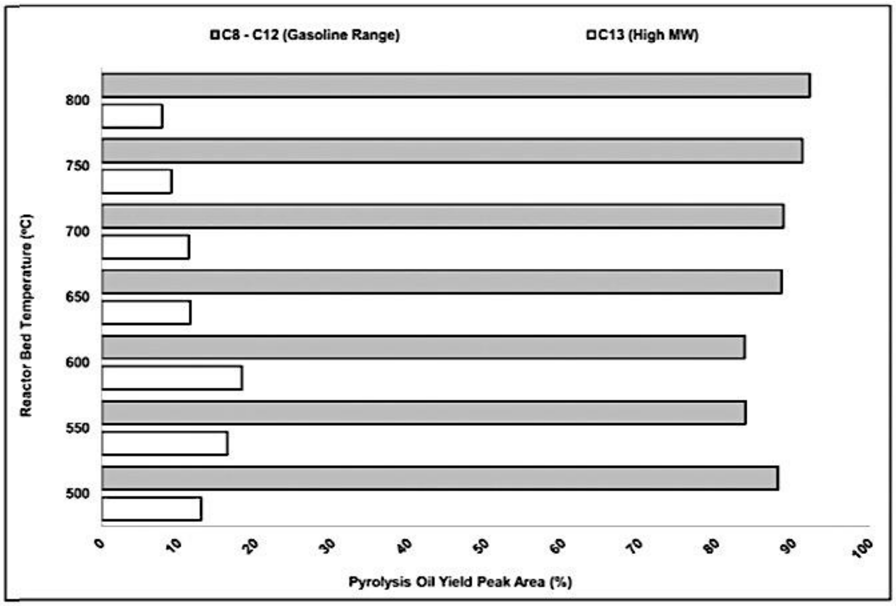


Figure 4: Influence of temperature on the gasoline range product (Al-Salem, 2019)

Pyrolytic oil was mostly aliphatic and its percentage decreased as temperature increased. The maximum yield of aliphatic compound was 98.38% at 500°C with and the maximum yield of aromatics was at 600°C as observed in Figure 5.

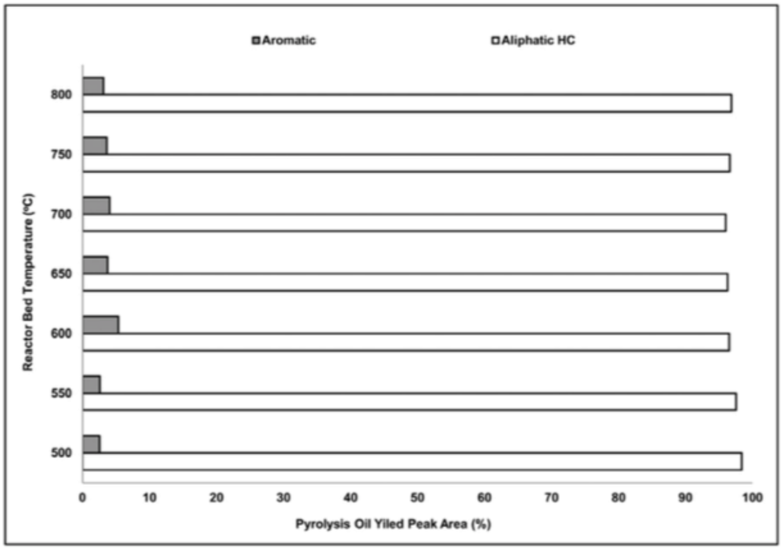


Figure 5: Distribution of aliphatic and aromatics hydrocarbons at different temperature (Al-Salem, 2019)

The gases collected from these experiments were also evaluated, and it was noted that the main components were olefins and alkanes in the C_2-C_4 range. The optimum gas yield was measured at 750°C to be 36 wt%.

Figure 6 shows that the gas product concentration was mainly a mixture of paraffin and olefin hydrocarbons in the C_2-C_4 range and progressively increased with the increase in temperature. At 500°C, the yield of C_2-C_4 hydrocarbons was 70.63%, and it became with a 50°C increment 76.96%, 78.83%, 75.12%, 78.83%, 70.47% and 79.59% respectively.

On the other hand, C_5^+ products decreased with the increase in temperature due to their decomposition to low molecular weight compound. Aromatic compounds such as benzene were detected at an elevated temperature (800°C) with a very low percentage.

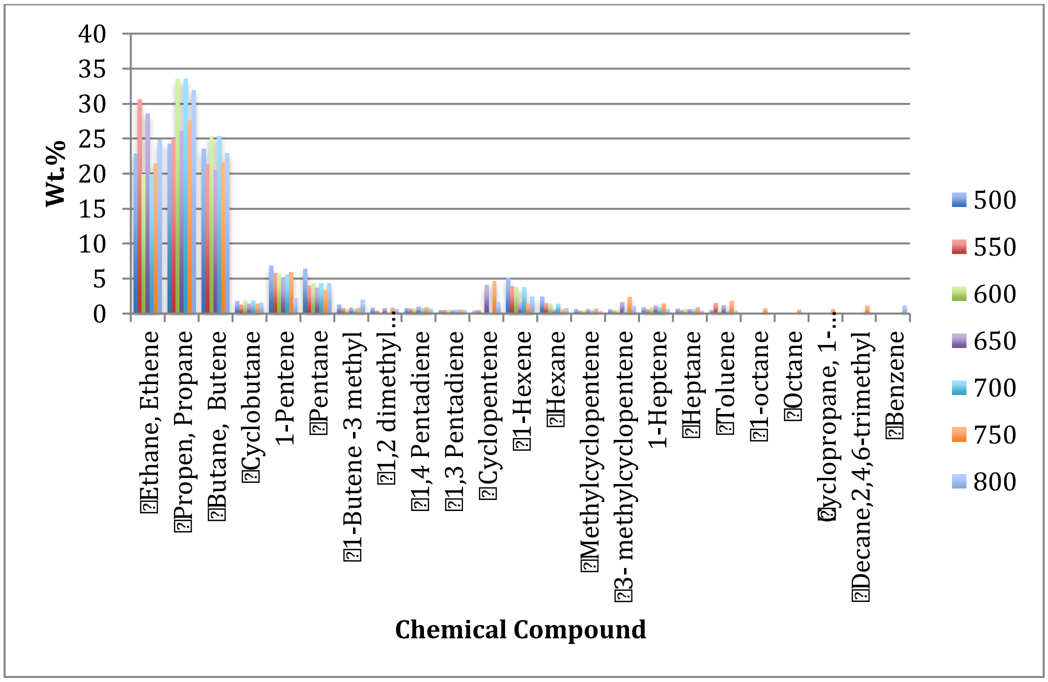


Figure 6: Identification of pyrolysis gas product with respect to temperature (Al-Salem, 2019)

b. Reaction time

In addition to temperature, residence time is an important factor that can affect the distribution of HDPE pyrolysis.

The definition of residence time varies between fast and slow pyrolysis. In the case of fast pyrolysis, residence time refers to the contact time of the HDPE on the hot surface, while, in the case of slow or batch pyrolysis, it refers to the period of time from when the feedstock of HDPE begins to be heated until the products are removed.

Hernandez et al. (2006) investigated the effect of residence time on the yield of HDPE cracking. They found that the gas yield increased with the increase in residence time during thermal pyrolysis. In this type of cracking some compounds were found to be released more with the increase of residence time while others are released less.

Table 1 shows that some compounds' yield increased with the increase of the residence time such as methane, ethene, ethane, propene, isobutane, isobutene, isopentane and benzene. When the residence time was around 0, only primary reactions took place, however, with the increase of the residence time to the 200-400 range the occurence of secondary reactions was more significant. The same trend was also observed when the residence time reached a higher value of 1500.

Table 1: Compounds whose yields increase with the residence time Hernandez et al. (2006)

V/m	0	207	401	1154	1500
Methane	0.66	2.4	4.8	5.5	12.6
Ethane	0.97	2.2	3.0	3.8	4.2
Ethene	3.1	6.3	16.5	17.2	24.3
Propene	2.0	5.0	10.5	12.2	11.0
Isobutane	0.0	0.06	0.01	0.01	0.04
Isobutene	004	0.17	0.24	0.24	0.58
Isopentane	0.02	0.05	0.02	0.04	0.03
Benzene	0.09	0.44	2.2	2.4	8.2

On the contrary, some products witnessed a decrease in their yield such as propane, n-butane, n-pentane, 1-hexene and 1-heptene. This can be attributed to the cracking of these compounds to generate lower molecules. This fact verifies that the compounds whose yield increases with residence time are released from the cracking of C_3-C_7 hydrocarbons.

c. Carrier gas

Fluidizing gas or carrier gas, also known as inert gas, is used in pyrolysis to transport the vaporized products without taking part in the pyrolysis.

Nitrogen is the most widely used carrier gas since it is safer and easier to handle in comparison to more reactive gases such as hydrogen and ethylene due to their flammability hazard. Although helium is capable of producing a high liquid yield, it is rarely used due to its limited availability and expensive cost.

3. Cracking mechanism

The cracking of C-C bonds occurs in the unstable bond. Methane has the highest stability followed by primary, secondary, and tertiary carbon (Sobko, 2008). The energy required to break the C-C bonds of primary, secondary, and tertiary carbons are 355, 351 and 339 KJ/mol respectively, thus, the tertiary carbon is broken first (McMurry, 2000). Through understanding the concept of bond breaking, the cracking mechanism can be understood further. The main cracking mechanisms in the pyrolysis reactions are random cracking, chain strip cracking, and end chain cracking.

- Random cracking

Long straight carbon chains such as high-density polyethylene have secondary carbon atoms; these C-C bonds are cracked by a random cracking mechanism since there is an equal chance of cracking for these carbons. The polymer is randomly broken down into smaller fragments of uneven length (Saha & Ghoshal, 2005).

- Chain strip cracking

Chain stripping is based on the concept of the elimination of reactive or side groups in the branched and cross-linked polymer. Therefore, the unsaturated chains undergo further reactions such as cracking and aromatization or even coke formation (Buekens & Huang, 1998).

- End chain cracking

This type of cracking occurs at the end groups successively leading to the formation of monomers such as volatile products (Buekens & Huang, 1998). At high temperature, the movements of molecule are more intense, and therefore shorter end chains are broken from the main carbon chains.

a. Thermal cracking mechanism

Various reactions occur during the pyrolysis of plastic. They consist mainly of four stages: initiation, propagation, hydrogen chain transfer, and termination (Blazso, 2006).

- Initiation reactions

During the initiation reaction, the carbon chain is broken into smaller free radicals and molecules through the three cracking mechanisms described above. However, in the pyrolysis of polyethylene, initiation reactions follow either randomly or through the end chain-cracking mechanism as shown in Figures 7 and 8.

Figure 7 Random cracking of polymer (Marongiu et al, 2007)

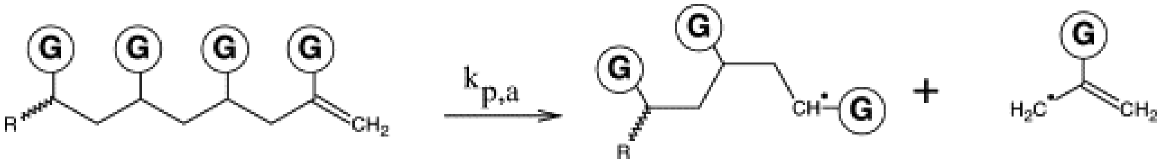


Figure 8 End chains cracking of polymer (Marongiu et al, 2007)

These free radicals produced in the initiation reaction then undergo the propagation and termination reactions.

- Propagation reactions

The free radicals formed at the initiation stage are split into intermediate compounds; this phenomenon is known as the scission of free radicals. During the pyrolysis, the main propagation reaction is the β-scission reaction, which refers to the breaking of covalent bond in the β position relative to the position of the unpaired electron. The β-scission reactions include the end chain β-scission and the mid chain β-scission. The main type of product is olefins since the large free radicals formed in the initiation stage are converted into alkene and another smaller free radicals as shown in Figures 9 and 10.

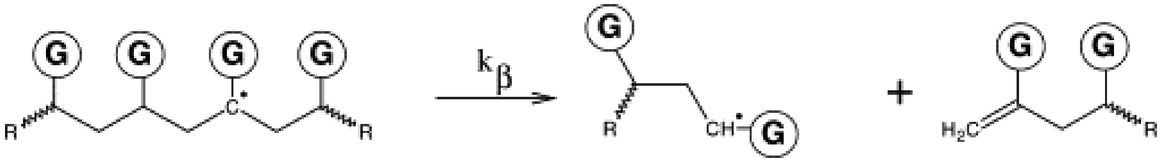


Figure 9: Mid chain β-scission reaction (Marongiu et al, 2007)

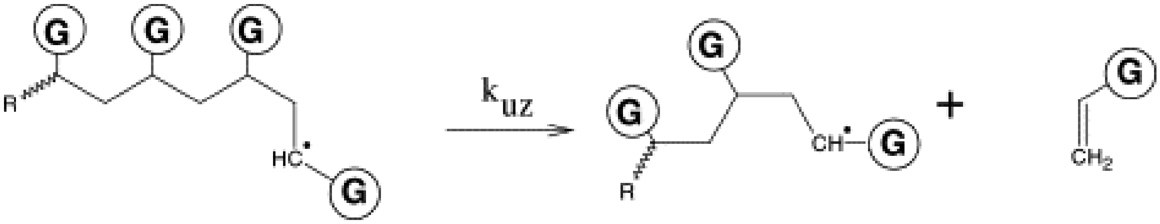


Figure 10: End chain β-scission reaction (Marongiu et al, 2007)

- Hydrogen chain transfer reactions

During a hydrogen chain transfer reaction, the radical formed at the initiation reaction abstracts hydrogen from an alkane. This type of reaction includes intermolecular and intra-molecular transfer reactions where the intermolecular occurs between free radicals and other compounds, and therefore, the radical is converted into saturated molecule as shown in Figures 11 and 12. During intra-molecular transfer reaction, free proton is transferred from the end to the middle of the free radicals. The intra-molecular transfer reaction enhances isomerization in the pyrolysis process as shown in Figure 13.

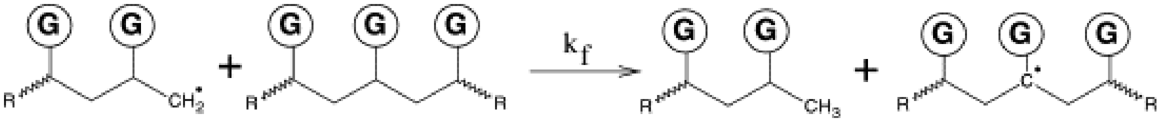


Figure 11 Intermolecular transfer reaction on the end chain radical (Marongiu et al, 2007)

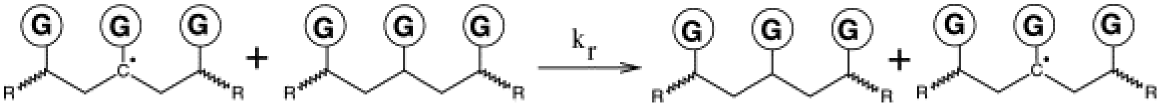


Figure 12 Intermolecular transfer reaction on the mid chain radical (Marongiu et al, 2007)

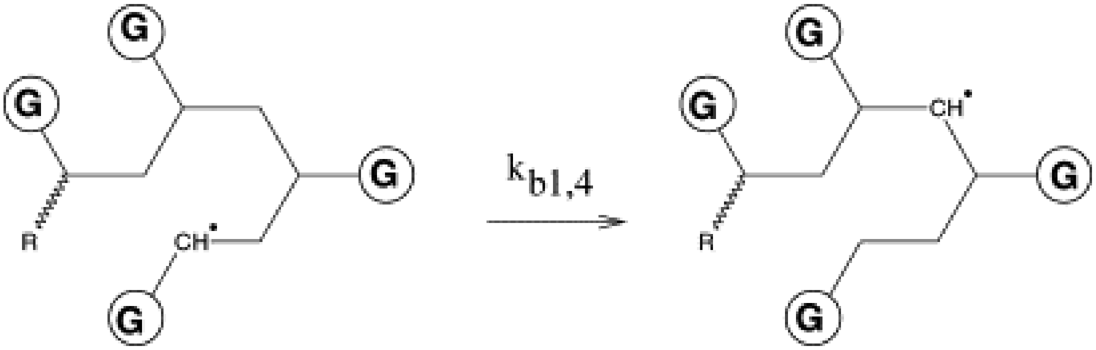


Figure 13 Intra-molecular transfer reactions (Marongiu et al, 2007)

- Termination reactions

The last step in the chain reaction is the termination step where radical combination (Figure 14) or disproportionation of the free radicals (Figure 15) occur. This reaction affects the length of the end products produced.

