Kinetic and Thermodynamic Studies on Pyrolysis of Waste HDPE Polymers

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Thunder Bay, ON

September 1st, 2017

A dissertation submitted in partial fulfillment of requirements

of the degree of

Doctor of Philosophy, Biotechnology

Abstract

Pyrolysis is a promising technology for converting waste plastic into high-value hydrocarbons, which can help to protect the environment and improve the waste management industry. Available methods for finding kinetic parameters and heat of solid state reactions are not compatible with the complexity of pyrolysis reactions, and do not give reliable parameters to design an industrial pyrolysis reactor. This work developed two new techniques to determine kinetic parameters and heat of solid state reactions with high-certainty.

The proposed kinetic study method is a differential isoconversional technique that finds activation energy and pre-exponential factor at different extents of reaction using isothermal Thermogravimetric Analysis (TGA) datasets. Employing this method, kinetic parameters of pyrolysis of high-density polyethylene (HDPE) were determined at different reaction conversions. The obtained apparent activation energy values were obtained in the range of 270 to 290 kJ/mol.

The developed method for finding heat of reaction employs Differential Scanning Calorimetry (DSC) technique at constant temperatures. This method involves a new procedure to find heat loss from the DSC instrument as function of temperature and sample weight. The method was employed to find heat of cracking of HDPE at constant temperature of 400, 410, 420 and 430 °C, and the average heat of reaction was determined to be 1375±233 kJ/kg.

Based on available recommendations in the literature for using ZSM-5 catalysts in polymer pyrolysis, catalytic cracking of high-density polyethylene was studied using three ZSM-5 catalysts with different Si/Al ratios of 25, 38 and 80. Using a TGA instrument and altering the variables such as temperature and the catalyst to HDPE ratio, catalytic activity of the catalysts was investigated, and proper operating conditions were estimated. ZSM-5 catalysts with Si/Al ratios of 25 and 38 at constant temperatures of 330, 340, 350, 360 and 370 °C, and cat/HDPE ratio of 15 %

showed considerably high catalytic activity in cracking of HDPE (especially the ZSM-5 with Si/Al ratio of 25). Using the developed kinetic study method, kinetic parameters of catalytic cracking of HDPE were determined at the aforementioned conditions, and apparent activation energy values were dropped dramatically to the range of 20 to 90 kJ/mol.

In addition, catalytic activity, deactivation behavior, regenerability and reuse of the ZSM-5 catalyst with Si/Al ratio of 25 in consecutive cracking tests were also investigated. When activity of the used catalyst dropped to 20% of its initial value, a catalyst regeneration at 480 °C for 5 h was conducted; however, due to dealumination reactions occurred in the regeneration step, the initial catalytic activity could never be recovered. After catalyst regeneration, the regenerated catalyst was used in the same cracking tests. With 10 regeneration cycles, the ZSM-5 was used in 54 cracking tests. The effect of calcination temperature on the activity of ZSM-5 in cracking of high-density polyethylene was then explored. Calcination at 600 and 700 °C reduced acidity and activity of the ZSM-5 mainly due to catalyst dealumination. On the contrary, no drop in activity of the 500 °C-calcined catalyst was detected.

Overall, the findings of this study can be employed to design an industrial reactor for pyrolysis of waste polymers. Additionally, the methods developed in this study for obtaining kinetic parameters and heat of pyrolysis can be used in any other solid state reactions.

Acknowledgments

I would like to express my sincere thanks to my PhD supervisor Dr. Siamak Elyasi, who has provided motivation and continuous support throughout my PhD. Many thanks to him for sharing his knowledge with me and accepting me as his PhD student. Words cannot describe my sincere gratitude to him.

I would like to thank Dr. Sudip Rakshit and Dr. Baoqiang Liao for agreeing to be my internal committee members and for their insightful comments. I also wish to thank Dr. Mehrab Mehrvar for serving as an external examiner from Ryerson University.

My especial thanks to Dr. Brenda Magajna, Science and Environmental Studies PhD Programs facilitator, for her patience and advice. In addition, I further extend thanks to Mr. Garry Rathje, technician of Chemical Engineering Lab for his support and helpful, technical training.

I would like to acknowledge the financial support provided by Graduate Assistantship at Lakehead University, President Award, Faculty Research scholarship and NSERC throughout my doctoral study.

I owe a great debt to all of my friends for their constant support and understanding while writing this thesis.

Finally, I would like to thank my mother and brothers, without their support and encouragement, I never would have been able to accomplish my goals.

Dedication

To my beloved mother.

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Chapter 1: Literature Review

1.1. Plastics

Plastics are inexpensive, waterproof and versatile materials that are produced in different shapes, weights, durability, color, strength and transparency. Owing to their excellent properties, they have become an inevitable commodity in our today's lifestyle. Plastics have found a wide range of uses in different fields, including agriculture, construction, electronics, automobile and packaging (mainly) industries [1-4].

In spite of all the benefits taken from plastics, its negative effects cannot be ignored. Since plastics are not made by nature, they are not digested by microorganisms and enzymes (except plastic eating microbes which are very rare). For this reason, most polymers are not biodegradable and do not break down naturally and last for a long time or maybe forever [1]. Therefore, plastic waste brings dark issues to societies and demands further advances in the recycling technology.

The polymer used in this work is high-density polyethylene (HDPE) since it is one of the most common household wastes. Same as many kinds of polyethylene, the chemical formula of HDPE is $(C_2H_4)_n$.Its cheap price and appropriate attributes qualify it to be used in a wide range of applications such as light shopping bags, milk and water jugs, vitamin containers, detergent bottles, shampoo containers, toys, water and gas pipes, thermal and electrical insulations, electrical wires, chairs, fuel tanks, etc. High-density polyethylene is a thermoplastic and consists of carbon and hydrogen. It has a high molecular weight and its linear structure with or without little branching (Figure 1.1) gives it a higher density, strength and crystallinity, and therefore, a broader range of applications than other types of polyethylenes [1].

Linear HDPE   Branched HDPE
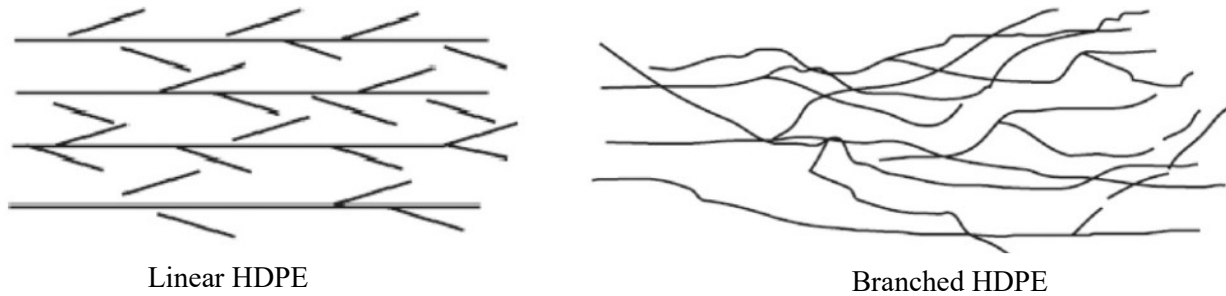
Figure 1.1. Schematic of linear and branched HDPE [1].

1.2. Landfilling, incineration and cracking

The rapid increase in plastic consumption, and consequently the ever-lasting plastic wastes, has led to serious environmental problems. Landfilling and incineration are the most popular methods for disposing polymer waste in developing and industrialized countries, respectively [2]. Nevertheless, since plastics are not biodegradable, landfilling is not the best solution in waste plastic management. With progressive production of one-use plastics, especially plastic bags and containers, declining landfill sites is a major concern [6-9]. Although incineration of plastic waste is an alternative to reduce the amount of landfilling, it has always been subjected to many criticisms and brought up a number of environmental concerns towards the release of toxic and greenhouse gases [10-11].

Besides the environmental concerns from waste polymers, the world's increase in energy demand and depletion of fossil fuels have inspired many researchers to find new technologies to convert waste polymers into energy [1,4,10,12]. Cracking is a thermochemical process that employs heat in an inert atmosphere to decompose waste polymers into different hydrocarbons. Cracking of waste polymers provides an opportunity to enhance waste plastic management and preserve the fossil fuels by converting waste polymers into high-value chemicals. Significant efforts, many of which have been successful, have been made to transform waste polymers into

liquid fuels or valuable hydrocarbons that can be used as a feedstock for existing refinery and petrochemical plants [10,13-22].

Cracking of waste polymers breaks down the molecular structure of polymers and produces a mixture of hydrocarbons in an inert atmosphere and under high temperature. This method is a promising technology to recover valuable hydrocarbons including paraffins, olefins, naphthenes and aromatics from the waste plastic [23-29]. The literature review on pyrolysis of HDPE has revealed promising results [11,14-16,18,24,27,30,31].

The product of plastic pyrolysis might appear in gas, liquid and solid phases. The liquid fraction, has properties and composition similar to different petroleum streams in the range of gasoline, kerosene or diesel oil. It can also be fed into hydrocarbon processing industries as raw material. The gas fraction can be burnt to provide the required energy for the process [10,14-16,22,32-40].