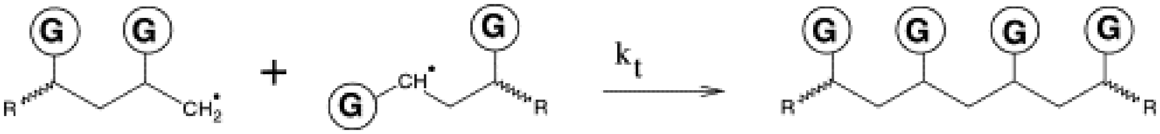


Figure 14 Radical combination reaction (Marongiu et al, 2007)

$$2R_4^\bullet \rightarrow \text{olefin} + \text{alkane} \qquad \text{disproportionation}$$

Figure 15: Disproportionation reaction (Dutton)

The number of unsaturated compounds generated at the end of the reaction indicates the magnitude of the initiation and termination reactions. In addition, the number of 1-alkenes shows the magnitude of propagation β-scission reactions.

4. Catalytic pyrolysis

In order to improve the pyrolysis of plastic reactions and optimize the distribution of products, catalysts are used in industrial pyrolysis processes. It has been noted that the degradation temperature needed to achieve a certain conversion is reduced significantly when a catalyst is inserted (Lee, 2009). The main role of a catalyst in the pyrolysis of HDPE, for example, is to decrease the length of the carbon chain produced and then decrease the boiling point of the products (Williams & Williams, 1997).

a. Zeolite

Thermal pyrolysis mainly generates olefins and di-alkenes. The presence of some types of catalysts reduces the proportion of unsaturated hydrocarbons and produces more aromatics and naphthenes. This can greatly enhances the stability and the cetane number of the oil (Garforth, 1998).

The most used catalyst in plastic pyrolysis is zeolite because it enhances the formation of aromatic compounds.

Zeolites are microporous crystalline alumino-silicates composed of primary structural units such as SiO_4, AlO_4, and PO_4 linked by an oxygen atom, forming a tetrahedron shape. Each oxygen atom is linked to two silicone or aluminum atoms to form a three-dimensional microporous structure (Manos, 2006). The pores of zeolites are molecular sieves that block the diffusion of bulk and large molecules into the internal surface of the catalyst. These molecular sieves are characterized by their high acidity and their selectivity (Mastral et al., 2006).

Artexe et al. (2012) conducted catalytic pyrolysis on HDPE using a HZSM-5 zeolite catalyst at 500°C. They found that the ratio of SiO_2/Al_2O_3 of the HSZM-5 greatly affected the product yield during HDPE pyrolysis. The catalyst with the highest acidity (SiO_2/Al_2O_3 = 30) was more active in wax degradation and therefore produced higher light olefins and low heavy fraction C_{12}-C_{20}. When the ratio was reduced from 280 to 30, the yield of light olefins improved from 35.5 to 58 wt.% and the yield of C_{12}-C_{20} decreased from 28 to 5.3 wt.%.

Additionally, the reduction of the ratio in zeolites increased the production of light alkanes and aromatics. Table 2 compares the properties of gasoline fraction resulted from the use of three types of HZSM-5 zeolite with different degrees of acidity. The lowest SiO_2/Al_2O_3 corresponding to the highest acidity gave a higher octane number with a high content of benzene and aromatics and a low content of olefins.

Table 2 Comparison of fuel properties of gasoline fraction Artetxe et al (2012)

SiO_2/Al_2O_3	Octane number	Olefins (vol%)	Aromatics (vol%)	Benzene (vol%)
30	94.1	33.1	43.3	4.2
80	86.7	61.2	13.5	1.3
280	85.9	68.9	6.9	0.46
Required	95	<18	<35	<1

Likewise, Zeaiter (2014) studied the catalytic pyrolysis of HDPE using zeolites. It was discovered that the catalytic pyrolysis of waste HDPE over HUSY and HBeta zeolites is a good method to convert waste HDPE to more valuable chemicals and fuel-like products. High gas fraction (90%) was produced using these catalysts containing mainly propene and butene (51% in total), however, the liquid product was rich with trimethylbenzene (36 %) that is classified as aromatic and the remaining compounds were C11-C23 alkanes.

To sum up, the catalysts used in the catalytic degradation were mainly zeolites due to their acidic sites, which aid in the process of breaking the polymer macromolecules and in the production of aromatics, which can be used as fuel-like products.

D. Oxidative cracking

1. Role of oxygen

Although polymer degradations are frequently studied in an inert atmosphere (pyrolysis), degradation in an oxygen environment is equally important. Oxidative cracking is considered as an alternative route to enhance the conversion and product distribution of the process. In addition, it can provide important knowledge about how polymers behave under atmospheric conditions (Peterson et al., 2001).

Peterson et al. (2001) studied thermal and thermo-oxidative degradation of PE. Figure 16 shows TGA data of PE cracked in nitrogen and air. It was found that in a nitrogen atmosphere, polyethylene, degraded in a single and smooth step which started at 350°C and reached zero mass at 490°C. In air, the degradation curve contained some irregularities. The inset plot indicates several degradation steps: the first is defined at 220°C followed by a small shoulder found at 320°C, and then, an irregular third peak arose at 400°C and continued smoothly above 475°C. An increase in mass was also detected at 200°C before any degradation under air atmosphere.

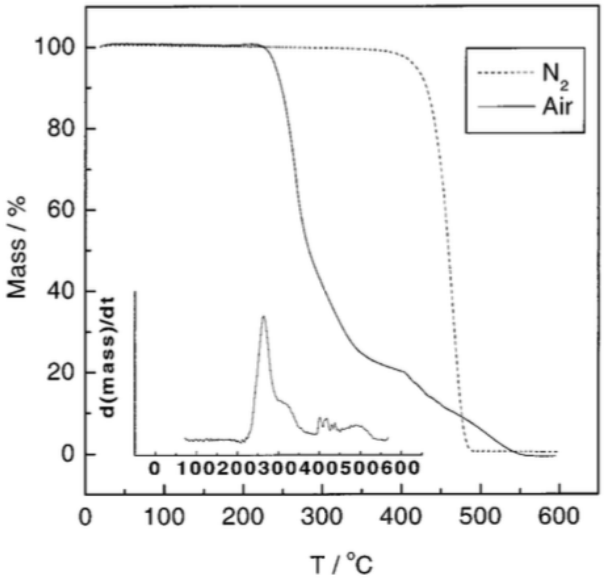


Figure 16: TGA curves for the thermal decomposition of PE in nitrogen (dashed line) and air (solid line). Inset plot is derivative graph of mass loss for degradation in air. Heating rates of 9.2 and 9.0 K.min-^{1} for nitrogen and air, respectively (Peterson et al., 2001).

The DSC scans of PE degraded in nitrogen and air are shown in Figure 17. Both curves demonstrate melting endotherms at 110°C. Then, the two traces differ significantly. Under a nitrogen atmosphere, PE revealed a board endotherm that expanded up to 500°C where the minimum endotherm was found at 470°C. In air, however, DSC traces showed a large exothermic peak whose maximum is at 330°C followed by another sharp exotherm peak at 410°C.

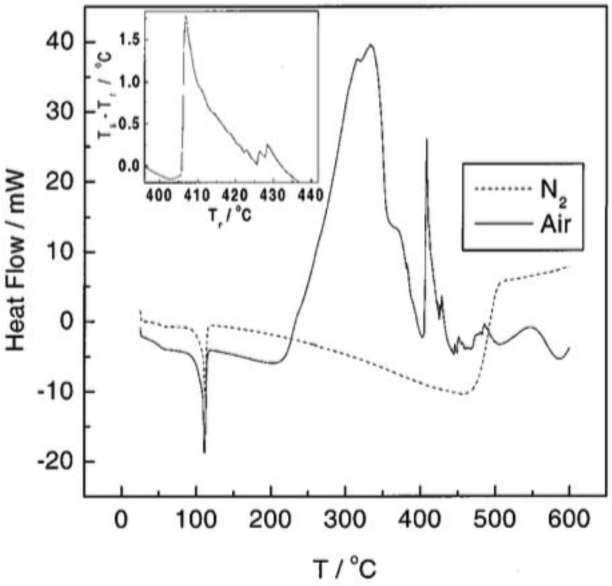


Figure 17: DSC scans of measured heat flow for degradation of PE in nitrogen (dashed line) and air (solid line). Heating rates of 20.0 K.min^{-1} for both nitrogen and air. Inset plot show the difference between sample temperature, T_s and reference temperature, T_r (Peterson et al., 2001).

Thereafter, Peterson et al. (2001) applied the isoconversional methods to calculate the activation energy of polymer degradation under nitrogen and air atmospheres as shown in Figure 18. Under a nitrogen atmosphere, the activation energy slowly increased from 150 to 240 KJ/mol throughout the degradation process. In air, however, the activation energy slightly increased from 80 to 125 KJ/mol during the initial degradation ($\alpha < 0.5$).

Based on this data, it may be concluded that oxygen plays a key role in providing a large amount of heat for oxidative cracking and allowing the process to run in an autothermal way.

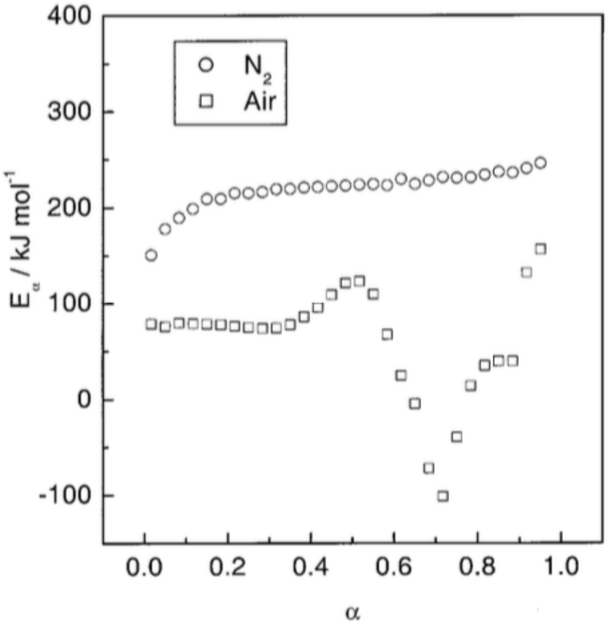


Figure 18: E_a-dependencies obtained by isoconversional analysis of TGA data for PS degradation in nitrogen (circles) and air (squares) (Peterson et al., 2001).

The gas phase oxidative dehydrogenation (ODH) of lower alkanes to produce lower olefins has attracted much attention and many studies have been conducted to investigate the role of oxygen on ethane, propane, and butane cracking. In these studies, most of the work was focused on the break of C-H bonds; however, the process, differs with higher hydrocarbons such as heavy hydrocarbon and polymers, since the most remarkable type of cleavage in these molecules is C-C bonds.

Therefore, Zhu et al. (2006) considered decalin and tetraline as the model compounds for heavier naphtene and arene, and investigated their gas oxidative cracking (GOC) processes to produce light fuels. They found that the introduction of the oxygen molecule changes the thermodynamic equilibrium and greatly enhances the conversion of decalin and tetraline. This study also highlights the role of oxygen in reducing the activation energy of the initial step of chain reactions, boosting the formation of hydrocrbon radicals, and accelerating the following C-C bond scission. During GOC, O_2 attacks the C-C bonds and produces CO_X. The formation of CO_X plays an important role in eliminating the carbon deposition in this system. During gas phase oxidative cracking, the reactor wall remains clean while black residue is formed during pyrolysis. High CO_X formation during oxidative cracking signifies high decoking ability.

2. Olefins production

Light olefins, mainly ethylene and propylene are the building blocks for many chemical industries. They are the raw materials for both the production of polymers such as polyethylene and polypropylene and the synthesis of chemicals such as ethylene oxide.

The increase in the production of modern materials such as plastic increases the global demand for ethylene and propylene. According to the Ministry of Economy, Trade and Industry of Japan (2018), the global supply and demand for petrochemical products such as ethylene and propylene derivatives have progressively increased by 3.8% in 2016 from the previous year, to reach 142.3 million tons for ethylene derivatives only. It is also mentioned that in the Middle East, the annual growth rates are estimated to be 4.2% in the coming years for ethylene equivalent demand and 4.7% for propylene equivalent demand. This increase in light olefins production in this region is attributed to the effort done to expand downstream industries in order to acquire domestic demand, produce high-value-added products, and realize globalization.

Continuous development in the production of synthetic materials and thus the increase in light olefins global demand has encouraged researchers to substantially investigate the development of efficient routes for the production of light olefins.

Although steam cracking is the major route for the production of light olefins today, it is a less attractive process as it requires high-energy consumption and leads to high emission of CO_2.

The oxidative cracking of hydrocarbons is found to be a potential alternative to steam cracking because the presence of oxygen in the reaction makes it exothermic and helps in minimizing coke formation in addition to enhancing olefins production.

Liu et al. (2004) observed that the thermal cracking of hexane without oxygen was negligible when the temperature is lower than 750°C. However, this cracking was greatly enhanced by the introduction of the oxygen to the feed even at relatively low temperatures. The conversion of hexane and yield of olefins in the absence of oxygen were 2.3% and 1.4% respectively, while in the gas oxidative cracking process, they reached 72.2% and 39.1% respectively at 650°C. Although the oxidative cracking of hexane gave a high conversion, the selectivity to light olefins was lower than that in the pyrolysis due to the formation of CO_X. It has been reported that the selectivity to CO_2 in this process is usually less than 1%, while the selectivity of CO can be as high as 17%. It should be noted here that CO is considered to be a valuable petrochemical feedstock and that the CO_2 released from GOC is much lower than that from pyrolysis. Pyrolysis is a high-energy consumption process that requires a great amount of fuels to be combusted externally in order to attain the high cracking temperature inside, leading to enormous release of CO_X.

Another study conducted by Pogosyana et al.(2014) aimed to investigate the effect of oxygen concentration on the cracking of propane to produce lower olefins. The results showed that the increase in temperature increased the conversion of propane to reach more than 90% at 800°C. Above 650°C, the process became mainly in the gas phase, where the yield of ethylene slightly increased and that of propylene attained its maximum at 650°C and then decreased sharply. Thus, the total yield of ethylene and propylene decreased at an elevated temperature. Moreover, high temperatures were found to be capable of reducing the production of CO_2 since it is mainly formed in heterogeneous reactions on the surface of the reactor, and the yield of CO was also reduced when the temperature exceeded 750°C due to the contribution of thermal cracking.

Then, Pogosyana et al. (2014) studied the effect of oxygen concentration in the initial mixture at a constant temperature 650°C. The data indicated that propane conversion increased with the increase in oxygen concentration. The use of molecular oxygen significantly increased the relative yield of propylene compared with that of ethylene due to the high influence of oxidative dehydrogenation compared to the conventional C-C or C-H bonds cleavage in thermal cracking, which have much higher activation energy. Secondary reactions of profound oxidation of primary products became dominant when the oxygen content in the initial mixture increased leading to an increase in carbon oxide formation.

In summary, the production of light olefins with low emissions of carbon dioxide through the oxidative cracking of heavy feed seems to be an environmentally friendly and efficient route.

3. *Catalytic Oxidative Cracking*

Researchers have found that a combination of heterogeneous (catalytic) and homogeneous (gas phase) reaction may be a promising route to obtaining commercially acceptable yields of light olefins.

The presence of catalyst helps tune the product selectivity towards the formation of light olefin under conditions where the gas phase cracking gives minimal olefins formation. Additionally, the catalyst plays an important role in the initiation and acceleration of cracking reaction. Researchers have been looking for an active and selective catalyst, which does not produce large amounts of CO_x in the presence of oxygen in light of the current challenge of finding a selective catalyst for oxidative cracking.

A non-redox alkali metal based oxide catalyst such as Li/MgO catalyst has been extensively used in literature for the oxidative conversion of the lower alkanes C_2-C_4 into olefins. The Li/MgO catalyst has only been tested on lower alkanes and it has shown a significant improvement in alkane conversion and olefins yield, but it has never been tested on long aliphatic chains and plastics.

Boyadjian et al. (2010) were interested in studying the catalytic oxidative cracking of naphtha using Li/MgO in order to produce olefins such as propylene and ethylene, and they used hexane as a model compound of naphtha. It was found that at temperatures as low as 575 °C, hexane conversion was about 28% and olefins selectivity was 60 mol% with a $\frac{C_4^= + C_3^=}{C_2^=}$ ratio of 1.6 in comparison to the 0.8 ratio with the steam cracking. The Li/MgO catalyst was shown to have high selectivity by inhibiting consecutive deep oxidation of the olefins produced. These results are justified by the basic and non-red-ox properties of the catalyst where Li^+ and Mg^{2+} cations are not prone to oxidation state changes in the presence of oxygen and they reduce the re-adsorption and hence the combustion of the produced olefins.

It was also demonstrated that the rise in temperature, CO_x formation decreased and C_2- C_4 olefin formation continuously increased. This was due to the increase in the rate of the propagation reactions, with temperature increasing the ratio of homogeneous to heterogeneous reactions. On the other hand, at low temperatures, the radicals can interact with unselective O_2^- sites producing alkoxy as precursors for carbon dioxide.

Leveles (2002) found that the presence of oxygen has two essential effects. The first role of oxygen is in the homogeneous gas phase, where it enhances both the number and the intensity of the chain carrier radicals ($OH^{\cdot}$). The second role of oxygen is to regenerate the active site of the Li/MgO catalyst after the abstraction of hydrogen during initiation stage.

4. *Mechanism*

a. Oxidative cracking mechanism

Oxidative cracking of polymers is mainly activated via hydrogen abstraction resulting in the formation of an alkyl radical and a hydroxyl radical.

$$\mathrm{R-H} + O_2 \longrightarrow \mathrm{R}^{\cdot} + \mathrm{H}O_2{}^{\cdot}$$

In the presence of an oxygen molecule, the propagation step starts with the formation of an alkene and a hydroperoxy radical $(HO_2^{\cdot})$. This radical abstracts a hydrogen atom from another polymer to form a hydroperoxide. The latter breaks up into two hydroxyl$(\mathrm{OH}^{\cdot})$, which are the main chain propagators in the oxidative cracking mechanism (Leveles, 2002). This alteration in the cracking mechanism enhances alkane conversion.

$$\mathrm{R}^{\cdot} + \mathrm{O_2} \longrightarrow \text{alkene} + HO_2^{\cdot}$$

$$HO_2^{\cdot} + \mathrm{RH} \longrightarrow \mathrm{R}^{\cdot} + H_2O_2$$

$$H_2O_2 \longrightarrow 2\ \mathrm{OH}^{\cdot}$$

b. Catalytic oxidative cracking over Li/MgO mechanism

In the case of Li/MgO, Li^+ ions diffuse and substitute Mg^{2+} cations, and the excess of cations on the MgO matrix form an oxygen vacancy which in the presence of molecule oxygen and high temperature oxygen transforms into $[Li^+ O]$ active sites. These defect sites play a key role in catalytic activity by initiating hydrogen from alkane and they become $[Li^+ OH^-]$. Then, the formed radical undergoes the oxidative cracking mechanism described before.

E. Research Objective

The extensive amount of plastic bottles in the environment has routed the scientific research towards the cracking concept. However, this process is dependent on many parameters that may affect its product yield and distribution, such as temperature, pressure, residence time, type of carrier gas… and the type of reactor used.

Moreover, it is noteworthy that the main focus in the previous work has been on the production of valuable oil from the cracking of HDPE to be used as fuel. Therefore, this work deviates from the extant literature, as it is focused on the oxidative cracking of octadecane to produce olefins. In this research, the aim was to investigate the effect of oxygen concentration on the oxidative cracking of HDPE into C_2-C_4 olefins. In this study, octadecane was chosen to be the model compound of HDPE since it has been found to be the major compound of pyrolytic oil of HDPE pyrolysis as shown in Table 3 (Kumar & Singh, 2013).

Table 3: GC-MS of HDPE pyrolytic oil

R.time (min)	Area %	Name of compound	Molecular formula
6.301	1.24	1-Decene	$C_{10}H_{20}$
6.450	1.12	Decane	$C_{10}H_{22}$
8.105	2.04	1-Undecene	$C_{11}H_{22}$
8.238	1.78	n-Undecane	$C_{11}H_{24}$
9.735	3.50	1-Dodecanol	$C_{11}H_{26}O$
9.855	3.19	n-Dodecane	$C_{11}H_{26}$
11.541	4.62	1-Tridecene	$C_{13}H_{26}$
12.615	5.30	1-Tetradecene	$C_{14}H_{28}$
12.711	4.82	Tetradecane	$C_{14}H_{30}$
12.772	0.65	7-Tetradecene	$C_{14}H_{28}$
13.909	5.40	1-Pentadecene	$C_{15}H_{30}$
13.997	5.13	Pentadecane	$C_{15}H_{30}$
15.039	0.48	1,19 Eicosadiene	$C_{20}H_{38}$
15.130	5.36	1-Hexadecene	$C_{16}H_{32}$
15.210	5.60	n-Octadecane	$C_{18}H_{38}$
15.261	0.51	Cyclohexadecane	$C_{16}H_{32}$
16.203	0.49	1,19 Eicosadiene	$C_{20}H_{38}$
16.283	5.09	1-Nonadecene	$C_{19}H_{38}$
16.357	5.52	n-Heptadecane	$C_{17}H_{36}$
17.406	0.51	1-Heptadecene	$C_{17}H_{34}$
17.378	4.43	1-Octadecene	$C_{18}H_{36}$
17.447	5.47	Octadecane	$C_{18}H_{38}$
17.493	0.69	1-Octadecene	$C_{18}H_{36}$
18.419	3.26	1-Nonadecene	$C_{19}H_{38}$
18.482	4.67	Nonadecane	$C_{19}H_{40}$

CHAPTER III

METHODOLOGY

To succeed in achieving the research objectives, several actions were performed consecutively and in parallel as follows:

- Preparation of the experimental setup for the cracking process.
- Optimization of the operating conditions such as temperature, residence time, flow of the carrier gas, and the amount of the octadecane loaded in the reactor.
- Testing of effect of different oxygen concentrations on the cracking of octadecane.
- Calculation of the amount of gas and oil produced and and analysis of the products using GC-MS techniques.
- Preparation of Li/MgO catalyst using different synthesis methods. In addition catalyst behavior was predicted by measuring its surface area using BET isotherm method.

CHAPTER IV

THERMAL AND OXIDATIVE CRACKING

Oxidative cracking of HDPE is an alternative process to thermal cracking. The effect of oxygen in the oxidative cracking of octadecane as a model compound of HDPE has been studied and compared to thermal cracking results. At temperatures as low as 600°C, a low volume of oxygen (10 vol%) has shown good octadecane conversion (68 wt%) and a high area percentage of light olefins (43.57%). It was proposed in this paper that the presence of molecular oxygen in the feed plays an important role in accelerating radical chemistry where the hydoperoxide radical is the main chain propagator. In addition, optimum oxygen concentrations are needed, increasing oxygen concentrations shifts product distribution towards formation of more CO_X.

A. Material

Octadecane (99.99% purity) was purchased from Sigma Aldrich as a model compound of HDPE pyrolytic oil.

B. Oxidative Cracking experiments set-up

The setup used to study the cracking of the model compound octadecane is shown in Figure 19. It consists of a semi batch reactor made of quartz tube (ID: 0.8 cm, L: 70cm) packed with 0.8 g of octadecane bounded by two quartz wool. The octadecane was placed just before the entrance of the reactor so it could be vaporized using a heating gun before entering the furnace as a pre-heating zone.

Figure 19: Oxidative cracking set-up

A flow of nitrogen or a mixture of nitrogen and oxygen supplied from gas tanks (pure nitrogen, 40% O_2 in nitrogen) was fed into the reactor with a total flow rate of 50ml/min controlled by two Omega mass flow controllers. The reactor was connected to the mass flow controller by a 1/8 inch stainless steel tubes and swagelok connectors.

The reactor was mounted in a programmable electrical furnace “Carbolite - Gero” (Serial No. 21-900253) to heat it and maintain a constant temperature.

The cracking experiment was divided into two consecutive stages. First, the reactor was placed inside the furnace for 15 minutes to ensure proper heating and proper oxygen concentration in the whole tube, and then the heating gun was turned on for another 15 minutes to vaporize the octadecane placed at the edge of the reactor (outside the furnace). The vaporized octadecane was mixed with the gas flow at the entry of the reactor and pushed into the reactor.

During the experiment, the condensable liquid product was collected through a pre-weighed condenser connected to the reactor end, while the gaseous product was collected in a tedlar bag connected to the other periphery of the condenser.

At the end of the experiment, the solid residue left in the reactor tube was weighed by subtracting the mass of the reactor after the experiment from the mass of the reactor while it was empty. The mass of the liquid oil collected in the condenser was also measured by subtracting the mass of the condenser after the experiment from the mass of the condenser before the experiment. Finally, the mass of gaseous products produced was calculated by mass balance.

At the end of the experiment, unreacted octadecane was present as solid or liquid mixed with the oil sample. Therefore, GC-MS of the oil sample was performed to detect the area of octadecane in the liquid sample. The mass percentage of unreacted material was evaluated from the oil analysis results.

After each experiment, the quartz tube reactor and the collector were weighed using a balance to calculate the amounts of non-condensable gas and liquid produced.

$$m_{liquid} = m_{collector\ before} - m_{collector\ after}$$

$$m_{gas} = m_{octadecane} - m_{liquid}$$

$$conversion\ to\ liquid = \frac{m_{liquid} - m_{unreacted\ octadecane\ (GC-MS)}}{m_{octadecane}} \times 100$$

$$conversion\ to\ gas = \frac{m_{gas}}{m_{octadecane}} \times 100$$

$$conversion = \frac{m_{gas} + m_{oil}}{m_{octadecane}} \times 100$$

C. Characterization method

1. *Gas Chromatography-Mass Spectrometry (for gas analysis)*

The GC-MS analysis of gas samples was carried out using a 5975C GC MSD gas chromatograph mass spectrometry from Agilent Technologies in the Environment Laboratory. The installed column was an Agilent DB-624 capillary column (30 m × 0.32 mm × 1.8 µm). Samples were injected in a split mode with a split ratio of 45:1 and split flow of 79.1 mL/min with an injection volume of 5 µL.

The oven temperature program was set to be initially held at 26°C for 10 minutes, then programmed to 255°C at a ramp of 25°C/min with a hold time of 4 minutes. Helium was used as the carrier gas with a flow of 1.8 mL/min. The injector and detector temperatures were maintained at 200 and 255°C, respectively and the interface temperature was held at 300°C

2. *Gas Chromatography-Mass Spectrometry (for oil analysis)*

GC–MS analysis of oil samples was performed using a 5975C GC MSD gas chromatograph mass spectrometry from Agilent Technologies equipped with a Thermo scientific column TR-5MS (30 m × 0.25 mm × 0.25µm) in the Central Research Science Laboratory. The column temperature was initially held at 40 °C for 5 min, following which it was programmed to 300 °C at a rate of 8°C/min with a final hold time of 5 min. Helium was used as the carrier gas. The injector and detector temperatures were maintained at 200 and 350 °C, respectively, and the injection volume was 1 μL in splitless mode. The interface temperature was held at 250 °C. Mass spectra were scanned from m/z 50 to 650 at a rate of 0.817 scans/s.

D. Results and Discussion

1. *Thermal cracking of octadecane*

a. Effect of temperature on octadecane conversion

During thermal cracking, temperature was the only driving force responsible for the degradation of octadecane into smaller molecules. Cracking of octadecane was studied in the temperature range of 450 and 650°C and the products obtained were non-condensable gas fraction, liquid fraction and unreacted material.

Table 4 shows the results of the thermal cracking of octadecane in the temperature range 450 - 650°C. Results clearly show the impact of temperature on octadecane conversion. With the increase in temperature from 450 to 550°C, a minor increase in conversion was noted, however, experiments at temperatures above 600°C have shown measurable improvement in octadecane conversion to a maximum of 86% at 650°C.

The gas and oil yield percentages displayed in the table 4 show that only gas was produced at all temperatures below 600°C and only low amounts of oil (9.30wt.%) were produced at 650°C.

Due to the increase in conversion with temperature, the gas yield followed the same trend of octadecane conversion.

Table 4: Influence of temperature on octadecane conversion and distribution of different fractions during cracking. Reaction conditions: 50 mL/min nitrogen, 15 minutes reaction time.

Temperature (°C)	Octadecane Conversion (%)	Gas (wt. %)	Oil (wt. %)
450	15.37	100	0
500	19.85	100	0
550	25.31	100	0
600	39.45	100	0
650	86	90.7	9.30

b. Effect of temperature on gaseous products

The majority of products formed during thermal cracking of octadecane were found to be gaseous compounds. Therefore, the gas collected from each experiment was analyzed using GC-MS to determine product distribution at different temperatures.

Table 5 shows the composition of gaseous products obtained from the cracking of octadecane at different temperatures. It was found that the increase in temperature induced a significant alteration in product distribution. At a low temperature (500°C), only C_2-C_4 olefins (ethene and propene) were produced and octadecane conversion to gas was low (19.85%). With the increase in temperature, more components were detected, accompanied by the increase in the gaseous yield. Alkane and branched olefins were first observed at 550°C, and di-alkenes appeared at 600 and 650°C.

The GC area percentages of products at different reactor temperatures were investigated (Table 5). From 500 to 550°C, a decrease in C_2-C_4 olefins selectivity (100% - 51.52%), accompanied by a significant increase in methane (0-7.12%) and C_5^+ olefins (0-41.35%), was observed. A further increase in temperature broadened the product distribution seen by the production of die-alkenes and cyclic components.

The increase in temperature enhanced octadecane conversion, and therefore more products were formed and lower area percentages of olefins were observed.

Table 5: Composition of gas products obtained during the cracking of octadecane at different temperatures. Reaction conditions: 50 mL/min nitrogen, 15 minutes reaction time.