One factor that plays an important role in the yields and composition of gas and liquid products is the operating temperature. Miskolczi et al. (2004) studied thermal pyrolysis of high-density polyethylene at different temperatures of 400, 420 and 450 °C [18]. The phase distribution of the products at the mentioned temperatures are presented in Figure 1.2. At 400 °C, after 20 min, the extent of cracking reactions was negligible (around 5%). Yields of both gas and liquid products increased with the increasing temperature of decomposition, and amount of residue decreased considerably when temperature increased to 450 °C. Similar trends were observed by the other researchers as well [14,15].
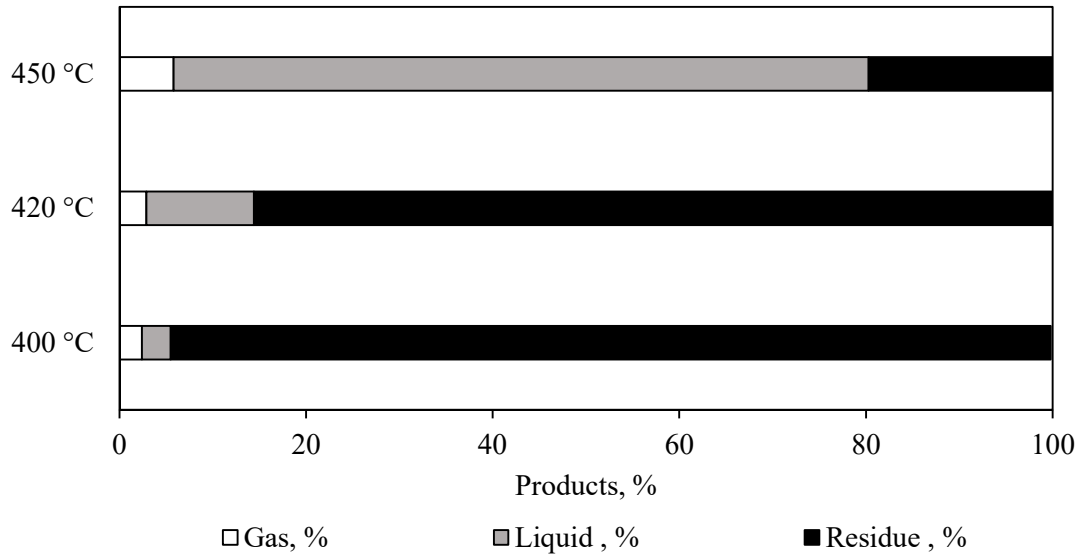
Figure 1.2. The yields of cracking of HDPE waste (at 20 min cracking time) [18].

In terms of effect of temperature on carbon atom number distribution, Miskolczi et al. (2004) did not observe any considerable change in gaseous products. On the contrary, composition of liquid phase, as shown in Figure 1.3, was clearly affected by operating temperatures. The main liquid products were recognized in the range of gasoline and kerosene at lower temperature, diesel oil and heavy oil at higher temperature. Therefore, higher cracking temperature led to higher density of liquids. This was explained by this fact that cracking of polymers in a batch reactor acts as reactive distillation; therefore, at higher temperature there is more driving force to decompose and volatilize heavier fractions of the liquefied polymer [18].

In addition to the cracking temperature, presence of a catalyst can also increase yields of lighter products. This subject is explained in the next section.
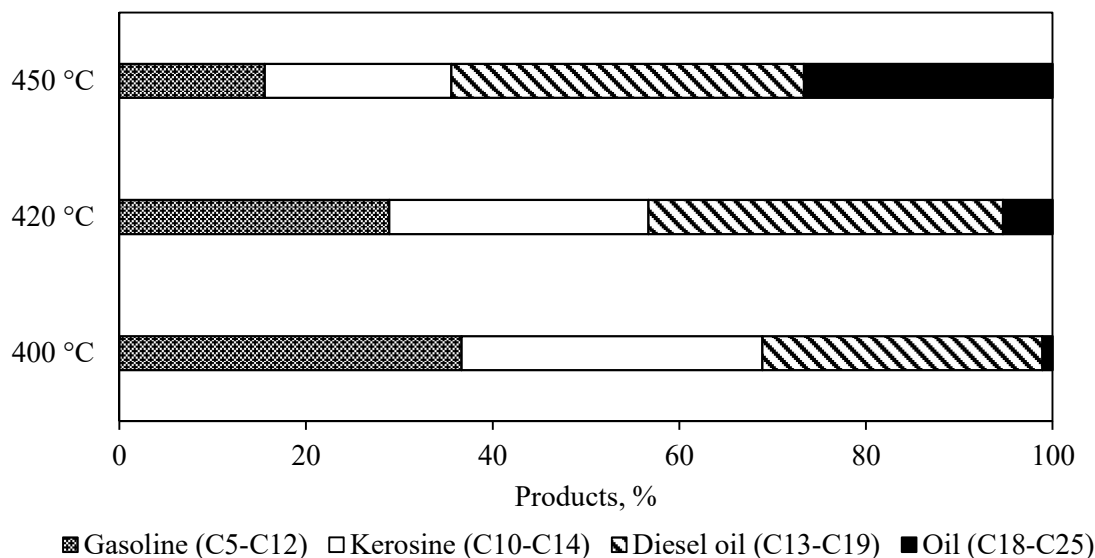
Figure 1.3. The possibilities of further utilization of liquids produced at 400, 420 and 450 °C [18].

1.3. Catalytic cracking vs. thermal cracking

Thermal recycling of waste polymers carries some particular problems. As it was discussed, the higher yields of liquid and gas products from cracking of waste polymers demand higher operating temperature. The second issue with thermal cracking of polymers is a very diverse range of products from C_5 to C_{28} [18,41]. On the other hand, employment of a proper catalyst can decrease both reaction temperature and time considerably [14,15,42]. In addition, the shape selectivity of certain catalysts can enhance the quality of the products by restricting them in the range of high-value hydrocarbons (gasoline) [4,14,16,28,30,38,43-46]. In addition, yield of gaseous products from catalytic cracking of waste polymers is higher than that of thermal cracking [16,43,47]. Therefore, pyrolysis of waste polymers in the presence of catalysts has several advantages as it promotes the cracking reactions to take place at milder conditions and produces more valuable hydrocarbons.

Several studies have been conducted concerning the cracking of polymers in the presence of acid solids like zeolites [17,23,46,48-51], non-zeolitic mesostructured solids [46] and clays [52,53]. Catalytic activities of catalysts can be attributed to many factors, mainly to the strength and number of acid sites, accessible surface area, particle size and pore size distribution [46]. In pyrolysis of polymers and especially HDPE, zeolite catalysts, in particular ZSM-5, have demonstrated certain advantages of high catalytic activity, strong acidity, excellent shape selectivity, and high thermal stability [18,24,27,28,31,48,54-59]. The great use of ZSM-5 in polymers pyrolysis should be attributed to its strong acidity and selectivity for producing gasoline range hydrocarbons, as well as its striking resistance to coke formation because of its small pores and restricted channels [23,60]. The reactions of catalytic cracking of polymers are similar to those of crude oil. Since in both of them long chain hydrocarbons are broken up or cracked into smaller and more valuable hydrocarbons, the FCC reactions shown in figure 1.4 can express the mechanism of catalytic cracking of polymers as well.

1. Alkane Mild Thermal Cracking
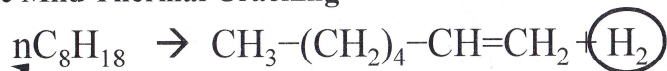
$$nC_8H_{18} \rightarrow CH_3-(CH_2)_4-CH=CH_2 + \boxed{H_2}$$

1.1. Proton Shift

$$CH_3-(CH_2)_4-CH=CH_2 + \quad H-O-H \quad + \quad Al-O-Si \rightarrow$$

Zeolite (Catalyst)

$$\rightarrow CH_3-(CH_2)_4-CH^+-CH_3 \quad + \quad H-O-Al-O-Si$$

Carbenium Ion

1.2. Beta Scision

$$CH_3-(CH_2)_4-CH^+-CH_3 \rightarrow CH_3-CH=CH_2 + CH_2{}^+-CH_2-CH_2-CH_3$$

1.3. Propagation

$$CH_2{}^+-CH_2-CH_2-CH_3 + nC_8H_{18} \rightarrow CH_3-(CH_2)_4-CH^+-CH_3 + C_4H_{10}$$

New Carbenium Ion

1.4. Termination

$$CH_2{}^+-CH_2-CH_2-CH_3 + H-Coke \rightarrow CH_3-(CH_2)_4-CH_2-CH_3$$

Hydrogen Donor

2. Olefins Cracking

$$CH_3-(CH_2)_7-CH=CH_2 \rightarrow CH_3-CH-CH=CH_2 + CH_3-CH=CH_2 + H_2$$
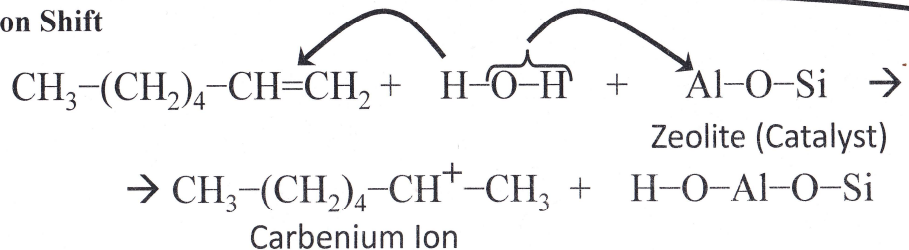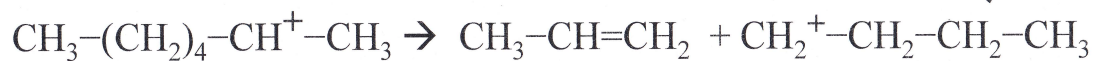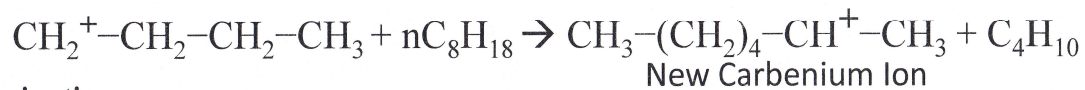
3. Alkylaromatics-Dealkylation
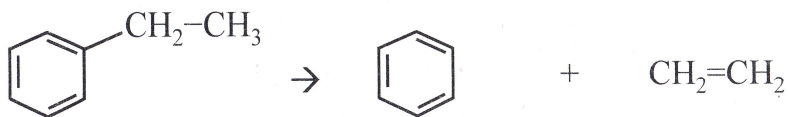
4. Alkylaromatics- Side Chain Cracking
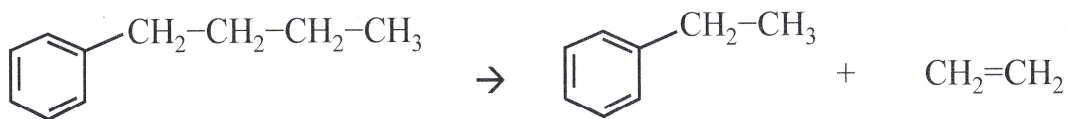
5. Intermolecular (bimolecular) Hydrogen Transfer

$$3CH_3-(CH_2)_6-CH_2=CH_2 \;+\; \underset{\text{Naphthenes}}{\text{(cyclohexane–R)}} \;\rightarrow\; 3CH_3-(CH_2)_7-CH_3 \;+\; \underset{\text{Aromatics}}{\text{(benzene–R)}}$$

Olefins Naphthenes Paraffins Aromatics

6. Hydrogenation

$$CH_3-(CH_2)_6-CH_2=CH_2 \;+\; H_2 \;\rightarrow\; 3CH_3-(CH_2)_7-CH_3$$
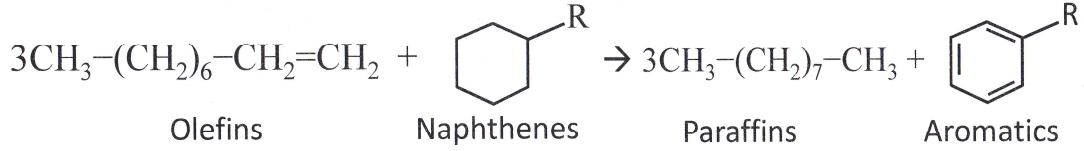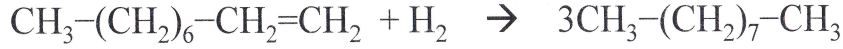
7. Alkylation, Condensation, Polymerization then Coking

$$\underset{\text{Aromatics}}{\text{(benzene–R)}} \quad \text{Or} \quad \underset{\text{Cyclo-Olefins}}{\text{(cyclohexene–R)}} \quad \rightarrow \quad COKE \;+\; H_2$$

$$2\;\underset{\text{n-butyl naphthalene}}{(\text{naphthalene–}C_4H_9)} \quad \rightarrow \quad \underset{\text{COKE precursor}}{(\text{polycyclic aromatic})} \;+\; 2C_3H_8$$

8. Isomerisation

$$\underset{\text{Carbenium Ion}}{R-CH_2-CH_2-CH^+-CH_3} \;\rightarrow\; \underset{\substack{\text{Tertiary}\\\text{Carbenium Ion}}}{R-CH_2-\overset{CH_2}{\underset{+}{C}}-CH_3}$$

9. Cyclisation
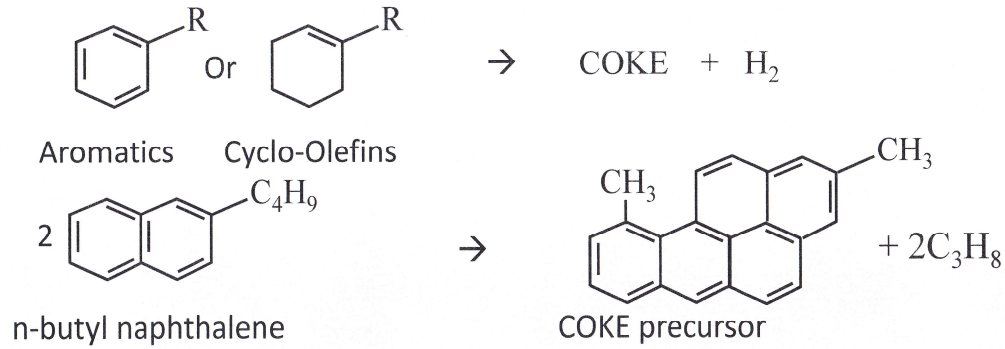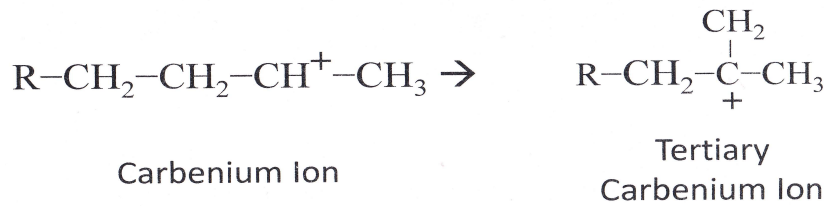
$$CH_3-CH^+-(CH_2)_3-CH=CH-CH_3 \;\rightarrow\; \text{(methylcyclohexyl carbenium ion)}$$
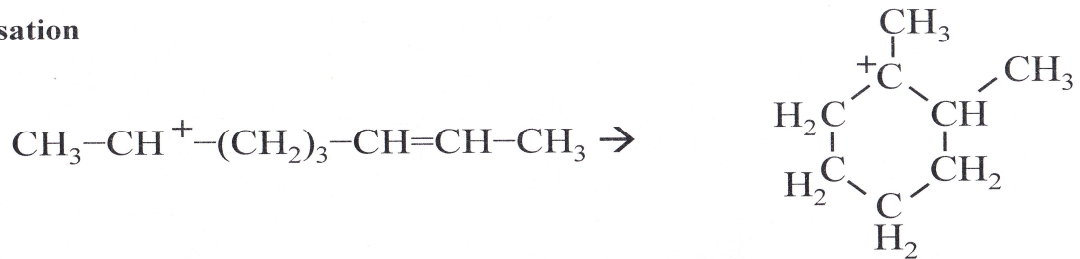
Figure 1.4. The mechanism of catalytic cracking of crude oil

1.4. Catalyst deactivation

In catalytic cracking of waste polymers, the conversion of reactions highly depends on the number of strong acidic sites and the pore structure. While strong acidity of the catalysts is a requirement to accelerate cracking reactions, it also increases the opportunity of deactivation reactions by coke formation [61]. On the other hand, it is known that the pore structure is the main determinative characteristic for coke formation [31,61,62]. As a result, although ZSM-5 has high acidity, its pore structure strongly resists coke formation in the pores [18,27,63-66]. The deposited coke on the catalyst surface can be burnt in a regeneration process with an oxidative atmosphere at high temperatures [31,54,61].

However, higher regeneration temperatures can initiate further deactivation by dealumination or agglomeration of the catalyst. Catalyst dealumination changes the number and strength of the acidic sites and it can cause considerable drop in catalytic activity. On the other hand, agglomeration of the catalyst decreases catalytic activity by increasing the mass transfer barrier between plastic species and the catalyst pores [67,68]. In these cases, the initial activity of the catalyst cannot be recovered, and catalyst undergoes irreversible deactivation. Considering this fact that coke burning is an exothermic phenomenon, the regeneration conditions should be chosen wisely to minimize dealumination and agglomeration of the catalyst and maximize the coke burning.

1.5. Kinetic parameters and Thermogravimetric Analysis (TGA)

In order to optimize a reaction/reactor and design any industrial process involving a reaction, having known kinetic parameters is required for conducting mass balance around the reactor. The kinetic parameters including apparent activation energy (E_a), pre-exponential factor (A_0) and reaction order (n) can be determined by different kinetic study methods. For the systems involving

multiple reactions with production of different intermediates, such as pyrolysis of polymers, using isoconversional methods has been recommended. Isoconversional methods produce kinetic parameters at different extent of the reaction [69-73]. The extent of the reaction can be determined from the weight loss curves recorded by Thermogravimetric Analysis (TGA) [56,70,74-83].

TGA is a thermal analysis technique which records the mass of a substance during a thermal regime as a function of temperature or time in a controlled atmosphere. Most of the kinetic study methods work with two types of TGA datasets, non-isothermal (dynamic) and isothermal (static) tests [84].

Non-isothermal TGA tests are fast, and therefore, they are very practical for quick investigations [75,83,85-87]. However, since temperature is continuously changing, there is uncertainty associated with non-isothermal data, and their results are not reliable for complex reactions.

On the other hand, in the isothermal approach, since temperature is constant, lesser variables exist. As a result, the nature of reactions at different conversions are more similar, and therefore, more reliable kinetic parameters can be determined [62,63,85,88-91]. Furthermore, isothermal kinetics data are needed since most of the pyrolysis processes work under isothermal conditions [92].

Despite the negative aspects of non-isothermal methods, they have been widely employed in different fields of solid state reactions [32,56,75-77,85-87,93,94]. The only isoconversional technique, working with isothermal data, is the model-free method [71,78,92,95], which has been used in a few polymer pyrolysis studies as well [78,92,96,97]. The main criticism on this method is its mathematical assumption [78,92]. Since the model-free method is an isoconversional

technique, activation energy is defined as a function of conversion. However, in the integration employed in this method, activation energy is treated as a constant number, and it can initiate uncertainty in the obtained results.

As a result, it is required to develop a new kinetic study method for solid state reactions, which firstly does not contain any of the aforementioned drawbacks, and secondly works with high-certainty isothermal measurements.

1.6. Heat of reaction and Differential Scanning Calorimetry (DSC)

Another necessary factor for designing a pyrolysis process is the heat of solid state reaction [98]. There are only few data that have been published for heat of polymer pyrolysis. Traditionally, heat of reaction is calculated from thermodynamic data. In this method, all the reactants and products should be known.

However, there are some reactions such as pyrolysis of plastic waste having a wide range of products and knowledge of all the products is sometimes impractical. For this kind of reactions, heat of reaction can be measured experimentally. Differential scanning calorimetry (DSC) is a fundamental tool in thermal analysis that can be used to determine heat of reactions. In a DSC instrument, a substance and an inert reference are subjected to the same thermal program, and the difference in heat flow into/from the two species is recorded at different times/temperatures. Since DSC works with a very small amount of sample, there is no mass and heat transfer barriers affecting the results, and reliable data can be obtained regardless of any restricting phenomena [99].

It is important to note that for finding the heat of decomposition reactions using a DSC instrument, the change in the sample weight must be known. Therefore, TGA results at the same

operating conditions (sample weight, flow rate of purging gas, thermal program, etc.) must be combined with DSC results [100].