Temperature (°C)	500	550	600	650
C_{18} conversion to gas (%)	19.85	25.31	39.45	78
Area %				
CO_X	0	0	0	0
Methane	0	7.12	10.28	2.90
C_2-C_4 alkanes	0	0	0	0
C_2-C_4 olefins	100	51.52	51.47	58.93
Alkynes	0	0	0	0
$\leq C_4$ di-alkenes	0	0	2.52	6.37
$\geq C_5$ alkanes	0	0	0	0
$\geq C_5$ olefins	0	41.35	35.72	25.49
$\geq C_5$ di-alkenes	0	0	0	3.28

Cyclic components	0	0	0	3.04
Oxygenates	0	0	0	0

Figure 20 presents the areas of the main gaseous products as a function of temperature. The amounts of methane, C_2-C_4 olefins, and C_5+ olefins clearly increased with temperature. However, the extent of increase in C_2-C_4 olefins and octadecane conversion to gas was massive at 650°C. It may thus be concluded that in thermal cracking, high temperatures above 650°C are needed to achieve acceptable yields of C_2-C_4 olefins.

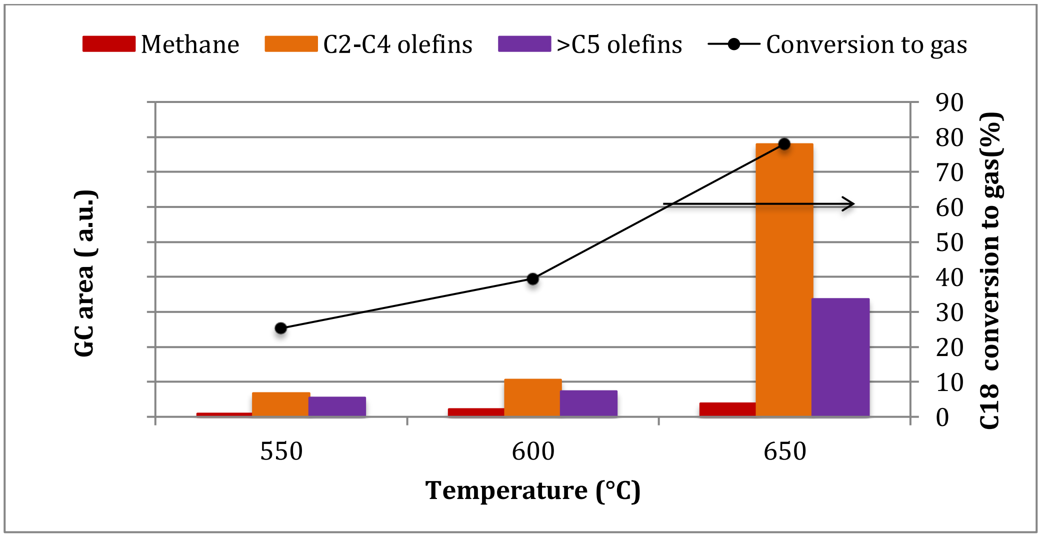


Figure 20: Influence of temperature on methane, C_2-C_4 olefins, >C_5 olefins yields and octadecane conversion to gas. Reaction conditions: 50 mL/min nitrogen, 15 minutes reaction time.

2. *Oxidative cracking of octadecane*

a. Effect of temperature

i. Effect of temperature on octadecane conversion

Table 6: Influence of temperature on octadecane conversion and product distribution. Reaction conditions: 50 mL/min total flow rate,10% oxygen,15 minutes reaction time.

Temperature (°C)	Octadecane Conversion (%)	Gas (wt. %)	Oil (wt.%)
450	17.84	100	0
500	22.53	100	0
550	65	46.33	53.67
600	69	67.19	32.81
650	87	91.32	8.68

In a quartz reactor, the cracking of octadecane without oxygen was modest when the temperature was below 600 °C. Table 6 displays the influence of temperature on octadecane cracking at 10% oxygen concentration. Results show that with the increase in temperature and the introduction of a low volume of oxygen to the feed ($C_{18}H_{38}$ / O_2 = 14.1 molar ratio), octadecane conversion increased. At temperatures below 500°C, the intensity of cracking was insignificant and low amounts of gaseous products were produced. An increase in temperature from 550°C to 650°C resulted in a significant increase in octadecane conversion from 65 to 87wt%. Gas wt. % increased from 46.33% to 91.32% and oil wt. % decreased from 53.67% to 8.68%.

ii. Effect of temperature on gaseous product

As previously mentioned, in thermal cracking, the increase in temperature increases octadecane conversion and gas wt. %, with the addition of molecular oxygen, the effect of temperature on product distribution was also studied. C_2-C_4 olefins, di-alkenes, alkanes, cyclic, and oxygenated compounds were produced at higher temperatures (Table 7). The production of oxygenated compounds was justified by the addition of molecular oxygen to the feed.

Table 7: Composition of gas products obtained during the cracking of octadecane at different temperatures. Reaction conditions: 50 mL/min total flow rate, 10% oxygen, 15 minutes reaction time.

Temperature (°C)	550	600	650
C_{18} conversion to gas (%)	30.12	46.36	79.45
Area %			
CO_X	10.63	4.46	5.57
Methane	4.92	3.45	2.36
C_2-C_4 alkanes	0	0	0
C_2-C_4 olefins	43.25	43.57	51.83
Alkynes	0	0	0.067
$\leq C_4$ di-alkenes	2.71	4.19	6.95
$\geq C_5$ alkanes	0	0	0.39
$\geq C_5$ olefins	35.45	37.73	26.29
$\geq C_5$ di-alkenes	0	0.52	2.27
Cyclic components	0	1.84	3.44
Oxygenates	3.05	4.23	0.81

As shown in Table 7, the increase in temperature decreased the CO_x area % (10.63-5.57 wt. %) and increased the C_2-C_4 olefins area % (43.25- 51.83wt. %). Furthermore, an increase in the formation of both di-alkenes and cyclic compounds was observed with the increase in temperature. For C_5^+ olefins, the area percentage was almost constant between 550°C and 600°C and then decreased vastly from 37.73% to 26.29% when the temperature increased from 600°C to 650°C.

Figure 21 demonstrates that the main product of the 10% oxidative cracking of octadecane was C_2-C_4 olefins at all temperatures. With the increase in octadecane conversion to gas, there was an increase in the formation of CO_x, methane, C_2-C_4 olefins and C_5^+ olefins. From 600 to 650°C, the conversion to gas was remarkable (46.36-79.45%) accompanied by the same trend of C_2-C_4 olefins production.

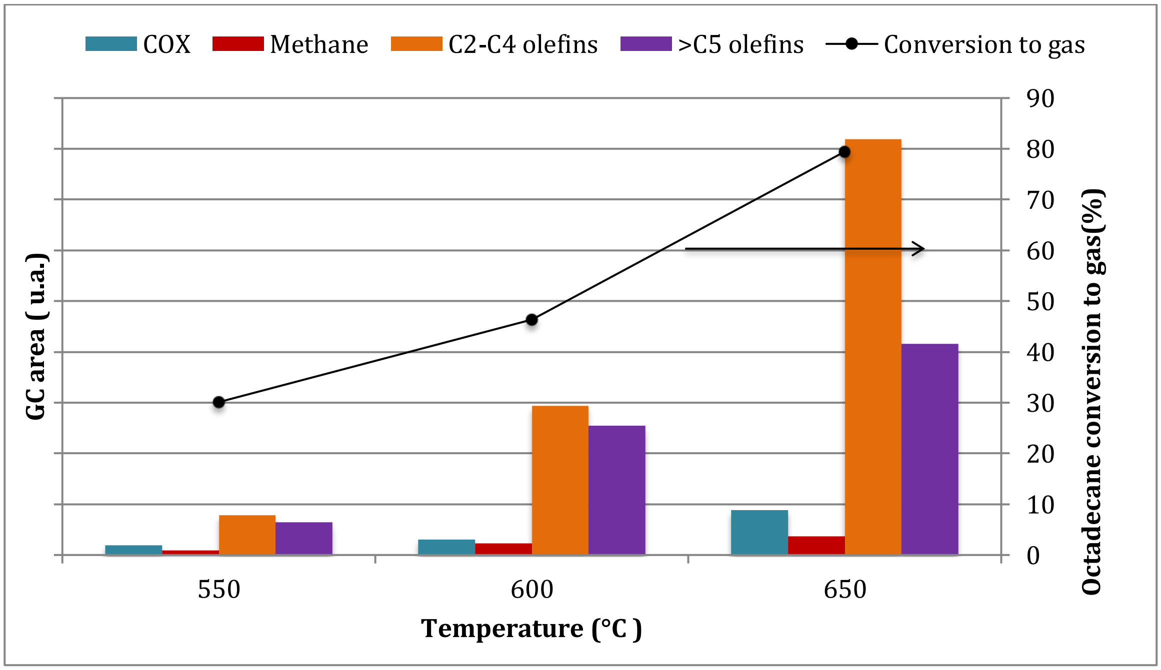


Figure 21: Influence of temperature on CO_x. methane, C_2-C_4 olefins, >C_5 olefins yields and octadecane conversion to gas. Reaction conditions: 50 mL/min total flow rate, 10% oxygen, 15 minutes reaction time.

iii. Effect of temperature on liquid products

The cracked oils derived from the 10% oxidative cracking experiments were evaluated in terms of carbon number and hydrocarbon group area percentage as depicted in Figure 22.

The alteration in oil product distribution with respect to furnace temperature was remarkable. The oil composition in the range of 550°C and 600°C showed an increase in the formation of C_9-C_{11} and C_{12}-C_{15} hydrocarbons. However, from 600°C to 650°C an opposite trend was detected. This behavior was due to the increase in cracking intensity with the increase of temperature to shift the cracking towards lower hydrocarbons justified by the formation of C_1- C_6 hydrocarbons in the gaseous product. At all temperatures, the majority of liquid products consisted of C_{12}-C_{15} hydrocarbons.

The oil analysis of all oil samples mainly exhibited two groups of hydrocarbons olefins and oxygenated compounds (alcohols, aldehydes and ketones), but olefins were the main products.

Similar to carbon number, the group of products changed with temperature at 10% oxygen. When the temperature increased from 550°C to 600°C, the area percentage of olefins increased while that of oxygenates decreased. A further increase in temperature to 650°C, led to opposite results. The use of oxygen was the reason behind the existence of oxygenated compounds such as alcohols, ketones, and aldehydes in spite of the small percentages.

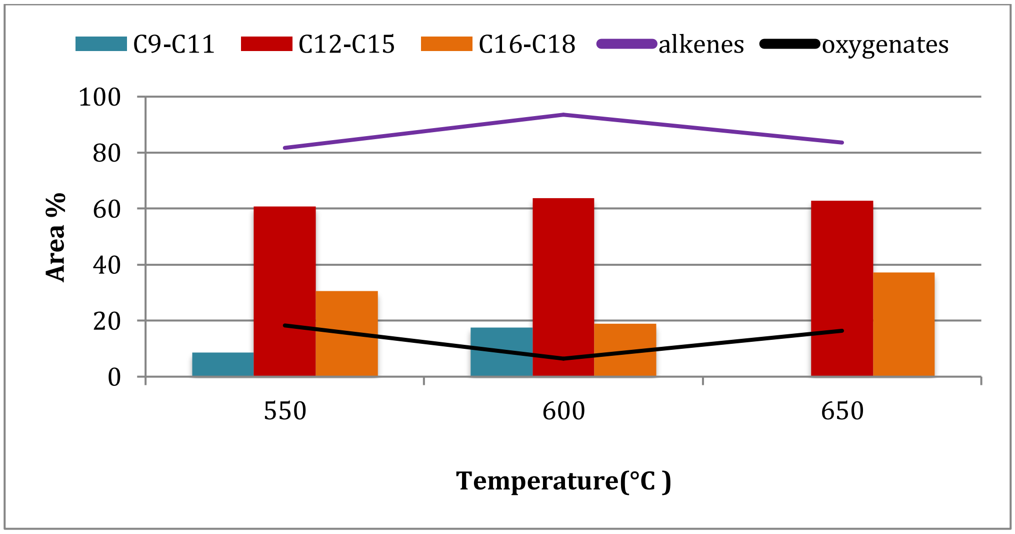


Figure 22: Influence of temperature on liquid products. Reaction conditions: 50 mL/min total flow rate, 10% oxygen, 15 minutes reaction time.

b. Effect of oxygen concentration

i. Effect of oxygen on octadecane conversion

Table 8: Influence of oxygen concentrations on octadecane conversion and product distribution. Reaction conditions: 50 mL/min total flow rate, T= 600°C, 15 minutes reaction time.

Oxygen concentrations (vol.%) at 600°C	Octadecane Conversion (%)	Gas (wt.%)	Oil (wt.%)
10%	69	67.19	32.81
20%	77	68.1	31.9
40%	86	76.74	23.26

The effect of oxygen concentrations on octadecane conversion and fraction wt. % distribution at 600°C is summarized in Table 8. The conversion and gas fraction (wt.%) increased when the concentration of oxygen increased in the feed. In fact, the increase in oxygen concentration from 10% to 40% at the constant temperature 600°C induced higher octadecane conversion, higher gas fraction, and lower oil fraction.

ii. Effect of oxygen concentration on gaseous product

Table 9 shows the GC-MS analysis results of the gaseous products at different oxygen concentrations and the relative product percentage for each run. The most abundant components were C_2-C_4 and C_5^+ olefins. At all oxygen concentrations, almost the same categories of hydrocarbons were detected at 600°C, but the selectivity towards them differed.

Table 9: Composition of gas products obtained during the oxidative cracking of octadecane at different oxygen concentrations. Reaction conditions: 50 mL/min total flow rate, T= 600°C, 15 minutes reaction time.

Oxygen concentration (%)	10	20	40
C_{18} conversion to gas (%)	46.36	52.44	66
Area %			
CO_X	4.46	6.16	14.40
Methane	3.45	5.81	6.63
C_2-C_4 alkanes	0	0	0
C_2-C_4 olefins	43.57	32.89	44.73
Alkynes	0	0	0
$\leq C_4$ di-alkenes	4.19	2.88	3.93
$\geq C_5$ alkanes	0	1.44	0
$\geq C_5$ olefins	37.73	36.04	20.11
$\geq C_5$ di-alkenes	0.52	1.96	2.72
Cyclic components	1.84	2.94	1.52
Oxygenates	4.23	9.87	5.96

CO_x selectivity increased with the increase in oxygen concentration from 4.4% to 14.4%. When the oxygen concentration was raised from 10% to 40% C_2-C_4 olefins selectivity decreased from 43.57 % to 32.89% and then increased to 44.73% at a 40% oxygen concentration. However, oxygenated compounds followed an opposite trend whereby their maximum percentage was reached at 20% oxygen. Methane selectivity was improved in the presence of oxygen from 3.4%-6.6%, while that of C_5^+ olefins was reduced 37.73%-20.11%.