A literature review on heat of solid state reactions reveals the predominant use of non-isothermal DSC measurements [98,101-108], and only a few works on the heat of polymer pyrolysis [101-103,108]. As it was discussed in Section 1.5, non-isothermal datasets have been recognized by uncertainty. In addition, in non-isothermal measurements especially at high heating rates, the temperature gradient between sample and furnace can cause ambiguity in the result [89,90]. Some data [101-103,108] for heat of polymer pyrolysis are shown in Table 1.1. They were all determined from non-isothermal DSC measurements. Considerable discrepancy can be observed for heat of decomposition of HDPE that will be discussed thoroughly in Chapter 6.

Table 1.1. Heat of cracking of polymers in literature.

Polymer	Heat (kJ.kg^{-1})	Reference
Poly(methyl methacrylate)	870±200	[101]
	800	[108]
Poly(oxymethylene)	2540±300	[101]
High-density polyethylene	920±120	[101]
	670	[108]
	649	[103]
	365-556	[102]
Polypropylene	1310±70	[101]
	630	[108]
Polystyrene	1000±90	[101]
	820	[108]
Polyamide 6,6	1390±90	[3]
	560	[4]
Poly(ethylene terephthalate)	1800±80	[101]
Bisphenol A polycarbonate	830±140	[101]
Poly(vinylidene fluoride)	2120±250	[101]
Poly(vinyl chloride)	170±170	[101]
	540±390	

One crucial point missing in most of decomposition studies is the fact that DSC instrument loses heat to its environment, and any heat flow curve recorded by DSC instrument should be corrected by the heat loss. This is more important when the reaction is slow and DSC instrument has more time to lose heat. A procedure should be developed to measure amount of the heat loss.

This issue was addressed in one non-isothermal calorific study on polymers gasification; prior to the reaction temperature, heat loss values were found experimentally at different temperatures, and then the obtained results were extrapolated for higher operating temperatures. Since the heat

loss measurements were performed prior to the decomposition temperature range, sample weight did not change. Therefore, it was assumed that heat loss is only temperature dependent [101]. However, it is not a valid assumption since heat loss is also affected by the area of the object. In the decomposition zone, when the reaction exceeds, amount and height of sample in the sample pan decline, and somehow it reduces the area of the sample too. Since measuring the area of the sample in a DSC instrument is not applicable, sample weight can be used as the representative of the area. In other words, heat loss from a DSC instrument depends on both temperature and sample weight.

Therefore, it is essential to develop an accurate experimental procedure and calculation method to determine the heat of solid state reactions using DSC apparatuses; an isothermal procedure that includes a reliable technique to find amount of heat loss in the reaction zone.

1.7. Distinguished contribution of this research

In order to design and optimize industrial reactors for pyrolysis of polymer waste, the kinetic parameters (apparent activation energy, pre-exponential factor and reaction order) and the heat of involved reactions have to be determined accurately. Known kinetic parameters and heat of reaction aid to simulate and predict response of the process beyond the employed temperature range.

In solid state reactions such as pyrolysis of polymers, TGA and DSC have demonstrated to be important analytical tools to determine kinetic parameters and heat of reaction. However, since TGA and DSC play important roles in finding fingerprints for reactions, further considerations and procedures are required to obtain precise and reproducible results. Most of the analytical methods employed for finding kinetic parameters and heat of polymer pyrolysis are either oversimplified or associated with major conflicts with the nature and mechanisms involved in the phenomenon.

The main contribution of this study is to develop two new analytical methods to determine kinetic parameters and heat of pyrolysis of polymers and any other solid state reactions. These two methods do not carry any of the drawbacks and limitations of the available methods for both kinetic study and heat of solid state reactions. All the experiments in this study were conducted four times to ensure the reproducibility of the results. The values of Standard deviations were calculated using Eq. 1.

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \mu)^2}$$ (1)

where σ is the standard deviation, N is the number of the measurements (in this study N=4), x_i is the value of each measurement, and μ is the average result of the N measurements.

As discussed, using a catalyst in cracking of polymers has several benefits over non-catalytic cracking. However, from an industrial point of view, catalytic activity, deactivation rate, regeneration and reuse of the employed catalyst should be well-understood. In this regard, this study addresses the main causes of deactivation of ZSM-5 in catalytic cracking of high-density polyethylene. It helps to maintain catalytic activity, resist catalyst deactivation and increase the number of reuse of the ZSM-5 in consecutive catalytic cracking reactions.

1.8. Objectives and organization of this thesis

Based on the gaps and opportunities described in the provided literature review, the main objectives of this thesis are classified in the following chapters:

Chapter 3:

This chapter gives, firstly, a critical study of the previous kinetic study methods in solid state reactions, and evaluates their validity and adaptability with thermal pyrolysis of HDPE.

Subsequently, it establishes a new kinetic study method to overcome the limitations and drawbacks of the previous methods. It will be shown that the new kinetic study approach is compatible with the nature, limitations and complexity of polymer pyrolysis.

Chapter 4:

This chapter evaluates catalytic activity of three ZSM-5 catalysts in cracking of HDPE, and aims to find a proper catalyst and mild operating conditions to proceed quick catalytic cracking. The developed kinetic study method in the second chapter is then employed to examine its validity for catalytic cracking reactions.

Chapter 5:

The focus of this chapter is on the deactivation behavior, regeneration and reuse of a ZSM-5 catalyst in consecutive catalytic cracking of HDPE. The effect of calcination temperature is investigated on activity of ZSM-5 in pyrolysis of HDPE, and recommendations for calcination temperature is stated.

Chapter 6:

This chapter develops a new procedure with high-certainty to determine the heat of solid state reactions. This procedure includes isothermal heat flow measurements (DSC), isothermal weight loss tests (TGA) and heat loss measurement (a new method). With the aid of this procedure, heat of decomposition of HDPE will be determined.

References

[1]   S. Kumar, A.K. Panda, R.K. Singh, A review on tertiary recycling of high-density polyethylene to fuel, Resources, Conservation and Recycling. 55 (2011) 893–910. doi:10.1016/j.resconrec.2011.05.005.

[2]   M. Arabiourrutia, G. Lopez, G. Elordi, M. Olazar, R. Aguado, J. Bilbao, Product distribution obtained in the pyrolysis of tyres in a conical spouted bed reactor, Chemical Engineering Science. 62 (2007) 5271–5275. doi:10.1016/j.ces.2006.12.026.

[3]   E. Espi, PLastic Films for Agricultural Applications, Journal of Plastic Film and Sheeting. 22 (2006) 85–102. doi:10.1177/8756087906064220.

[4]   S.M. Al-Salem, P. Lettieri, J. Baeyens, Recycling and recovery routes of plastic solid waste (PSW): A review, Waste Management. 29 (2009) 2625–2643. doi:10.1016/j.wasman.2009.06.004.

[5]   B. Johnke, Emissions from Waste Incineration, Good Practice Guidance and Uncertainty Management   (2009)   455–468. http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Emissions+From+Waste+inci neration#4.

[6]   M. El-Fadel, A.N. Findikakis, J.O. Leckie, Environmental Impacts of Solid Waste Landfilling, Journal of Environmental Management. 50 (1997) 1–25. doi:10.1006/jema.1995.0131.

[7]   PlasticsEurope, Plastics-The Facts 2013: An analysis of European latest plastics production, demand and waste data, Http:// www.plasticseurope.org/Document/plastics-the-Facts-2013.aspx. (2015) 1–40. doi:10.1016/j.marpolbul.2013.01.015.

[8]   X.F. Lou, J. Nair, The impact of landfilling and composting on greenhouse gas emissions - A review, Bioresource Technology. 100 (2009) 3792–3798. doi:10.1016/j.biortech.2008.12.006.

[9]   M.M. Taghiei, Z. Feng, F.E. Huggins, G.P. Huffman, Coliquefaction of Waste Plastics with Coal, Energy & Fuels. 8 (1994) 1228–1232. doi:10.1021/ef00048a010.

[10]   A.K. Panda, R.K. Singh, D.K. Mishra, Thermolysis of waste plastics to liquid fuel. A suitable method for plastic waste management and manufacture of value added products-A world prospective, Renewable and Sustainable Energy Reviews. 14 (2010) 233–248. doi:10.1016/j.rser.2009.07.005.

[11]   K.M. Zia, H.N. Bhatti, I. Ahmad Bhatti, Methods for polyurethane and polyurethane composites, recycling and recovery: A review, Reactive and Functional Polymers. 67 (2007) 675–692. doi:10.1016/j.reactfunctpolym.2007.05.004.

[12]   G. Lemoine, Comparison of Different Types of Zeolites Used As Solid Acid Catalysts in Jatropha-Type Oil for Biodiesel, (2013) 1–183.

[13]   S. Hardman, D.C. Wilson, Polymer cracking - New hydrocarbons from old plastics, Macromolecular Symposia. 135 (1998) 113–120. doi:10.1002/masy.19981350113.

[14]   M. Rasul Jan, J. Shah, H. Gulab, Catalytic conversion of waste high-density polyethylene into useful hydrocarbons, Fuel. 105 (2013) 595–602. doi:10.1016/j.fuel.2012.09.016.

[15]   M. Rasul Jan, J. Shah, H. Gulab, Degradation of waste High-density polyethylene into fuel oil using basic catalyst, Fuel. 89 (2010) 474–480. doi:10.1016/j.fuel.2009.09.007.

[16]   N. Miskolczi, L. Bartha, G. Deák, B. Jóver, Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons, Polymer Degradation and Stability. 86 (2004) 357–366. doi:10.1016/j.polymdegradstab.2004.04.025.

[17]   N. Miskolczi, L. Bartha, G. Deák, Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks, Polymer Degradation and Stability. 91 (2006) 517–526. doi:10.1016/j.polymdegradstab.2005.01.056.

[18]   N. Miskolczi, L. Bartha, G. Deák, B. Jóver, D. Kalló, Thermal and thermo-catalytic degradation of high-density polyethylene waste, Journal of Analytical and Applied Pyrolysis. 72 (2004) 235–242. doi:10.1016/j.jaap.2004.07.002.

[19]   N. Miskolczi, L. Bartha, G. Deák, B. Jóver, Chemical recycling of waste polyethylene and polypropylene, Petroleum & Coal. 45 (2003) 125–130.

[20]   A. Angyal, N. Miskolczi, L. Bartha, Petrochemical feedstock by thermal cracking of plastic waste, Journal of Analytical and Applied Pyrolysis. 79 (2007) 409–414. doi:10.1016/j.jaap.2006.12.031.

[21]   N. Miskolczi, A. Angyal, L. Bartha, I. Valkai, Fuels by pyrolysis of waste plastics from agricultural and packaging sectors in a pilot scale reactor, Fuel Processing Technology. 90 (2009) 1032–1040. doi:10.1016/j.fuproc.2009.04.019.

[22]   F. Paradela, F. Pinto, I. Gulyurtlu, I. Cabrita, N. Lapa, Study of the co-pyrolysis of biomass and plastic wastes, Clean Technologies and Environmental Policy. 11 (2009) 115–122. doi:10.1007/s10098-008-0176-1.

[23]   D.P. Serrano, J. Aguado, J.M. Escola, J.M. Rodríguez, Influence of nanocrystalline HZSM-5 external surface on the catalytic cracking of polyolefins, Journal of Analytical and Applied Pyrolysis. 74 (2005) 353–360. doi:10.1016/j.jaap.2004.11.037.

[24]   W.C. Huang, M.S. Huang, C.F. Huang, C.C. Chen, K.L. Ou, Thermochemical conversion of polymer wastes into hydrocarbon fuels over various fluidizing cracking catalysts, Fuel. 89 (2010) 2305–2316. doi:10.1016/j.fuel.2010.04.013.

[25]   A.G. Buekens, H. Huang, Catalytic plastics cracking for recovery of gasoline-range hydrocarbons from municipal plastic wastes, Resources, Conservation and Recycling. 23 (1998) 163–181. doi:10.1016/S0921-3449(98)00025-1.

[26]   S. Jiao, J. Zhu, M.A. Bergougnou, M. Ikura, M. Stanciulescu, 99/03613 Investigation and modeling of the thermal cracking of waste plastics derived oil in a downer reactor, Fuel and Energy Abstracts. 40 (1999) 383. doi:10.1016/S0140-6701(99)98819-7.

[27]   J.F. Mastral, C. Berrueco, M. Gea, J. Ceamanos, Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite, Polymer Degradation and Stability. 91 (2006) 3330–3338. doi:10.1016/j.polymdegradstab.2006.06.009.

[28]   A.. Garforth, Y.-H. Lin, P. Sharratt, J. Dwyer, Production of hydrocarbons by catalytic degradation of high density polyethylene in a laboratory fluidised-bed reactor, Applied Catalysis A: General. 169 (1998) 331–342. doi:10.1016/S0926-860X(98)00022-2.

[29]   K.H. Lee, N.S. Noh, D.H. Shin, Y. Seo, Comparison of plastic types for catalytic degradation of waste plastics into liquid product with spent FCC catalyst, Polymer Degradation and Stability. 78 (2002) 539–544. doi:10.1016/S0141-3910(02)00227-6.

[30]   Y. Seo, K. Lee, D. Shin, Investigation of catalytic degradation of high- density polyethylene by hydrocarbon group type analysis, Journal of Analytical and Applied Pyrolysis. 70 (2003) 383–398.

[31]   A. López, I. de Marco, B.M. Caballero, A. Adrados, M.F. Laresgoiti, Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes, Waste Management. 31 (2011) 1852–1858. doi:10.1016/j.wasman.2011.04.004.

[32]   G. Yan, X. Jing, H. Wen, S. Xiang, Thermal cracking of virgin and waste plastics of PP and LDPE in a semibatch reactor under atmospheric pressure, Energy and Fuels. 29 (2015) 2289–2298. doi:10.1021/ef502919f.

[33]   M. Syamsiro, H. Saptoadi, T. Norsujianto, P. Noviasri, S. Cheng, Z. Alimuddin, K. Yoshikawa, Fuel oil production from municipal plastic wastes in sequential pyrolysis and catalytic reforming reactors, Energy Procedia. 47 (2014) 180–188. doi:10.1016/j.egypro.2014.01.212.

[34]   G. Elordi, M. Olazar, G. Lopez, M. Amutio, M. Artetxe, R. Aguado, J. Bilbao, Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor, Journal of Analytical and Applied Pyrolysis. 85 (2009) 345–351. doi:10.1016/j.jaap.2008.10.015.

[35]   N. Carmo, D. Afonso, E. Santos, I. Fonseca, F. Lemos, M.A.N.D.A. Lemos, Coprocessing of Waste Plastic and Hydrocarbons over MFI (HZSM-5), International Journal of Chemical Kinetics. 48 (2016) 329–336. doi:10.1002/kin.20993.

[36]   J. Walendziewski, Continuous flow cracking of waste plastics, Fuel Processing Technology. 86 (2005) 1265–1278. doi:10.1016/j.fuproc.2004.12.004.

[37]   J. Walendziewski, Engine fuel derived from waste plastics by thermal treatment, Fuel. 81 (2002) 473–481. doi:10.1016/S0016-2361(01)00118-1.

[38]   N. Kiran, E. Ekinci, C.E. Snape, Recyling of plastic wastes via pyrolysis, Resources, Conservation and Recycling. 29 (2000) 273–283. doi:10.1016/S0921-3449(00)00052-5.

[39]   G.M. JENG, Y.Y. YIN, J.B. LI, Manufacture of Liquid Fuel by Catalytic Cracking Waste Plastics in a Fluidized Bed, Energy Sources. 25 (2003) 577–590. doi:10.1080/00908310390195642.

[40]   J.M. Arandes, I. Abajo, D. López-Valerio, I. Fernández, M.J. Azkoiti, M. Olazar, J. Bilbao, Transformation of Several Plastic Wastes into Fuels by Catalytic Cracking, Industrial & Engineering Chemistry Research. 36 (1997) 4523–4529. doi:10.1021/ie970096e.

[41]   W.C. McCaffrey, M.R. Kamal, D.G. Cooper, Thermolysis of polyethylene, Polymer Degradation and Stability. 47 (1995) 133–139. doi:10.1016/0141-3910(94)00096-Q.

[42]   H. Ohkita, R. Nishiyama, Y. Tochihara, T. Mizushima, N. Kakuta, Y. Morioka, A. Ueno, Y. Namiki, S. Tanifuji, Acid properties of silica-alumina catalysts and catalytic degradation of polyethylene, Industrial & Engineering Chemistry Research. 32 (1993) 3112–3116. doi:10.1021/ie00024a021.

[43]   D. Park, E. Hwang, J. Kim, J. Choi, Y. Kim, H. Woo, Catalytic degradation of polyethylene over solid acid catalysts, Polymer Degradation and Stability. 65 (1999) 193–198. doi:10.1016/S0141-3910(99)00004-X.

[44]   F. Pinto, P. Costa, I. Gulyurtlu, I. Cabrita, Pyrolysis of plastic wastes. 1. Effect of plastic waste composition on product yield, Journal of Analytical and Applied Pyrolysis. 51 (1999) 39–55. doi:10.1016/S0165-2370(99)00007-8.

[45]   K. Gobin, G. Manos, Polymer degradation to fuels over microporous catalysts as a novel tertiary plastic recycling method, Polymer Degradation and Stability. 83 (2004) 267–279. doi:10.1016/S0141-3910(03)00272-6.

[46]   J. Aguado, D.P. Serrano, G.S. Miguel, J.M. Escola, J.M. Rodríguez, Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins, Journal of Analytical and Applied Pyrolysis. 78 (2007) 153–161. doi:10.1016/j.jaap.2006.06.004.

[47]   J.J. Park, K. Park, J.-W. Park, D.C. Kim, Characteristics of LDPE pyrolysis, Korean Journal of Chemical Engineering. 19 (2002) 658–662. doi:10.1007/BF02699313.

[48]   A. Garforth, S. Fiddy, Y.-H. Lin, A. Ghanbari-Siakhali, RN. Sharratt, J. Dwyer, Catalytic degradation of high density polyethylene: An evaluation of mesoporous and microporous catalysts using thermal analysis, Thermochimica Acta. 294 (1997) 65–69. doi:10.1016/S0040-6031(96)03145-0.

[49]   D.P. Serrano, J. Aguado, J.M. Escola, E. Garagorri, J.M. Rodríguez, L. Morselli, G. Palazzi, R. Orsi, Feedstock recycling of agriculture plastic film wastes by catalytic cracking, Applied Catalysis B: Environmental. 49 (2004) 257–265. doi:10.1016/j.apcatb.2003.12.014.

[50]   J. Aguado, D.P. Serrano, J.M. Escola, E. Garagorri, J.A. Fern??ndez, Catalytic conversion of polyolefins into fuels over zeolite beta, Polymer Degradation and Stability. 69 (2000) 11–16. doi:10.1016/S0141-3910(00)00023-9.

[51]   C. Muhammad, J.A. Onwudili, P.T. Williams, Catalytic pyrolysis of waste plastic from electrical and electronic equipment, Journal of Analytical and Applied Pyrolysis. 113 (2015) 332–339. doi:10.1016/j.jaap.2015.02.016.

[52]   G. Manos, A. Garforth, J. Dwyer, Catalytic degradation of high-density polyethylene over different zeolitic structures, Ind Eng Chem Res. 39 (2000) 1198–1202. doi:10.1021/ie990512q.

[53]   G. Manos, I.Y. Yusof, N. Papayannakos, N.H. Gangas, Catalytic Cracking of Polyethylene over Clay Catalysts. Comparison with an Ultrastable Y Zeolite, Industrial & Engineering Chemistry Research. 40 (2001) 2220–2225. doi:10.1021/ie001048o.

[54]   N. Rahimi, R. Karimzadeh, Catalytic cracking of hydrocarbons over modified ZSM-5 zeolites to produce light olefins: A review, Applied Catalysis A: General. 398 (2011) 1–17. doi:10.1016/j.apcata.2011.03.009.