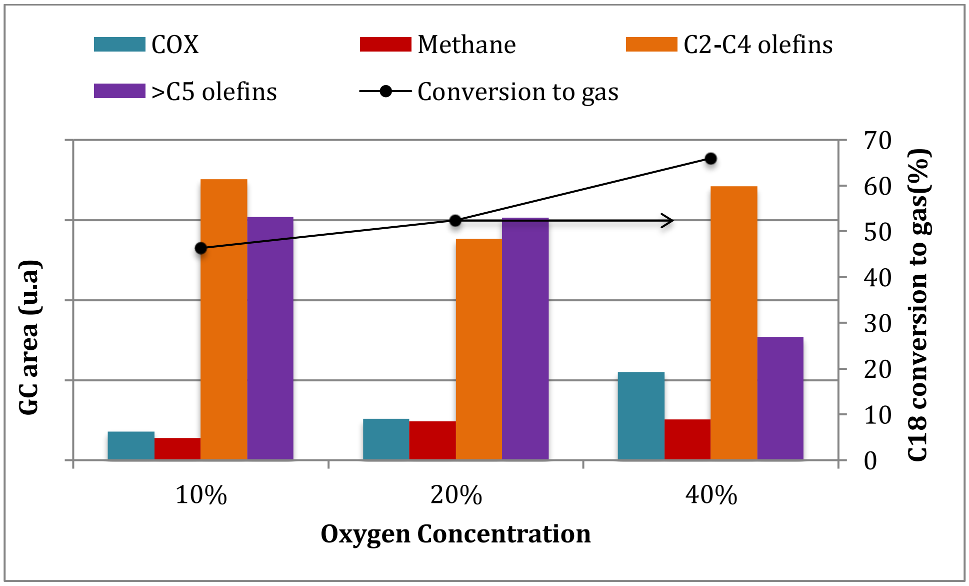


Figure 23: Influence of oxygen concentration on CO_x. methane, C_2-C_4 olefins, >C_5 olefins yields and on octadecane conversion to gas. Reaction conditions: 50 mL/min total flow rate, T= 600°C, 15 minutes reaction time.

The effect of oxygen concentrations on GC areas of products is summarized in Figure 23. Regardless of oxygen concentration olefins were the dominant compounds. The largest area of C_2-C_4 olefins was noted at 10% oxygen concentration. A further increase in oxygen content in the feed did not show a clear effect while a higher oxygen content in the feed was found to boost CO_x and methane production.

iii. Effect of oxygen concentrations on liquid product

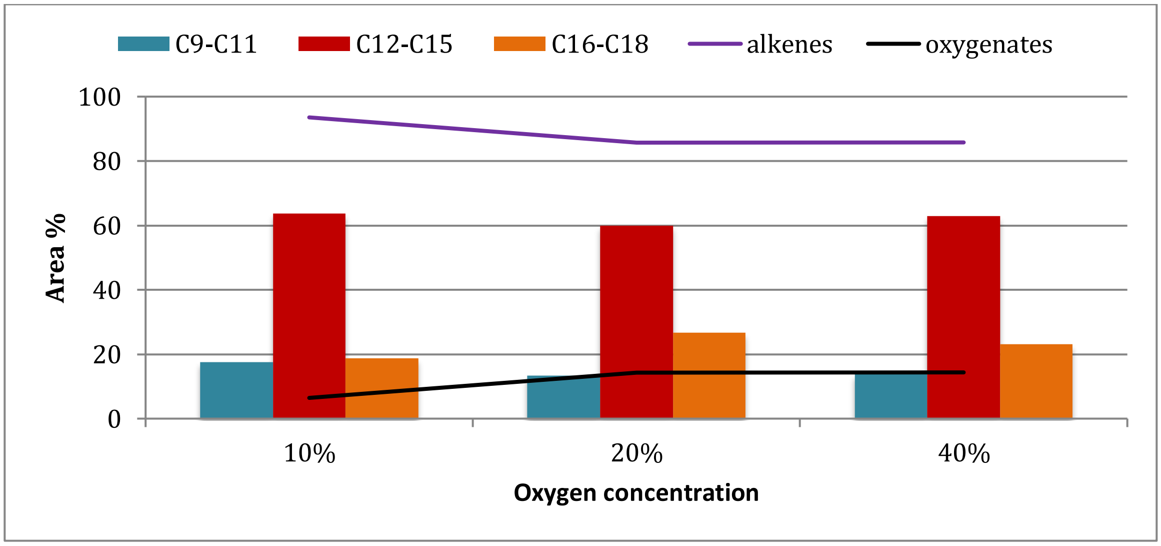


Figure 24: Influence of oxygen concentration on liquid products. Reaction conditions: 50 mL/min total flow rate, T= 600°C, 15 minutes reaction time.

The content of the liquid oil remained approximately the same at all oxygen concentrations. From 10% to 20% oxygen, a slight decrease in olefins production was observed, counterbalanced by a slight increase in oxygenated products. However, it remained constant from 20 to 40% oxygen.

The classification of detected compounds per carbon numbers in Figure 24 shows that C_{12}-C_{15} is the major class of carbon number. Oxygen concentration did not alter the carbon number and carbon type significantly.

3. *Comparison of thermal cracking with oxidative cracking*

a. Octadecane conversion

The introduction of oxygen led to a significant impact on the cracking process. Octadecane conversion at all temperatures increased upon the introduction of oxygen as shown in Figure 25. At 500°C, the effect of oxygen was observed at a 20% oxygen concentration and above. At higher temperatures, the addition of low volume of oxygen makes a huge difference. For example, at 600°C, the conversion was 39.45% in thermal cracking and then increased to 69%, 77%, and 86% with 10%, 20% and 40% oxygen concentrations respectively. It is important to mention that the amount of oxygen added in these experiments was relatively low compared to the amount of octadecane used, where the highest molar ratio of octadecane to oxygen was around 3.5.Thus, a low volume of oxygen can achieve significant improvement in the cracking process.

Figure 25 shows that the increase in temperature increased the cracking of octadecane in thermal and oxidative cracking. However, the effect of oxygen concentration at 650°C was negligible, as the conversion remained the same. Above 600 °C, thermal cracking achieves high conversions to which the addition of oxygen did not bring any further improvements. The activation energy at this temperature was adequate enough that addition of oxygen was no longer needed.

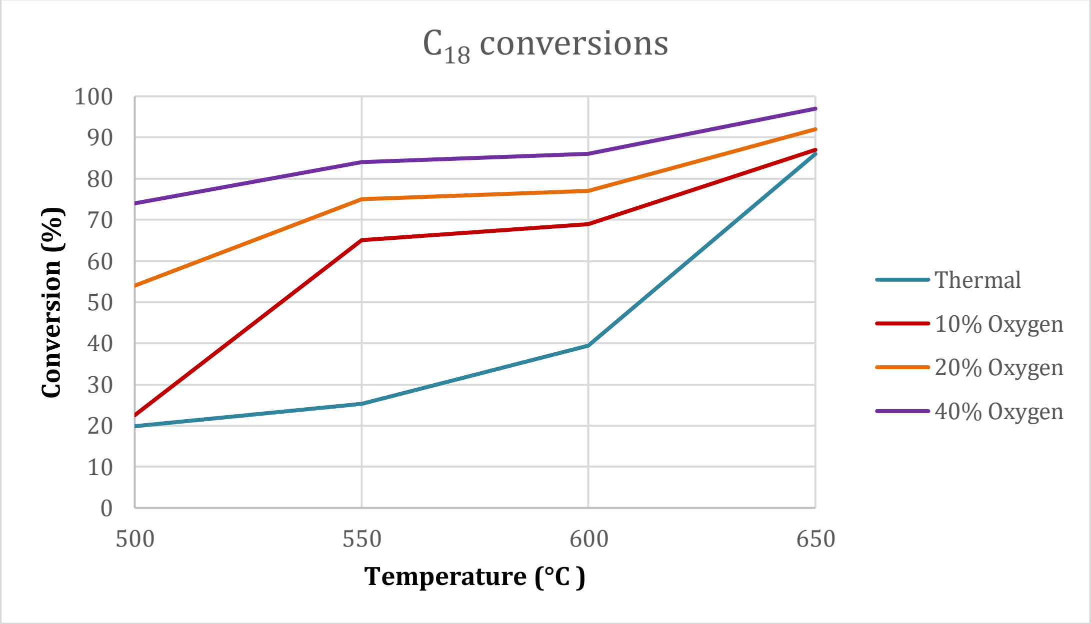


Figure 25: Octadecane conversion at different temperatures and different oxygen concentrations. Reaction conditions: 50 mL/min total flow rate, 15 minutes reaction time.

Figure 26 presents octadecane conversion to gas resulting from the cracking of octadecane at different temperatures and different oxygen concentrations. It was found that the conversion to gas increased with both temperature and oxygen concentration. A significant difference between thermal cracking and oxidative cracking at 600 °C was noted and this difference became larger with increase in oxygen concentration.

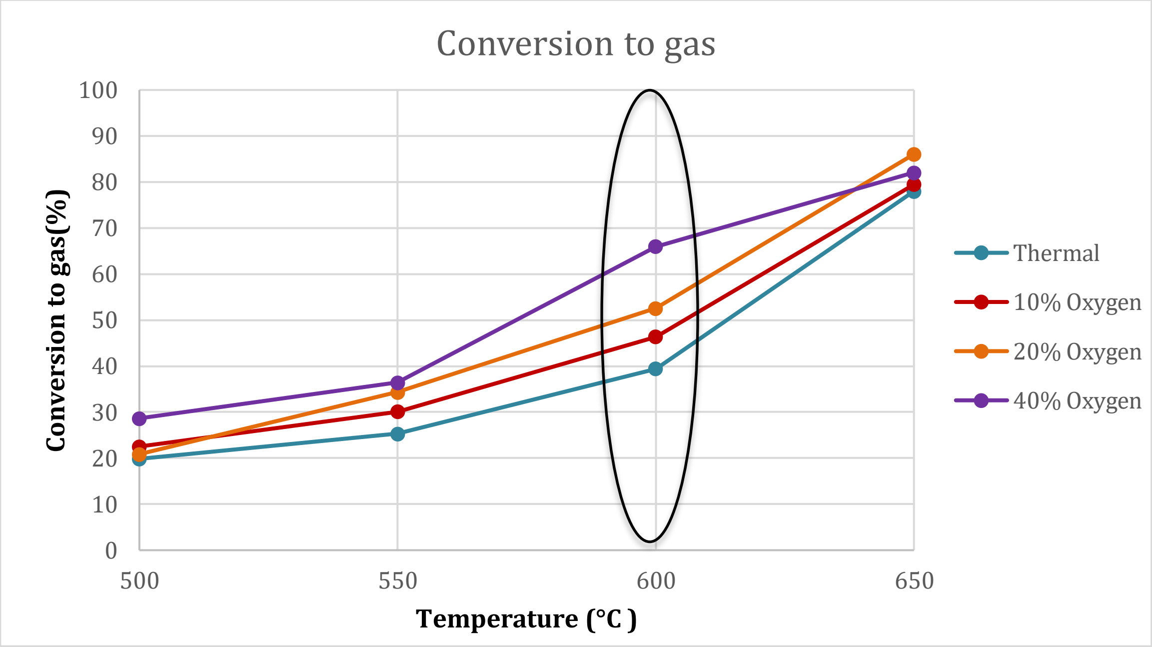


Figure 26: Conversion to gas at different temperatures and different oxygen concentrations. Reaction conditions: 50 mL/min total flow rate, 15 minutes reaction time.

In addition to octadecane conversion to gas, its conversion to oil was also investigated as shown in Figure 27. In thermal cracking, oil was only produced at high temperature (650°C) while oxidative cracking showed improvement in oil production even at low temperatures. The addition of oxygen had significant impact on oil production mainly at low temperatures and this impact decreased with temperature.

To conclude, our results show that oxygen plays an important role in enhancing octadecane cracking and maximizing gas and oil production.

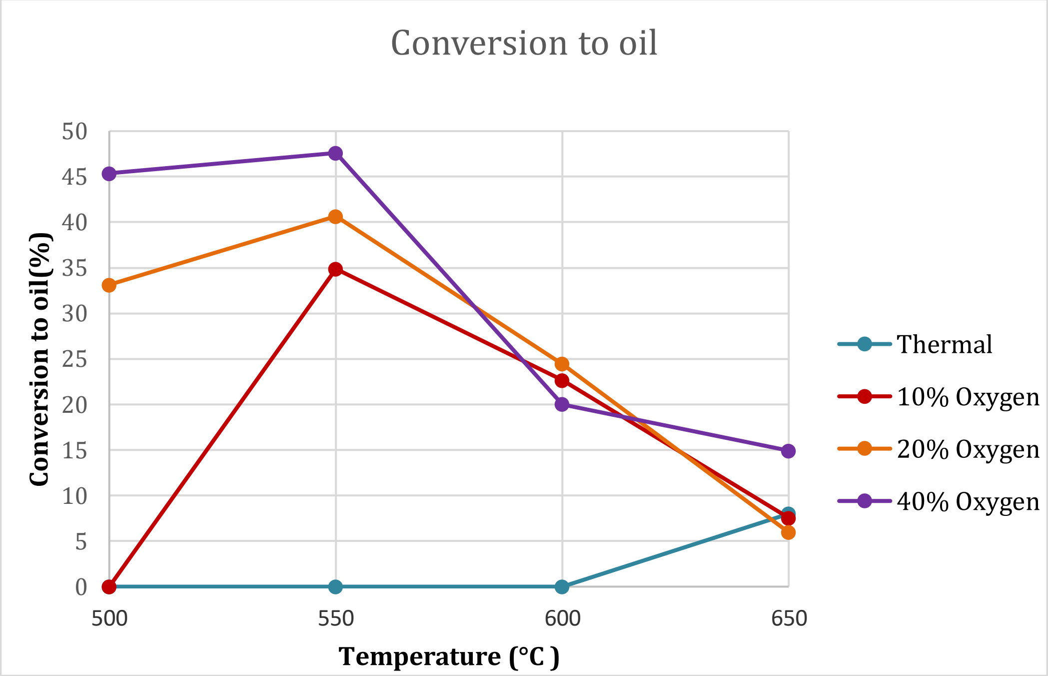


Figure 27: Conversion to oil at different temperatures and different oxygen concentrations. Reaction conditions: 50mL/min total flow rate, 15 minutes reaction time.

b. Product distribution of the gas fraction

In order to assess the optimum conditions for the production of C_2-C_4 olefins, a series of experiments were performed at the optimal temperature chosen (600°C) in the absence and the presence of oxygen. It was found that the relative percentage of C_2-C_4 olefins in the gaseous product was maximal in the absence of oxygen (51.4%) and decreased to 36% with 20% oxygen concentration. A further increase in oxygen concentration to 40% improved the selectivity to 44.7%. This increase was justified by the massive decrease in C_5^+ olefins (36%-20%) from 20% to 40% oxygen concentration as shown in Figure 28. Upon the addition of oxygen to the initial reaction mixture, the relative percentage of olefins decreased with oxygen due to the increase in CO_x and oxygenated compounds.

Although, the increase in oxygen concentration decreased the relative percentage of C_2-C_4 olefins, it significantly increased the octadecane conversion to gas. According to this data, the presence of oxygen plays an important role in increasing octadecane conversion at low temperatures and improves its conversion to gas leading to a broad range of gaseous components, mainly olefins.

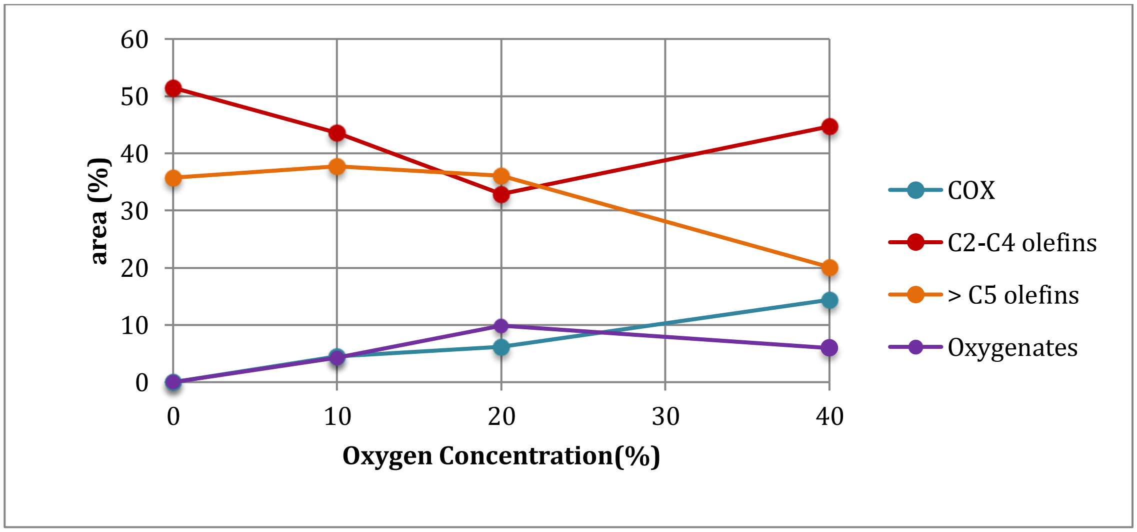


Figure 28: Influence of oxygen concentration on the area % of CO_X, C_2-C_4 olefins, C_5+ olefins and oxygenates. Reaction conditions: 50 mL/min total flow rate, T= 600°C, 15 minutes reaction time.