[55]   C. Muhammad, J.A. Onwudili, P.T. Williams, Thermal degradation of real-world waste plastics and simulated mixed plastics in a two-stage pyrolysis-catalysis reactor for fuel production, Energy and Fuels. 29 (2015) 2601–2609. doi:10.1021/ef502749h.

[56]   I.C. Neves, G. Botelho, A. V. Machado, P. Rebelo, Catalytic degradation of polyethylene: An evaluation of the effect of dealuminated Y zeolites using thermal analysis, Materials Chemistry and Physics. 104 (2007) 5–9. doi:10.1016/j.matchemphys.2007.02.032.

[57]   Z. Zhi-heng, F.A.N. Tian-bo, L.I.U. Yun-yi, The Deactivation and Regeneration of HZSM-5 Zeolite Catalysts for Synthesis of Dichlorophenylphosphine in the Gas Phase, (n.d.) 3–6.

[58]   E.Y. Hwang, J.R. Kim, J.K. Choi, H.C. Woo, D.W. Park, Performance of acid treated natural zeolites in catalytic degradation of polypropylene, Journal of Analytical and Applied Pyrolysis. 62 (2002) 351–364. doi:10.1016/S0165-2370(01)00134-6.

[59]   J. Schirmer, J.S. Kim, E. Klemm, Catalytic degradation of polyethylene using thermal gravimetric analysis and a cycled-spheres-reactor, Journal of Analytical and Applied Pyrolysis. 60 (2001) 205–217. doi:10.1016/S0165-2370(00)00197-2.

[60]   S. Ali, A.A. Garforth, D.H. Harris, D.J. Rawlence, Y. Uemichi, Polymer waste recycling over "used" catalysts, Catalysis Today. 75 (2002) 247–255. doi:10.1016/S0920-5861(02)00076-7.

[61]   Y. Uemichi, M. Hattori, T. Itoh, J. Nakamura, Deactivation Behaviors of Zeolite and Silica - Alumina Catalysts in the Degradation of Polyethylene, Industrial & Engineering Chemistry Research. 5885 (1998) 867–872.

[62]   Y. Sakata, M.A. Uddin, A. Muto, Degradation of polyethylene and polypropylene into fuel oil by using solid acid and non-acid catalysts, Journal of Analytical and Applied Pyrolysis. 51 (1999) 135–155. doi:10.1016/S0165-2370(99)00013-3.

[63]   A. Coelho, I.M. Fonseca, I. Matos, M.M. Marques, A.M. Botelho do Rego, M.A.N.D.A. Lemos, F. Lemos, Catalytic degradation of low and high density polyethylenes using ethylene polymerization catalysts: Kinetic studies using simultaneous TG/DSC analysis, Applied Catalysis A: General. 374 (2010) 170–179. doi:10.1016/j.apcata.2009.12.001.

[64]   A. Marcilla, A. Gómez-Siurana, D. Berenguer, Study of the early deactivation in pyrolysis of polymers in the presence of catalysts, Journal of Analytical and Applied Pyrolysis. (2007). doi:10.1016/j.jaap.2007.02.002.

[65]   K. Takuma, Y. Uemichi, M. Sugioka, A. Ayame, Production of Aromatic Hydrocarbons by Catalytic Degradation of Polyolefins over H-Gallosilicate, Industrial & Engineering Chemistry Research. 40 (2001) 1076–1082. doi:10.1021/ie000638j.

[66]   M. Guisnet, P. Magnoux, Organic chemistry of coke formation, Applied Catalysis A: General. 212 (2001) 83–96. doi:10.1016/S0926-860X(00)00845-0.

[67]   J. Lu, Z. Zhao, C. Xu, A. Duan, P. Zhang, Effects of calcination temperature on the acidity and catalytic performances of HZSM-5 zeolite catalysts for the catalytic cracking of n-butane, Journal of Natural Gas Chemistry. 14 (2005) 213–220. doi:10.1016/j.ijfoodmicro.2004.12.017.

[68]   D.P. Serrano, J. Aguado, J.M. Escola, Catalytic Cracking of a Polyolefin Mixture over Different Acid Solid Catalysts, Industrial & Engineering Chemistry Research. 39 (2000) 1177–1184. doi:10.1021/ie9906363.

[69]   P. Budrugeac, E. Segal, Problems Concerning Nonisothermal Kinetic Analysis of Heterogeneous Solid – Gas Reactions, International Journal of Chemical Kinetics. 33 (2001) 564–573. doi:10.1002/kin.1052.

[70]   P. Budrugeac, Thermal degradation of glass reinforced epoxy resin and polychloroprene rubber: The correlation of kinetic parameters of isothermal accelerated aging with those obtained from non-isothermal data, Polymer Degradation and Stability. 74 (2001) 125–132. doi:10.1016/S0141-3910(01)00112-4.

[71]   A. Khawam, D.R. Flanagan, Role of isoconversional methods in varying activation energies of solid-state kinetics: II. Nonisothermal kinetic studies, Thermochimica Acta. 436 (2005) 101–112. doi:10.1016/j.tca.2005.05.015.

[72]   S. Vyazovkin, Advanced isoconversional method, Journal of Thermal Analysis and Calorimetry. 49 (1997) 1493–1499. doi:10.1007/BF01983708.

[73]   S. Vyazovkin, On the phenomenon of variable activation energy for condensed phase reactions, New Journal of Chemistry. 24 (2000) 913–917. doi:10.1039/b004279j.

[74]   Z. Liu, Z. Jiang, B. Fei, X. Liu, Thermal Decomposition Characteristics of Chinese Fir, BioResources. 8 (2013) 5014–5024. doi:10.15376/biores.8.4.5014-5024.

[75]   V. Leroy, D. Cancellieri, E. Leoni, J.L. Rossi, Kinetic study of forest fuels by TGA: Model-free kinetic approach for the prediction of phenomena, Thermochimica Acta. 497 (2010) 1–6. doi:10.1016/j.tca.2009.08.001.

[76]   S. Ramukutty, E. Ramachandran, Reaction Rate Models for the Thermal Decomposition of Ibuprofen Crystals, Journal of Crystallization Process and Technology. 4 (2014) 71–78. doi:10.4236/jcpt.2014.42010.

[77]   O.S. Al-ayed, K. Mutah, Study of the Kinetics and Mechanisms of Thermal Decomposition of Ellajjun Oil Shale, (n.d.).

[78]   S. Vyazovkin, C.A. Wight, Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data, Thermochimica Acta. 340 (1999) 53–68. doi:10.1016/S0040-6031(99)00253-1.

[79]   C. Gamlin, M.G. Markovic, N.K. Dutta, N.R. Choudhury, J.G. Matisons, Structural effects on the decomposition kinetics of EPDM elastomers by high-resolution TGA and modulated TGA, J. Thermal Analy. Calorimetry. 59 (2000) 319–336.

[80]   Y. Han, Theoretical Study of Thermal Analysis Kinetics, (2014) 104. http://uknowledge.uky.edu/me_etds/35.

[81]   X. Zhang, W. de Jong, F. Preto, Estimating kinetic parameters in TGA using B-spline smoothing and the Friedman method, Biomass and Bioenergy. 33 (2009) 1435–1441. doi:10.1016/j.biombioe.2009.06.009.

[82]   J.C. De Jesus, I. González, A. Quevedo, T. Puerta, Thermal decomposition of nickel acetate tetrahydrate: An integrated study by TGA, QMS and XPS techniques, Journal of Molecular Catalysis A: Chemical. 228 (2005) 283–291. doi:10.1016/j.molcata.2004.09.065.

[83]   M. Venkatesh, P. Ravi, S.P. Tewari, Isoconversional kinetic analysis of decomposition of nitroimidazoles: Friedman method vs Flynn-Wall-Ozawa method, Journal of Physical Chemistry A. 117 (2013) 10162–10169. doi:10.1021/jp407526r.

[84]   S. Sauerbrunn, P. Gill, Decomposition kinetics using TGA, Am. Lab. (Shelton, Conn.). 26 (1994) 29–30,32,34.

[85]   S. Maitra, S. Mukherjee, N. Saha, J. Pramanik, C. Technology, A.C.B. Lane, Non-isothermal decomposition kinetics of magnesite (Decomposição não isotérmica de magnesita), 53 (2007) 284–287.

[86]   S.M. Mušanić, Applicability of non-isothermal DSC and Ozawa method for studying kinetics of double base propellant decomposition, … European Journal of …. 7 (2010) 233–251. http://yadda.icm.edu.pl/baztech/element/bwmeta1.element.baztech-article-BAT6-0014-0004.

[87]   B. Saha, A.K. Ghoshal, Thermal degradation kinetics of poly(ethylene terephthalate) from waste soft drinks bottles, Chemical Engineering Journal. 111 (2005) 39–43. doi:10.1016/j.cej.2005.04.018.

[88]   W. Jang, A review of DSC kinetic methods, Du Pont Instruments. (1981) 1–6. http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:A+Review+of+DSC+Kinetics +Methods#3.

[89]   S. Chervina, G.T. Bodman, Mechanism and Kinetics of Decomposition From Isothermal DSC Data: Development and Application, Process Safety Progress. 16 (1997) 94–100. doi:10.1002/prs.680160211.

[90]   D.N. Waters, J.L. Paddy, Equations for Isothermal Differential Scanning Calorimetric Curves, Anal. Chem. 60 (1988) 53–57. doi:10.1021/ac00152a014.

[91]   T. Methods, Thermal Methods of Analysis Thermal Analysis, (n.d.) 1–15.

[92]   B. Saha, A.K. Maiti, A.K. Ghoshal, Model-free method for isothermal and non-isothermal decomposition kinetics analysis of PET sample, Thermochimica Acta. 444 (2006) 46–52. doi:10.1016/j.tca.2006.02.018.

[93]   M.V.S. Murty, P. Rangarajan, E.A. Grulke, D. Bhattacharyya, Thermal degradation/hydrogenation of commodity plastics and characterization of their liquefaction products, Fuel Processing Technology. 49 (1996) 75–90. doi:10.1016/S0378-3820(96)01040-5.

[94]   J. Yang, R. Miranda, C. Roy, Using the DTG curve fitting method to determine the apparent kinetic parameters of thermal decomposition of polymers, 73 (2001) 455–461.

[95]   L. Shuyan, E. Vuorimaa, H. Lemmetyinen, Application of isothermal and model-free isoconversional modes in DSC measurement for the curing process of the PU system, Journal of Applied Polymer Science. 81 (2001) 1474–1480. doi:10.1002/app.1574.

[96]   S.Y. Lee, J.H. Yoon, J.R. Kim, D.W. Park, Catalytic degradation of polystyrene over natural clinoptilolite zeolite, Polymer Degradation and Stability. 74 (2001) 297–305. doi:10.1016/S0141-3910(01)00162-8.

[97]   S. Vyazovkin, C.A. Wight, Kinetics of thermal decomposition of cubic ammonium perchlorate, Chemistry of Materials. 11 (1999) 3386–3393. doi:10.1021/cm9904382.

[98]   M. Van de Velden, J. Baeyens, A. Brems, B. Janssens, R. Dewil, Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction, Renewable Energy. 35 (2010) 232–242. doi:10.1016/j.renene.2009.04.019.

[99]   M.G. Wolfinger, J. Rath, G. Krammer, F. Barontini, V. Cozzani, Influence of the emissivity of the sample on differential scanning calorimetry measurements, Thermochimica Acta. 372 (2001) 11–18. doi:10.1016/S0040-6031(01)00438-5.

[100]   W. Kentucky, B. Green, Combining dsc and tg data for measuring of reaction, 166 (1990) 251–265.

[101]   S.I. Stoliarov, R.N. Walters, Determination of the heats of gasification of polymers using differential scanning calorimetry, Polymer Degradation and Stability. 93 (2008) 422–427. doi:10.1016/j.polymdegradstab.2007.11.022.

[102]   G. Agarwal, B. Lattimer, Method for measuring the standard heat of decomposition of materials, Thermochimica Acta. 545 (2012) 34–47. doi:10.1016/j.tca.2012.06.027.

[103] M.C. Bruns, O.A. Ezekoye, Modeling differential scanning calorimetry of thermally degrading thermoplastics, Journal of Analytical and Applied Pyrolysis. 105 (2014) 241–251. doi:10.1016/j.jaap.2013.11.010.

[104] F. He, W. Yi, J. Zha, Measurement of the heat of smoldering combustion in straws and stalks by means of simultaneous thermal analysis, Biomass and Bioenergy. 33 (2009) 130–136. doi:10.1016/j.biombioe.2008.05.006.

[105] J. Rath, M.G. Wolfinger, G. Steiner, G. Krammer, F. Barontini, V. Cozzani, Heat of wood pyrolysis, Fuel. 82 (2003) 81–91. doi:10.1016/S0016-2361(02)00138-2.

[106] R. Narayan, M.J. Antal, Thermal Lag, Fusion, and the Compensation Effect during Biomass Pyrolysis, Industrial & Engineering Chemistry Research. 35 (1996) 1711–1721. doi:10.1021/ie950368i.

[107] M. Stenseng, A. Jensen, K. Dam-Johansen, Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry, Journal of Analytical and Applied Pyrolysis. 58–59 (2001) 765–780. doi:10.1016/S0165-2370(00)00200-X.

[108] W.J. Frederick, C.C. Mentzer, Determination of heats of volatilization for polymers by differential scanning calorimetry, Journal of Applied Polymer Science. 19 (1975) 1799–1804. doi:10.1002/app.1975.070190702.

Chapter 2: Experimental Setups

2.1 Thermogravimetric Analysis (TGA)

TGA is a thermal analysis method to measure physical and chemical properties of materials as a function of increasing temperature at a constant heating rate, or as a function of time at a constant temperature. In fact, TGA is a batch reactor that records the weight (or weight loss) of a sample at different times and temperatures under inert atmosphere. Since a very small amount of sample is used in TGA, it can determine the net characterizations of the reaction regardless of mass transfer and heat transfer barriers. In this work, Perkin Elmer TGA7 was used to study decomposition of HDPE under an inert atmosphere of nitrogen. TGA7 was conducted non-isothermally and isothermally to find the specification of decomposition of HDPE such as kinetic parameters.

2.2. Differential Scanning Calorimetry (DSC)

DSC is a thermal analysis technique to measure the required heat flows into/from a known amount of sample during a heating or cooling procedure. The obtained results from DSC can provide the heat of reaction, which aids to simulate the heating characterization of a chemical reactor. A DSC apparatus is not an ideal isolated instrument, and therefore, it has heat loss to the environment. There is a need for a procedure to determine the heat loss experimentally, and then subtract it from the original DSC curve to obtain the net required heat for the process.

In this study, the heat flow (energetic) measurements were carried out in Perkin Elmer DSC7. Prior to using DSC, it was calibrated by the fusion heats and melting points of tin and indium as the reference materials. Figure 2.1 shows that DSC7 has a chamber where the sample and reference pans are located. Two separate heaters are under the sample and reference pans. The DSC outcome is the difference of the produced heats between the heaters versus time or temperature.

a: Platinum-Iridium sample furnace   f: Aluminum heat sink
b: Platinum-Iridium reference furnace   g: Swing cover
c: Sample pan   h: Latch
d: Reference pan   i: Knurled adjusting thumb nut
e: Purge gas exit
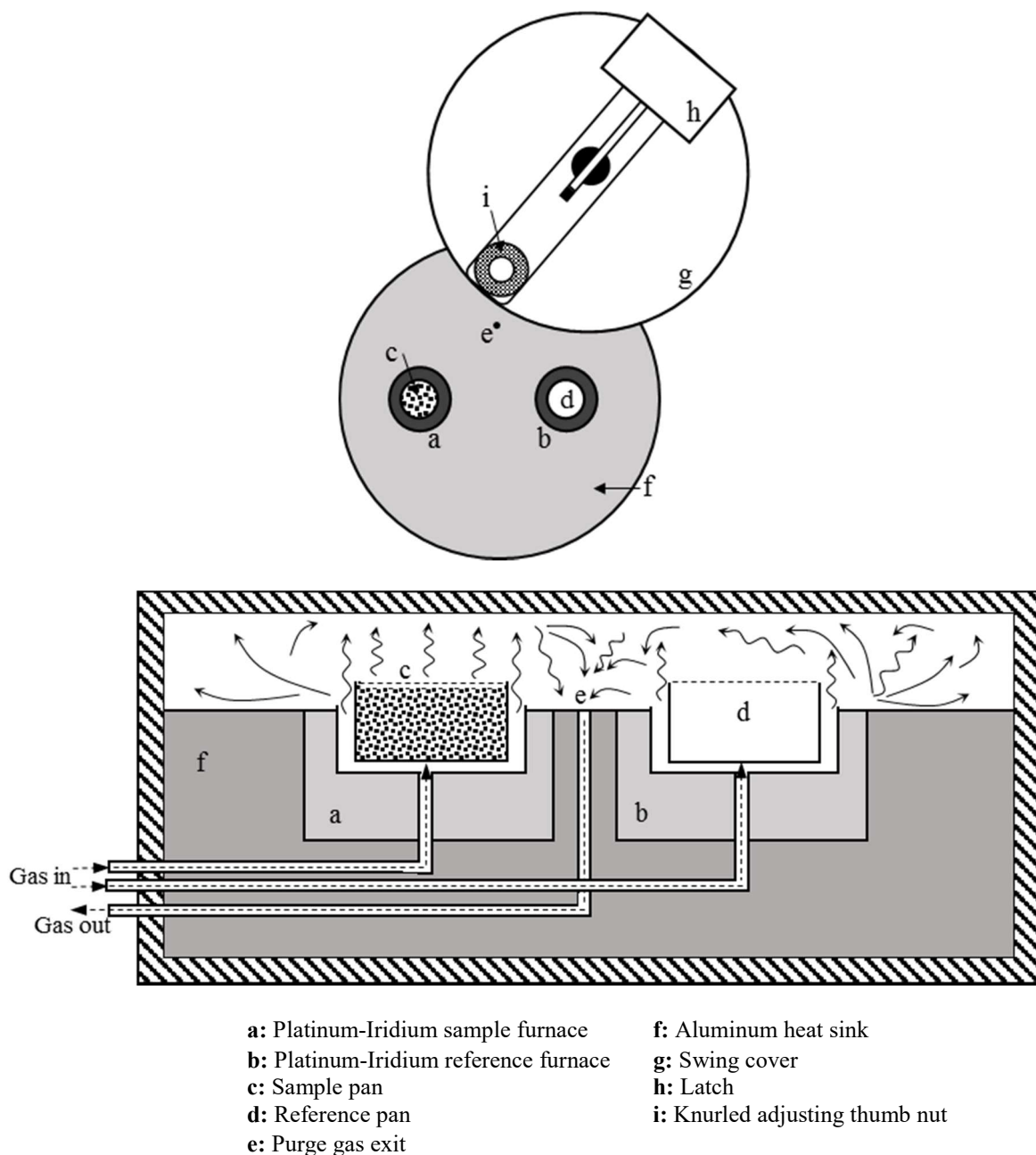
Figure 2.1. The DSC7 modified from the Perkin Elmer manual (no scale).

Figure 2.1 shows that DSC7 has two separate inlets for the purging gas, which go under the sample and reference holders. The purging gas removes the oxygen and the gaseous products from the system through a small hole, shown as "e" on the aluminum heat sink (f).