The GC areas of various products are presented in Figure 29. The production of CO_X increased with oxygen concentration as well as methane production. A vast improvement in C_2-C_4 olefins was witnessed from thermal to oxidative cracking. The GC area of light olefins (C_2-C_4) at 10% and 40% oxidative cracking was high, but at 40% oxidative, it produced also a considerable amount of CO_X. This shows that the best oxygen concentration to produce C_2-C_4 olefins is 10% oxidative, where the GC area and relative area percentage of these compounds are high.

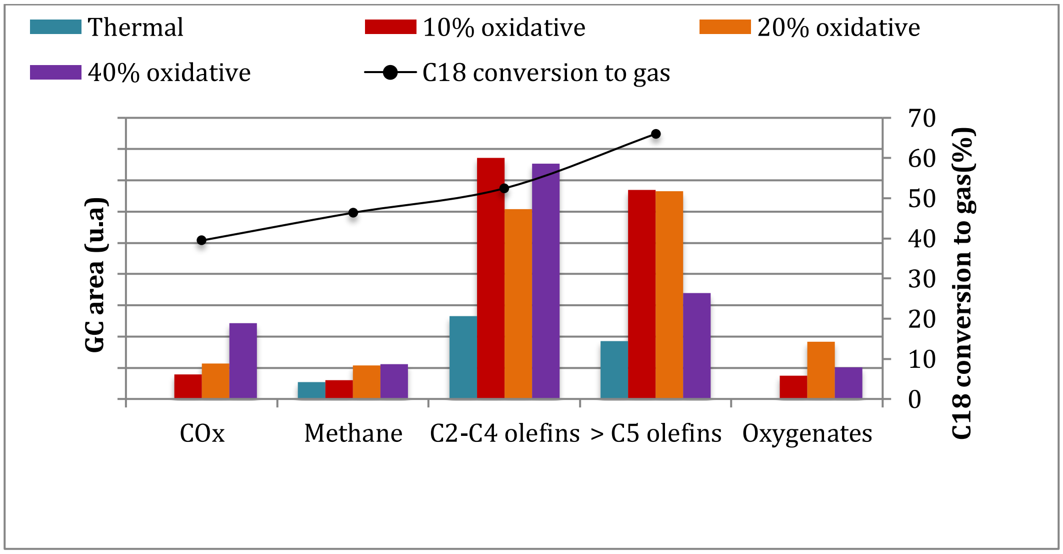


Figure 29: Influence of oxygen concentration on GC area of CO_X, C_2-C_4 olefins, C_5+ olefins and oxygenates. Reaction conditions: 50 mL/min total flow rate, T= 600°C, 15 minutes reaction time.

4. Mechanism

a. Thermal cracking

Thermal cracking is a process in which hydrocarbons are exposed to high temperature in order to break down long chained hydrocarbons into shorter chains. This process usually generates valuable products like fuels and chemicals. In our case, the thermal cracking of octadecane was performed at different temperature ranges from 450°C to 650°C to produce C_2-C_4 olefins.

The increase in cracking temperature improves octadecane cracking and enhances its conversion to gas since high temperature favors the end chain mechanism. The end chain mechanism leads to the formation of lower hydrocarbons due to the intense movements of molecules (Gao, 2010).

During thermal cracking, radical initiation is better achieved by C-C bond cleavage rather than C-H since the latter has higher activation energy (Pogosyana et al., 2014).

$$C_{18}H_{38} \rightarrow CH_3^{\cdot} + C_{17}H_{35}^{\cdot} \qquad (1)$$

$$C_{18}H_{38} \rightarrow C_2H_5^{\cdot} + C_{16}H_{33}^{\cdot} \qquad (2)$$

$$C_{18}H_{38} \rightarrow C_3H_7^{\cdot} + C_{15}H_{31}^{\cdot} \qquad (3)$$

The C-C bond cleavage can occur at any C-C bond to form two free radicals as shown in eq1→3. The two free radicals produced during thermal cracking undergo two different paths during propagation (Xu, et al., 2019). The first suggested path is hydrogen abstraction where the formed radicals abstract hydrogen from octadecane to form an alkane and a new radical such as methane, butane, pentane, and hexane (eq.3→6).

$$C_{18}H_{38} + CH_3^{\cdot} \rightarrow CH_4 + C_{18}H_{37}^{\cdot} \qquad (3)$$

$$C_{18}H_{38} + C_4H_9^{\cdot} \rightarrow C_4H_{10} + C_{18}H_{37}^{\cdot} \qquad (4)$$

$$C_{18}H_{38} + C_5H_{11}^{\cdot} \rightarrow C_5H_{12} + C_{18}H_{37}^{\cdot} \qquad (5)$$

$$C_{18}H_{38} + C_6H_{13}^{\cdot} \rightarrow C_6H_{14} + C_{18}H_{37}^{\cdot} \qquad (6)$$

The second suggested path is the beta scission known to be the weakest route and therefore the dominant one. During beta scission, the radical formed in the initiation step produces ethene and another radical. Hence, ethene is the major compound generated during thermal cracking (eq.7).

$$C_{17}H_{35}^{\cdot} \rightarrow C_2H_4 + C_{15}H_{31}^{\cdot} \qquad (7)$$

Propene is a major component found in the gas sample from octadecane cracking. Propene is produced via hydrogen abstraction from the propyl radical (eq.3) formed during the initiation step (eq.8).

$$C_3H_7^{\cdot} \rightarrow H^{\cdot} + C_3H_6 \tag{8}$$

And finally during the termination stage, the highly reactive alkyl free radicals are terminated by pairing two radicals to form new bond. For example, the methyl radical abstracts hydrogen radical to produce methane (eq.9) or reacts with another methyl radical to make ethane (eq.10).

$$\mathrm{CH}_3^{\cdot} + H^{\cdot} \rightarrow \mathrm{C}H_4 \tag{9}$$

$$\mathrm{CH}_3^{\cdot} + \mathrm{CH}_3^{\cdot} \rightarrow C_2H_6 \tag{10}$$

Finally, the formation of branched compounds such as methyl propene and methyl pentene is done by the reaction between a secondary radical and a methyl radical (eq.11-12).

$$\mathrm{CH_3}CH^{\cdot}\mathrm{CH_3} + \mathrm{CH}_3^{\cdot} \rightarrow \mathrm{CH_3CH(CH_3)CH_3} \tag{11}$$

$$\mathrm{CH_3CH_2CH_2}CH^{\cdot}\mathrm{CH_3} + \mathrm{CH}_3^{\cdot} \rightarrow \mathrm{CH_3CH_2CH_2CH(CH_3)CH_3} \tag{12}$$

This mechanism is proposed based on Xu et al. (2019)’s work. They were aiming to explore the role of the free radical mechanism in pentane cracking to produce light olefins.

b. Oxidative cracking

The use of oxygen in the initial feed is an alternative way to improve the conversion of octadecane and increase the tendency to form light hydrocarbons.

The enhancement in the degradation of octadecane between thermal and oxidative was clear in our experiments. In thermal cracking the initiation step is based mainly on C-C bond cleavage. However, the use of oxygen improves the initiation step since not only may C-C cleavage occur but also C-H cleavage (Gao, 2010). In addition, the nature of a main chain propagator differs between thermal and oxidative cracking. The radicals formed at the initiation reaction are the main chain propagators in the thermal cracking. On the other hand, the main chain propagator of the oxidative cracking is $OH^{\cdot}$ radicals (Leveles, 2002).

During oxidative cracking, molecular oxygen abstracts hydrogen from octadecane and forms an octadecyl radical (eq.13). The formed octadecyl radical reacts with the oxygen molecule to produce an alkene and a hydroperoxyl radical (eq.14). The latter reacts with another octadecane, thus forming a hydroperoxide molecule (H_2O_2) (eq.15), which by decomposition gives two hydroxyl radicals. $\mathrm{OH}^{\cdot}$ radicals are the main chain propagator in oxidative cracking(eq.16) (László, 2002).

$$\mathrm{C_{18}H_{38} + O_2 \rightarrow C_{18}H_{37}^{\cdot} + H}O_2^{\cdot} \tag{13}$$

$$\mathrm{C_{18}H_{37}^{\cdot} + O_2 \rightarrow C_{18}H_{36} + H}O_2^{\cdot} \tag{14}$$

$$\mathrm{C_{18}H_{38} + HO_2^{\cdot} \rightarrow C_{18}H_{37}^{\cdot} + H_2O_2} \tag{15}$$

$$\mathrm{H_2O_2 \rightarrow 2\ OH^{\cdot}} \tag{16}$$

This oxidative cracking mechanism proposed is analogous to that of oxidative cracking of propane by László (2002).

During oxidative cracking of octadecane, oxygenated compounds are minor products in the gas and oil samples. They consist mainly of aldehydes and ketones whose formation is done by the oxidation of alkane, as justified in a study by Câmara et al., (2010). In the study by Câmara et al. low-temperature 373 K oxidative cracking of n-hexadecane gave mainly oxygenated compounds such as ketones and aldehyde.

$$\mathrm{R-CH_3+\frac{1}{2}\,O_2\ \rightarrow\ R-CH_2-OH}$$

$$\mathrm{R-CH_2-OH+\frac{1}{2}\,O_2\ \rightarrow\ R-CHO}$$

$$R-CHO+R_1^{\cdot}\ \rightarrow\ R-CO^{\cdot}+R_1-H$$

$$R-CO^{\cdot}\ \rightarrow\ R^{\cdot}+CO$$

$$R-CHO+O_2\ \rightarrow\ R-COOH$$

$$R-COOH\ \rightarrow\ R-COO^{\cdot}$$

$$R-COO^{\cdot}\ \rightarrow\ R^{\cdot}\ +CO_2$$

$$R^{\cdot}\ +H\rightarrow\ R-H$$

$$R^{\cdot}\ +OH^{\cdot}\rightarrow\ R-OH$$

E. Conclusion

This study has found that the presence of oxygen in the feed significantly improved total octadecane conversion and its conversion to gas. The main role of oxygen in the cracking process was attributed to the formation of highly reactive chain carrier radicals ($OH^{\cdot}$). In addition, the presence of oxygen made the reaction exothermic and released in-situ heat for the endothermic cracking process. This minimized the external heat input and allows the process to run in an autothermal way.

Oxidative cracking of octadecane improved C_2-C_4 olefins production compared to thermal cracking; nonetheless, at higher oxygen concentrations, there was an increase in CO_X formation (from 4.46%-14.40%).

Oxidative cracking of octadecane at 600°C with 10% oxygen concentration in the initial mixture resulted in a significant conversion (69 wt%) with 46.36% conversion to gas and a promising area percentage of C_2-C_4 olefins (43.57%) in addition to a total area percentage of olefins in the gaseous product around which was roughly (81.3%). In addition, in these conditions, the oil produced mainly consisted of C_{12}-$C1_5$ olefins.

Therefore, oxidative cracking appears to be a promising alternative to increase alkane conversion and light olefin production. The drawback of oxidative cracking is the tendency to produce a noticeable amount of CO_X.

CHAPTER V

CATALYTIC OXIDATIVE CRACKING

A. Introduction

The cracking process can be improved by the addition of catalysts, which may promote the cracking reactions at lower temperatures and improve selectivity towards desired products. The pyrolysis of plastic wastes using catalysts has been widely investigated, leading to findings which show that acidic catalysts such as zeolites are ideal in the production of valuable fuels. Zeolites are mainly employed to alter the distribution of pyrolytic oil to aromatics and naphtenes, and therefore enhance the stability and increase the cetane number of the oil produced.

However, the aim of this study was to shift the cracking products from valuable fuels to light olefins such as ethene, propene, and butene since they are the building blocks of the petrochemical industry, as well as the basis for a wide range of consumables. As a consequence of the global demand for light olefins, the development of an alternative route drew researchers' attention.

The most recent studies on the cracking of lower alkanes using oxidic non red-ox catalysts have demonstrated improvement in olefin yields. Boyadjian et al. (2010) studied catalytic oxidative cracking of hexane as a model compound of naphtha using sol gel, which is synthesized Li/MgO. At a temperature as low as 575°C, Li/MgO gives reasonable hexane conversion (28 mol%) and excellent selectivity to light olefins (60% mol). Basic catalysts such as Li/MgO are widely used in the cracking of lower alkanes unlike acidic catalysts because basic catalysts have high selectivity to light olefins while acidic catalysts such as zeolite have high selectivity to aromatic compounds. Hence, testing was carried out to evaluate the performance of different Li/MgO synthesis methods in the oxidative cracking of octadecane as a model compound of HDPE. High surface area support MgO (290 m^2/g) was attained via the thermal decomposition of magnesium hydroxide precursors. But the impregnation of Li with the high surface area support resulted in a low surface area (10 m^2/g).

B. Materials

Commercially available magnesium nitrate hexahydrate (Sigma Aldrich, 99%, 4M), and Ammonium hydroxide (Sigma Aldrich, 99%) solution were used for synthesis of MgO via the ammonium precipitation method.

Commercially available magnesium hydroxide (Sigma Aldrich, 99%) was used for synthesis of MgO via the thermal decomposition method.

Commercially available magnesium oxide (Acros Organics, 98%) was used for the synthesis of MgO via the thermal decomposition method.

Lithium nitrate solution (Fisher Scientific) was used as precursor for Li impregnated on the MgO support.

C. Experimental procedure

1. Catalyst preparation

a. Synthesis of magnesium oxide support synthesis

Different synthesis methods were executed to produce high surface area magnesium oxide as support for the investigated catalyst Li/MgO.

i. Thermal decomposition with $Mg(OH)_2$ precursor

Commercially available magnesium hydroxide (Sigma Aldrich, 99%) was calcined at 600°C for 2 hours **(MgO-R)**. The magnesium oxide obtained was rehydrated through refluxing in distilled water (125ml) for 3 hours. The resultant solid, denoted as rehydrated $Mg(OH)_2$, was dried at 120°C overnight (**MgO-RO**) and then calcined at 450°C under dynamic vacuum for 2 hours. This material was designated as **MgO-ROH**.

ii. Thermal decomposition with MgO precursor

Commercially available MgO (ACROS ORGANICS, 98%) with low surface area was refluxed with 250 ml of distilled water for 24 hours. The mixture was then washed and dried at 120°C overnight to get $Mg(OH)_2$. This sample was divided into more hydrated and less hydrated parts. The more hydrated compound (MgO-C) was calcined at 450°C under dynamic vacuum for 2 hours. This sample was designated as MgO-CA.

iii. Ammonium precipitation method

A 4M aqueous solution of magnesium nitrate hexahydrate was taken in a glass bottle at room temperature. To maintain a NH_4OH-to-Mg mole ratio of 5, a calculated amount of an aqueous ammonium hydroxide solution was added to the magnesium nitrate solution, and the mixture was stirred magnetically for about 5 minutes at room temperature. The bottle was then tightly closed, gradually heated to 60°C, and maintained at this temperature for 6 hours with continuous stirring. After 6 hours, the cap of the reagent bottle was slowly opened. A brisk effervescence was observed due to a release of accumulated ammonia gas inside the bottle. The heating was stopped and slow stirring continued for the next 24 hours. The precipitate was then separated by centrifugation and repeatedly washed with distilled water several times. The precipitate was dried at 70°C for another 24 hours. The solid obtained was coded as MGO-A and then calcined at 450°C under dynamic vacuum for 2 hours. The obtained sample was coded as MGO-AC.

b. Synthesis of Li-MgO

After the synthesis of high surface area magnesium oxide, MgO was doped with lithium.

i. 1wt% Li-MgOROH

After the synthesis of the support, the lithium was impregnated on this support using the wet impregnation method to make 1wt% Li-MgO using $LiNO_3$ solution. The sample was stirred at room temperature for 1 hour then dried in a rotary evaporator for 24 hours and calcined at 700°C for 8 hours.

2. *Catalyst characterization method*

a. BET Isotherm Analysis

BET analysis was conducted using the Gemini VII 2390 p instrument. The gas used for physical adsorption was nitrogen. Before the analysis of the surface area, the catalyst sample was placed in the BET quartz tube and connected to the degassing unit FlowPrep060 for a period of 2 hours at a temperature of 200°C in order to remove gases and vapors that might be physically adsorbed onto the surface of the catalyst. The method loaded on Gemini VII version 3.04 contains 66 points for analysis: 46 points for adsorption and 20 points for desorption. The report of each analysis includes surface area, pore size, and volume in addition to the adsorption and desorption isotherm curve.

3. *Catalytic oxidative cracking setup*

The same setup used in the oxidative cracking of octadecane was used in the catalytic oxidative cracking. The difference was that the reactor was loaded with 0.15 g of a catalyst placed at a constant distance from the reactant and bonded by quartz wools. The oxygen concentration used was 10 vol%.

Before the beginning of the experiment, the reactor was kept under the experimental temperature for 30 minutes to ensure that the catalyst was active and the temperature was uniformed throughout the reactor.

D. Results and discussion

1. *Catalyst characterization*

a. BET Isotherm Analysis

The surface area of all synthesized supports was analyzed using the BET technique. The best synthetic method to produce high surface magnesium oxide support was found to be thermal decomposition with a $Mg(OH)_2$ precursor as shown in Table 10.

Table 10: BET results of MgO supports.

Support	Surface area (m^2/g)	Pore Size (nm)	Pore Volume (cc/g)
Commercial MgO	4.87	14.57	0.01002
MgO-ROH	290.23	7.5	0.54561
MgO-CA	156	6.60	0.22475
MgO-AC	57.29	10.06	0.09831

High surface area magnesium oxide prepared via the thermal decomposition of $Mg(OH)_2$ precursor was impregnated with lithium aiming to produce high surface area catalysts.

Table 11: BET results of Li/MgO

Preparation method	Surface area (m^2/g)	Pore Size (nm)	Pore Volume (cc/g)
Wet impregnation	10.53	15.97	0.02128

The Li/MgO catalyst prepared by wet impregnation required high temperature during calcination in order to incorporate lithium to magnesium lattice. At high temperature, two lithium ions replace one magnesium cations thereby forming an oxygen vacant site transforms into $[Li^+O^-]$ defect sites in presence of molecular oxygen. However, not all Li is incorporated as $[Li^+O^-]$ sites and some stay as Li_2O which easily absorbs CO_2 from the atmosphere and forms Li_2CO_3 on the MgO support. Since this catalyst needs a high calcination temperature, Li_2CO_3 melts and sinters the catalyst. This explains the reason behind the major decrease in the surface area after the impregnation of Li on the high surface area MgO support from 290.23 m^2/g to10.53 m^2/g as shown in Table 11.

Thus, other synthesis techniques such as sol-gel method might be a promising route for high surface area Li/MgO, but due to time constraint we could not prepare it.

2. *Cracking results*

a. Conversion of octadecane

A series of experiments were performed using different catalysts to study their effect on octadecane cracking and product distribution. According to Table 12, the use of high surface MgO and 1 wt. % Li-MgO-ROH increases the octadecane conversion from 69% in oxidative cracking to 83%-84%. The presence of the catalysts led to a decrease in octadecane conversion to gas and an increase in oil production.

Table 12: Conversion and distribution of gas and oil fractions over various catalysts. Reaction conditions: 50 mL/min total flow rate, T= 600°C, 10% oxygen (except H-Beta no oxygen), 15 minutes reaction time, mass of catalyst: 0.15g

Catalyst conditions	Octadecane conversion (%)	Octadecane conversion to gas (%)	Octadecane conversion to oil (%)
No catalyst	69	46.36	22.64
Blank	_	23.37	_
MgO-ROH	84.4	29.7	54.7
1% Li-MgO-ROH	83.11	23.77	59.34
H-Beta	100	95	5

These results show that high surface area MgO-ROH and low surface area 1wt% Li-MgO-ROH did not fulfill the purpose of this research purpose, which was to get high octadecane conversion to gas and high olefins production. A blank experiment was performed using sand to compare it with a catalytic oxidative cracking experiment. The total conversion of the blank experiment was not included since the oil sample was not analyzed. It was found that both catalytic and blank experiments gave approximately the same octadecane conversion to gas. This catalyst system might be playing the role of a physical barrier.

Moreover, the impregnation of Li on the high surface area MgO-ROH did not have a significant impact on the cracking of octadecane due to the low surface area and therefore the low active site concentration. Octadecane conversion and gas production were approximately the same as shown in Table 12.

Finally, catalytic cracking of octadecane with H-Beta was performed to compare it with the obtained results from the cracking of octadecane with MgO and Li/MgO. H-Beta showed excellent catalytic cracking of octadecane (100% conversion) with 95% conversion of octadecane to gas.

i. Gas analysis

Results in Table 13 clearly show the positive effect of H-Beta on C_2-C_4 olefins production. H-Beta resulted in the highest octadecane conversions and the highest yields to C_2-C_4 olefins. Therefore, H-Beta was the best catalyst in comparison to the MgO and LiMgO prepared by us.

Basic catalysts, which have been tested so far, have not shown promising results; this was mainly due to low surface area of these catalysts and the low concentration of active sites. The gaseous products formed when Li/MgO and MgO were used show high olefins production but the conversion to gas was low. Therefore, these catalysts were not acting as a physical barrier as proposed earlier since sand experiment gave only oxygenates. These results emphasize that basic catalyst can make olefins if prepared properly since preparation method affected catalysts properties. Time constraint has not allowed the exploration of other catalyst systems.

In oxidative cracking, in order to increase olefins yields further, the presence of an acidic catalyst would be needed.

However, zeolites would also lead to formation of aromatic compounds, which are not detected here with octadecane but mentioned in the literature.

Therefore, to improve the selectivity of Zeolites to C_2-C_4 olefins, the acidity of zeolites needs to be tuned by the addition of alkaline earth metals. Basic-acidic catalysts would be interesting to explore in future work.

Table 13: Gas area % over various catalysts. Reaction conditions: 50 mL/min total flow rate, T= 600°C, 10% oxygen (except H-Beta no oxygen), 15 minutes reaction time.

Experiments	No catalyst	MgOROH	1% Li-MgOROH	Sand	H-Beta
C_{18} conversion to gas	46.36	29.7	23.77	23.37	95
Area %					
CO_X	4.46	5.54	32.74	0	0
Methane	3.45	0	0	0	1.20
C_2-C_4 alkanes	0	0	0	0	0
C_2-C_4 olefins	43.57	55.03	61.66	0	72.76
Alkynes	0	0	0	0	0
$\leq C_4$ di-alkenes	4.19	3.49	0	0	0
$\geq C_5$ alkanes	0	0	0	0	3.37
$\geq C_5$ olefins	37.73	12.60	0	0	7
$\geq C_5$ di-alkenes	0.52	0	0	0	0.19
Cyclic components	1.84	4.20	0	0	14.11

Oxygenates	4.23	19.14	5.60	100	1.38
Benzene	0	0	0	0	0.38

E. Conclusion

Basic non-redox catalysts tested in this study show very low activity due to their low surface area. The addition of these catalysts results in low octadecane conversion but results in light olefins formation, contrary to the sand experiment where only oxygenates are produced. In addition, these results indicate that both MgO-ROH and Li/MgO were able to produce olefins compared to thermal cracking.

On the other hand, acidic catalysts remain the best in large hydrocarbon cracking and favor aromatic production. Therefore, it would be interesting in the future, for the oxidative cracking of HDPE, to investigate mesoporous acidic catalysts such as zeolites and attempt to tune their acidity with basic promoters such as calcium and lithium, in order to maximize light olefins production.

CHAPTER VI

OXIDATIVE CRACKING OF HIGH-DENSITY POLETHYLENE

A. Introduction

The purpose of this study was to find a suitable method to take advantage of HDPE plastic wastes by cracking them into valuable products. After testing the effect of oxygen on the cracking of the HDPE model compound (octadecane), it would be interesting to preform thermal and oxidative cracking on shredded HDPE plastic bottles.

B. Materials

To study the pyrolysis of high-density polyethylene, HDPE pellets were obtained from SIGMA-ALDRICH and domestic bottles made of HDPE were collected. The waste plastic bottles were cleaned and shredded into small pieces using a grinding machine.

C. High-Density Polyethylene properties

High-Density Polyethylene is formed of a chain of ethylene (Figure 30) and is known for its high strength-to-density ratio. The proximate and ultimate analysis of HDPE showed that the percentage of volatile matter is around 99.92% with a very low percentage of ash (0.08%), which made the cracking of HDPE nearly free of residue formation (Table 14). For the ultimate analysis, HDPE is mainly constituted of carbon and hydrogen; however, the presence of oxygen and nitrogen and other impurities was due to the ingredients added during production (Kumar & Singh, 2013).

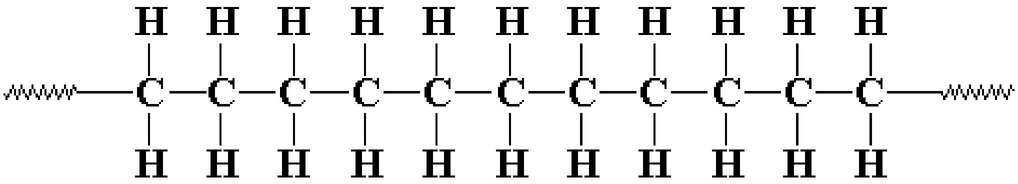


Figure 30: Common expression of polyethylene structure

Table 14: Proximate and ultimate analysis of HDPE (Kumar & Singh, 2013).

Properties	Virgin HDPE
Proximate analysis	
Moisture content	0.00
Volatile matter	99.92
Fixed carbon	0.00
Ash content	0.08
Ultimate analysis	
Carbon (C)	83.29
Hydrogen (H)	13.93
Nitrogen (N)	0.20
Sulphur (S)	0.07
Oxygen (O)/ others	2.51
GCV (MJ/kg)	47.64

Thermogravimetric analysis (TGA) was applied on Virgin HDPE pellets to investigate its weight loss as a function of temperature. As shown in Figure 31, the HDPE degradation started at 380°C and finished at 510°C. Furthermore, DTG was performed and the curve showed only one peak indicating that there was only one degradation step from 390°C to 510 °C where the conversion took place, and the maximum weight loss happened at 498°C (Kumar & Singh, 2013).

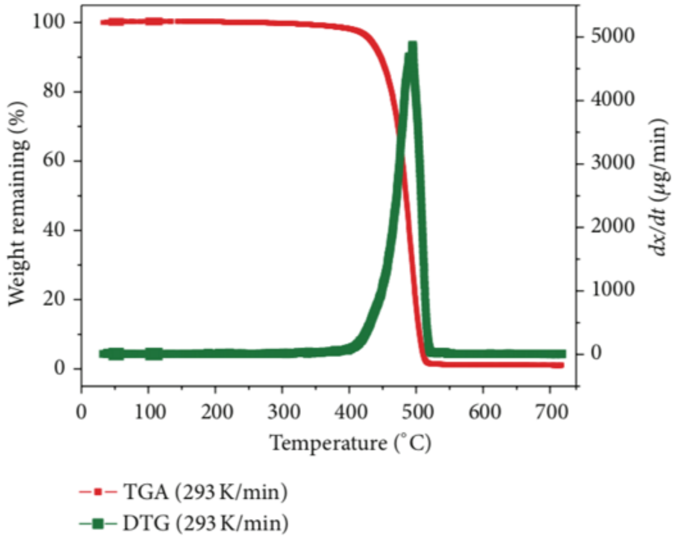


Figure 31: TGA and DTG curves of virgin HDPE (Kumar & Singh, 2013).

D. Characterization method

1. *Thermogravimetric Analysis*

Thermogravimetric analysis was conducted using TG 209 F1 Libra instrument by Netzsch. A given weight of the sample was heated in an Al_2O_3 crucible at a constant heating rate of 30 K/min carried out in a stream of nitrogen from 30°C to 750°C.

2. *Ultimate Analysis*

The ultimate analysis of HDPE pellets and waste plastic bottles was done using a CNH analyzer (Thermo Fisher Flash 2000 Organic element analyzer).

3. *Gas Chromatography-Mass Spectrometry (for gas analysis)*

The GC-MS analysis of gas samples was carried out using a 5975C GC MSD gas chromatograph mass spectrometry from Agilent Technologies in the Environment Laboratory. The installed column was an Agilent DB-624 capillary column (30 m × 0.32 mm × 1.8 μm). Samples and standards were injected in a split mode with a split ratio of 45:1 and split flow of 79.1 mL/min with an injection volume of 5 μL.

The oven temperature program was set to be initially held constant at 26°C for 10 minutes, and then programmed to 255°C at a ramp of 25°C/min with a hold time of 4 minutes. Helium was used as the carrier gas with a flow of 1.8 mL/min. The injector and detector temperatures were maintained at 200°C and 255°C respectively and the interface temperature was held at 300°C

4. Gas Chromatography-Mass Spectrometry (for oil analysis)

The GC–MS analysis for oil samples was performed using a 5975C GC MSD gas chromatograph mass spectrometry from Agilent Technologies equipped with a 30m TR-5MS column. The column temperature was initially held at 40°C for 5 minutes and then programmed to 300 °C at a rate of 8°C/min. with a final hold time of 5 minutes. Helium was used as the carrier gas. The injector and detector temperatures were maintained at 200°C and 350 °C respectively, and the injection volume was 1 μL in splitless mode. The interface temperature was held at 250 °C. Mass spectra were scanned from m/z 50 to 650 at a rate of 0.817 scans/s.

E. HDPE Cracking experiments set-up

The setup used to study the oxidative cracking of shredded plastic is shown in Figure 32. It consisted of a semi-batch reactor made of quartz tube packed with 1.5 g of shreds bounded by quartz wool. A mixture of nitrogen and oxygen was fed into the reactor with 10% oxygen and a total flow rate of 20ml/min. An electric furnace was used to heat up the reactor and maintain its temperature. The condensable liquid product was collected through a pre-weighted condenser connected to the reactor, while the gaseous product was collected in a tedlar bag connected to the other periphery of the condenser. At the end of the experiment, the solid residue left in the reactor tube was weighed and the gaseous product was measure using the material balance.

$$M_{Oil} = M_{Condenser\ after} - M_{Condenser\ before}$$

$$M_{Residue} = M_{reactor\ at\ the\ end} - M_{reactor\ empty} - M_{quartz\ wools}$$

$$M_{Gas} = M_{HDPE} - M_{Oil} - M_{residue}$$

Where M Oil is the mass of liquid collected in the condenser, M Condenser after and M Condenser before are the mass of the condenser after and before the experiment respectively; M Residue is the mass of residue found in the reactor after the experiment; M reactor at the end is the mass of the reactor at the end of the cracking experiment; M reactor empty is the mass of the reactor empty before preparation; M quartz wools is the mass of quartz wools added to the reactor; and M HDPE is the mass of the HDPE used during the experiment.

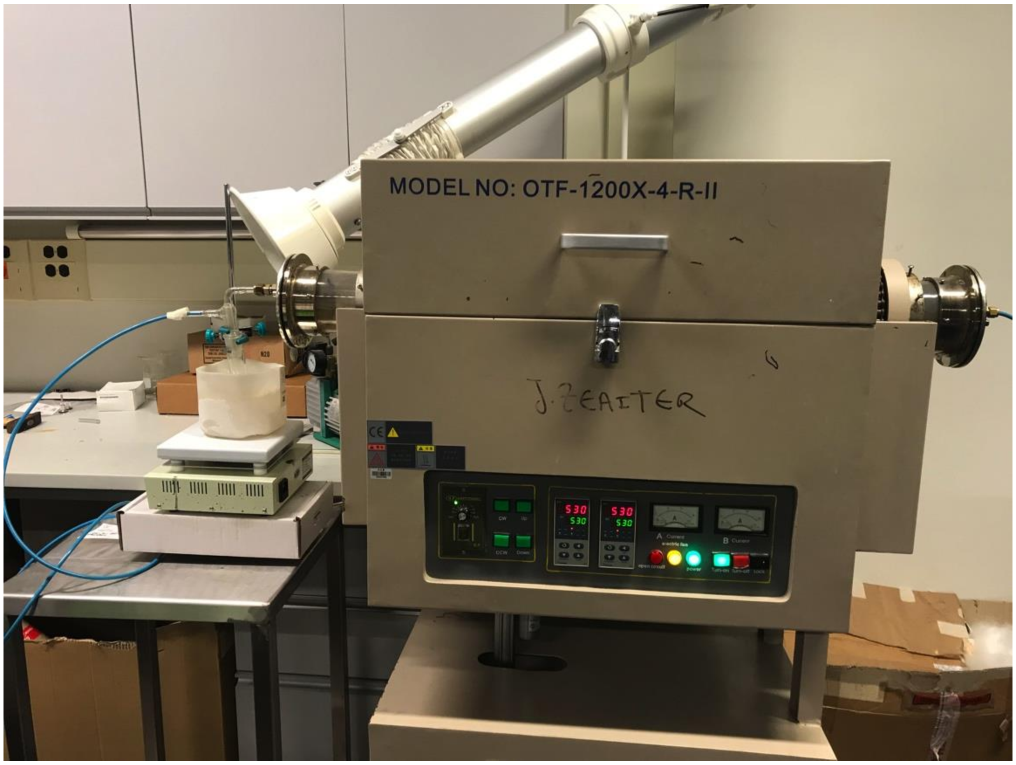


Figure 32: HDPE cracking set-up

F. Results and discussion

1. *Characterization of High Density Polyethylene Characterization*

a. Ultimate analysis of HDPE

The ultimate analysis of virgin HDPE pellets and shredded plastic bottle samples is shown in Table 15. The main elements of HDPE are carbon (C) and hydrogen (H). Each sample was tested twice for reproducibility and it was found that HDPE pellets and HDPE bottles had approximately the same content, which emphasizes that no significant additives were added during the production of HDPE domestic bottles. The calorific value of both samples was also comparable.

Table 15: Ultimate analysis of virgin HDPE pellets and shredded plastic bottles

Sample	Nitrogen	Carbon	Hydrogen	GCV (KJ/Kg)
HDPE (1)	0.0441	85.07	12.71	46264
HDPE (2)	0.0556	85.3	12.28	
Plastic bottles	0.0487	83.48	12.24	45708
Plastic bottles	0.0451	83.48	12.56	

b. TGA analysis of HDPE samples

Thermogravimetric analysis (TGA) was done for both materials to detect the decomposition of samples as a function of time and temperature in a controlled environment. This technique is used to study the behavior of a material and its thermal stability in different atmospheres. It was found that the decomposition of the waste plastic bottles started at 460 °C and ended at 520°C; that of HDPE was approximately the same.

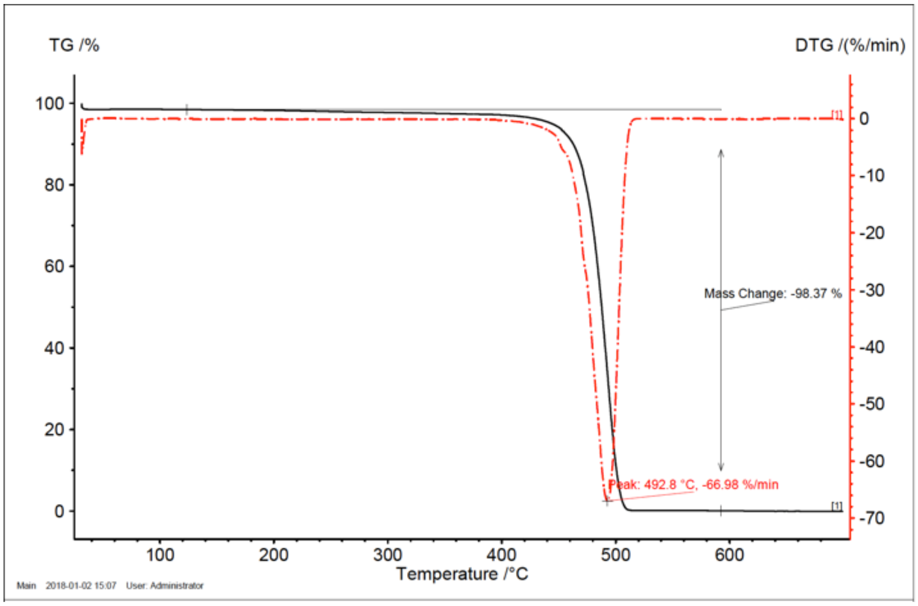


Figure 33: TGA curve of shredded plastic bottles

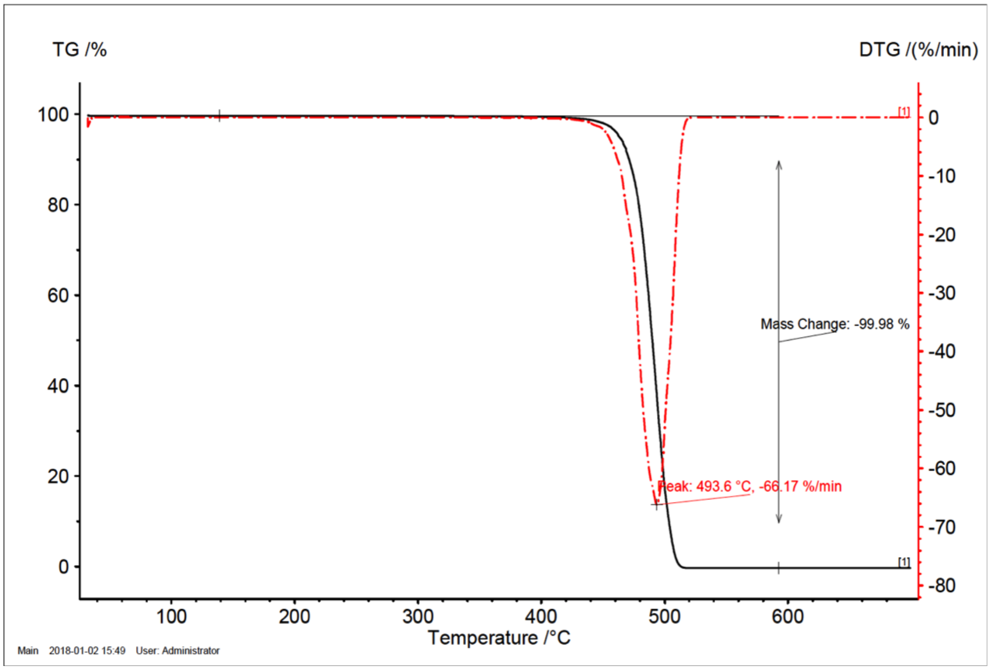


Figure 34: TGA curve of virgin HDPE pellets

2. HDPE preliminary cracking experiments

Preliminary experiments were performed on shredded HDPE bottles at different temperatures ranging from 470°C to 560°C. Results in Table 16 show that the increase in reactor temperature boosted the cracking of HDPE pellets from 28.31% to 93.13%. It was also noticed that the gas fraction followed the same trend as conversion, starting with 21.7% at 470°C to 80.87% at 560°C. However, oil fraction increased to a maximum at 530 °C (44.52%) and then decreased. This behavior was similar to that found in previous studies done by Abbas and Shubar (2008). They performed thermal pyrolysis of virgin HDPE at temperatures between 465°C to 500°C. The highest yield of oil was attained at 480°C while the yield of gas increased with the increase in temperature.

Table 16: Influence of temperature on shredded HDPE cracking conversion and gas and oil fraction. Reaction conditions: 20 mL/min total flow rate, 120 minutes reaction time.

Temperature (°C)	Conversion (%)	Gas wt.%	Oil wt.%	Unreacted material wt.%
470	28.31	21.7	6.57	71.69
500	76.91	38.65	38.26	23.09
530	88.08	43.56	44.52	11.92
560	93.19	80.87	12.31	6.81

After testing the influence of temperature on shredded HDPE, 10% oxidative cracking was performed to prove the concept and results achieved earlier with octadecane.

Although, the introduction of a low volume of oxygen did not show a remarkable improvement in the conversion of HDPE and the gas fraction (Table 17) a significant alteration in gas product distribution was found at 530°C.

Table 17: Influence of oxygen concentration on shredded HDPE cracking conversion and gas and oil fraction. Reaction conditions: 20 mL/min total flow rate, 10% oxygen, 120 minutes reaction time.

Temperature (°C)	Conversion (%)	Gas wt%	Oil wt%	Unreacted material wt%
500	80.82	46.86	33.96	19.18
530	88.76	45.55	43.21	11.24

As shown in Table 18, the addition of low concentration oxygen to the reactant mixture hugely affects the distribution of compounds produced in the gaseous phase. During thermal cracking, only C_5^+ compounds were detected (pentene and hexene); however, light olefins were the main compounds during 10% oxidative, with product percentage around 53.84%.

Table 18: Gas composition at 530°C oxidative cracking, 20 mL/min total flow rate, 10% oxygen, 120 minutes reaction time.

Experiments	Thermal	10% oxygen
HDPE conversion to gas (%)	43.56	46.86
Area %		
CO_X	0	0
Methane	0	0
C_2-C_4 alkanes	0	0
C_2-C_4 olefins	0	53.84
Alkynes	0	0
$\leq C_4$ di-alkenes	0	5.14
$\geq C_5$ alkanes	0	10.75
$\geq C_5$ olefins	100	25.11
$\geq C_5$ di-alkenes	0	1.82
Cyclic components	0	2.58
Oxygenates	0	0.76

Table 19 shows the GC-MS components for liquid products when 10% oxygen was introduced. It consisted mainly of olefins (48.69%) and alkanes (33.05%). In addition, the liquid contained mostly C16-C20 range (43.72%).

Table 19: Liquid composition at 530°C oxidative cracking, 20 mL/min total flow rate, 10% oxygen, 120 minutes reaction time.

R(min)	%Area	Compound
6.13	2.72	Nonene
6.42	1.65	Nonane
8.84	0.70	Octadecyne
9.07	4.06	Decene
9.29	1.99	Decane
11.23	0.64	Octadecyne
11.41	4.00	Dodecene
11.6	2.02	Undecane
13.27	0.24	Dodecadiene
13.45	5.39	Dodecene
13.61	2.89	Dodecane
15.12	0.95	Tridecadiene
15.26	4.45	Tridecene
15.41	0.93	Tridecane
16.83	1.47	Oleyl alcohol
16.96	6.29	Tridecene
17.1	3.06	Tetradecane
18.42	1.37	Oleyl alcohol
18.55	5.79	Pentadecene
18.67	3.06	Pentadecane
19.93	1.22	Oleyl alcohol
20.05	5.28	Hexadecanol
20.16	3.03	Heptadecane
21.36	1.12	Oleyl alcohol
21.46	4.84	Hexadecanol
21.56	2.88	Heptadecane
22.7	0.64	Oleyl alcohol
22.81	3.67	Nonadecene
22.91	3.06	Nonadecane
24.01	0.80	Eicosadiene
24.09	3.39	Nonadecene
24.17	2.05	Nonadecane
25.23	0.43	Oleyl alcohol
25.31	2.65	Nonadecene
25.4	1.92	Heneicosane
26.41	0.33	Eicosadiene
26.5	1.95	Nonadecene
26.56	1.32	Heneicosane
27.62	1.34	Nonadecene
27.68	1.24	Heneicosane

28.68	0.67	Nonadecene
28.74	0.91	Heneicosane
29.72	0.56	Eicosanol
29.78	0.68	Heneicosane
30.76	0.36	Heptacosane

3. Conclusion

The addition of molecular oxygen to the carrier gas produced a noteworthy improvement in the quality of gas produced from the cracking of shredded HDPE waste bottles.

The presence of oxygen in low concentrations alters the composition of the gaseous products from C_5-C_6 olefins to C_2-C_4 olefins. Thermal cracking of shredded HDPE did produce light olefins.

The oxidative cracking of HDPE showed to be a promising route to enhancing the quality of gaseous product produced in order to generate low olefins (C_2-C_4).

CHAPTER VII

CONCLUSION

The extensive use of plastic worldwide has raised concerns around plastic waste accumulation in the environment. Traditional techniques such as landfilling and incineration have been used for a long time to eliminate accumulated plastic wastes, however, these techniques are not environmentally friendly, and incineration requires high energy input. The need for energy efficient and environmentally friendly processes has impelled considerable research work towards the development of cracking technologies for plastic waste reduction.

Cracking processes such as pyrolysis and catalytic cracking technologies have been established as promising approaches to reduce plastic waste and produce valuable products such as fuel and light olefins.

In this thesis, oxidative cracking of octadecane as a model compound of HDPE has been studied as an alternative route to pyrolysis for the production of C_2-C_4 olefins and fuel.

This study resulted in several findings. The introduction of only small concentrations of molecular oxygen to the feed introduced a new radical initiation route and results in significant improvements in octadecane and shredded HDPE conversions, and hence a significant increase in yields of gaseous products, especially C_2-C_4 olefins. The oxidative cracking of octadecane was best at 600°C and 10 vol.% oxygen with 69% conversion and a 43.57 area % of light olefins. A higher oxygen concentration was found to increase CO_X formation. Moreover, oxidative cracking of octadecane significantly improved oil production.

The primary experiment was performed on shredded HDPE bottles waste as theoretical proof of the concept under study. It showed that the addition of a low concentration (10 vol%) of oxygen significantly affects the product distribution of gaseous product towards the production of C_2-C_4 olefins.

In order to achieve higher C_2-C_4 olefins yields the employment of a catalyst was essential. The catalytic cracking of high alkanes such as octadecane using Li/MgO did not result in significant conversion although it showed ability to produce C_2-C_4 olefin to some extent. The reason behind this performance can be attributed to the low surface area of the catalyst tested and to the relative large volume of octadecane vapor employed (high vapor-to-catalyst ratio) during cracking process. So far, acidic catalysts exhibit the best activity for cracking of HDPE, however to better tune the selectivity of the acidic catalysts towards light olefins, it is recommended in the future to develop basic-acidic mesoporous catalysts for the cracking of polymers.

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