Chapter 3: Kinetic Analysis for Thermal Cracking of HDPE: A New Isoconversional Approach

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3.1. Abstract

Converting waste plastic into marketable hydrocarbons is a promising way to protect the environment and earn financial gain. While several kinetic studies have examined the cracking of waste plastic, they are often oversimplified or inappropriate for designing an industrial reactor. This work proves the necessity of using isoconversional methods by using Differential Scanning Calorimetry (DSC). DSC verified that cracking of waste plastic involves the production of several intermediates, indicating that the kinetics is more complex and requires further studies. Several isoconversional methods such as Friedman, Ozawa, Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and model-free were applied to estimate the apparent activation energy and frequency factor of thermal cracking of high-density polyethylene (HDPE) using non-isothermal and isothermal Thermogravimetric Analysis (TGA). The determined kinetic parameters from each method were evaluated against the experimental data. In order to overcome the failures and shortages engaged with the employed methods, a new isothermal isoconversional model was proposed and good matching results was observed.

Keywords:

Thermal cracking; Kinetic parameters; HDPE; Isothermal TGAs; Non-isothermal TGAs; Isoconversional methods

3.2. Introduction

3.2.1. Waste plastic cracking

Nowadays, plastics can be found almost everywhere on our planet. Since plastics are produced in a variety of shapes, weights and strengths, and with different levels of durability, they have a wide range of applications in the packaging, automobile, construction, electrical and electronics

industries [1]. The global production of plastic increased by 300 times between 1950 and 2013 [2], generating a dramatic increase in waste plastic generation. Globally, 65–70% of waste plastic is buried in landfills, and the remaining 20–25% is incinerated [3]. Neither of these disposal methods are completely environmentally friendly; however, landfilling causes more environmental problems than incineration. As plastics are not biodegradable, they take hundreds of years to decompose in landfill sites. Moreover, pollutants in landfill sites may leak into underground water resources and soil and cause more problems such as contaminating drinking water [4].

Cracking of waste plastic is a promising process for converting waste plastic into fuel. This process decreases the landfilling of waste plastics, enhances the recycling industry and preserves virgin fuel resources [5]. Thermal cracking of waste plastic needs to meet high temperatures to produce more calorific products in the range needed for kerosene and diesel. Using a catalyst in thermo-catalytic cracking reduces the operating temperature and increases the production of more valuable hydrocarbons such as gasoline, ethylbenzene and styrene [6,7].

Since 1984, a number of studies have been performed on thermal and thermo-catalytic cracking of pure and waste plastics. Most researchers have focused on the product distribution and effect of operating conditions such as temperature, reaction time, type of catalyst and catalyst-to-plastic ratio on the yields of products [6-15].

Besides the operating conditions, the reactor's configuration, size and internals can also affect the product yields. However, an industrial reactor design for the cracking of waste polymers has not been studied in depth. Known reliable kinetic parameters including reaction order (n), apparent activation energy (E_a) and frequency factor (A_0) are the most important requirements for designing a reactor. While several kinetic studies have investigated the cracking of waste plastic [3,9,16-22], most have employed uncertain methods. As a result, they are not quite suitable to be employed in

the design of an industrial reactor. Moreover, these studies failed to evaluate the agreement of the estimated kinetic parameters with the experimental data [3,9,16-18].

Most pyrolysis studies have focused on virgin and waste polystyrene (PS), high-density polyethylene (HDPE) and low-density polyethylene (LDPE); however, different kinetic parameters were reported even for one kind of polymer [e.g. 18,19]. Apart from the experimental factors and instrumental accuracy, this diversity could be caused by the molecular structure of the plastic, as even one type of plastic, such as HDPE, is available in different ranges of molecular weight, density and specification. Consequently, characterizations such as the melting point [23], crystallinity [23,24], fusion heat [24], molecular weight and ash content should be reported to demonstrate a fingerprint of the plastic sample in every study.

3.2.2. TGA and kinetic study

TGA, which is a high temperature furnace measuring the weight (or weight loss) of a sample at different times and temperatures, is widely used for kinetic studies. TGA uses a very small sample weight to ensure the mass and heat transfer barriers are negligible. For this reason, TGA may find the net rate of the reactions and provide more accurate and reliable data compared with other methods [25].

TGA can essentially be employed in two different modes, isothermal and non-isothermal [26,27]. The choice of mode depends on the nature of the reactions [25]. Non-isothermal TGAs are considerably less time-consuming than isothermal TGAs, and are thus attractive for quick investigations [27]. In isothermal methods, the temperature of the sample after reaching a specified value remains constant during the decomposition of the sample. As fewer experimental variables are used in isothermal methods, compared to non-isothermal TGAs, the results are more reliable

[27,28]. In addition, the isothermal approach is recommended for observing the reaction with the production of different intermediates, such as the decomposition/pyrolysis of waste plastics [28].

Isoconversional and non-isoconversional methods can be used to analyze TGA datasets in order to estimate the kinetic parameters. In the non-isoconversional methods, kinetic parameters are constant throughout the reaction, whereas the isoconversional methods generate kinetic parameters as a function of the extent of the reaction [16,17,19-22,29-30]. Considering the nature of thermal/catalytic cracking, it can be concluded that polymer decomposition is not a single reaction and that it produces different intermediates. For this reason, several polymer researchers have applied isoconversional methods to conduct kinetic studies of polymer decomposition [16,17,19-22].

Polymer researchers have mostly studied non-isothermal TGAs by applying the isoconversional methods of Coats-Redfern, the modified Coats-Redfern [17,31], Friedman [16,18,21], Ozawa [16], Kissinger–Akahira–Sunose (KAS) [21], Flynn–Wall–Ozawa (FWO) [21] and model-free [19,20,29,30] to determine the kinetic parameters. In these methods, the activation energy slightly increases or decreases during the cracking of waste plastics, but the difference between the levels of activation energy at different conversion factors is not significant [16,17,19,20].

Nevertheless, the estimated kinetic parameters from non-isothermal TGAs are not applicable for isothermal measurements [30]. While most researchers confirm that pyrolysis reactors work under constant temperature [20], few have studied isothermal TGAs of waste plastics [3,19,20,22]. The common methods to analyze isothermal TGAs are the conventional method which generates constant kinetic parameters over the entire decomposition [3], and the isoconversional model-free method which is highly recommended in different works [19,20,22].

Despite the rich content of research on the kinetic study of polymer decomposition, it is difficult to find a reliable model for designing an industrial reactor. One question remains unanswered regarding which method is more precise for predicting the kinetic parameters of polymer decomposition. In this work, we attempt to bridge this gap by focusing on a comprehensive kinetic study of pyrolysis of HDPE and comparing different methods. The isothermal-differential method presented in this paper better fits the real case and provides more consistent results. This method involves fewer assumptions and thus prevents more errors. The findings of this paper are a step forward in the design of an industrial reactor.

This chapter employs and analyzes the following isoconversional methods for non-isothermal and isothermal TGAs to determine the kinetic parameters: Friedman, Ozawa, FWO, KAS, and model-free methods. We evaluate the results against the experimental data and discuss their reliabilities. Considering the limitations of the employed methods, we present a new differential isoconversional method to estimate the kinetic parameters.

3.3. Materials and methods

3.3.1. Plastic (raw material)

Table 3.1 shows the typical properties of the virgin HDPE used in this study. DSC and TGA were used to determine the melting point, fusion heat, crystallinity and ash content.

Table 3.1. Typical properties of the HDPE used in this study

Melting point (°C)	Fusion heat (J/g)	Crystallinity (%)	Specific gravity	Ash content (%)
134.5	178	64.23	0.93-0.94	2.5

3.3.2. TGA

Non-isothermal and isothermal TGAs were carried out for 13 mg of the HDPE in disposable aluminum pans by Perkin Elmer TGA7 under an inert atmosphere of 30 mL.min^{-1} N$_2$. Before each

measurement the TGA was purged with N_2 for 2 hrs to avoid any oxidation. If there was any interruption for TGA test in order to stop purging of nitrogen through TGA apparatus nitrogen purging was set at 24 hours before testing a new sample. This method guarantees that there is no oxygen in the reaction zone. The weight and furnace calibration were performed according to the Perkin Elmer TGA 7 instruction manual. Different heating rates of 40, 45, 50 and 55 °C.min^{-1} were applied in non-isothermal TGAs from 40 to 575 °C. Two sets of isothermal decompositions were studied at constant temperatures of 390, 400, 410, 420 and 430 °C. The heating rates before reaching the target temperatures (which could be called the pre-heating rate) were set at 50 and 25 °C.min^{-1} during the first and second attempts to obtain isothermal measurements, respectively. These isothermal measurements enabled us to predict the effect of the pre-heating rates on the decomposition rate and the kinetic parameters. In TGA, the molten plastic cracks into gaseous products, and the overall reaction of pyrolysis of HDPE is assumed first order (Eq. 1).

$$(C_2H_4)_{n\,(l)} \rightarrow (Mixture\ of\ products)_{(g)} \tag{1}$$

3.3.3. DSC

We employed Perkin Elmer DSC7 available in our lab to determine the melting point and fusion heat of the reacted HDPE at different conversions. For the DSC measurements, we heated a 5 mg sample from 50 °C to 160 °C at 10 °C.min^{-1}, and added Nitrogen (35 mL.min^{-1}) to avoid any unwanted oxidation. Prior to the DSC, TGA was used to prepare pyrolyzed HDPE at different conversions. For this, we programmed TGA using three steps: (1) heating the polymer from 40 °C to 430 °C at a constant hating rate of 50 °C.min^{-1}, (2) maintaining the temperature at 430 °C for different durations of 10, 30, 50, 70 and 85 min, and (3) cooling it down to the ambient temperature. As the cooling rate was not very high because of technical restrictions concerning the instrument, pyrolysis continued during the cooling step. The collected samples from the TGA

reaching ambient temperature were mixtures of reacted (cracked) and unreacted HDPE at different conversions of 20, 30, 56, 70, and 86.

3.4. Results and discussions

3.4.1. Non- isothermal TGAs of HDPE

Figure 3.1 shows the non-isothermal TG and DTG curves for the HDPE at the following heating rates: 40, 45, 50 and 55 °C.min^{-1}. While all the TG curves showed a similar trend, the starting (T_i) and completion (T_f) temperatures, and the temperature at the maximum degradation rate (T_p) of reactions for all the curves were different. Table 3.2 presents the aforementioned temperatures at the different heating rates.
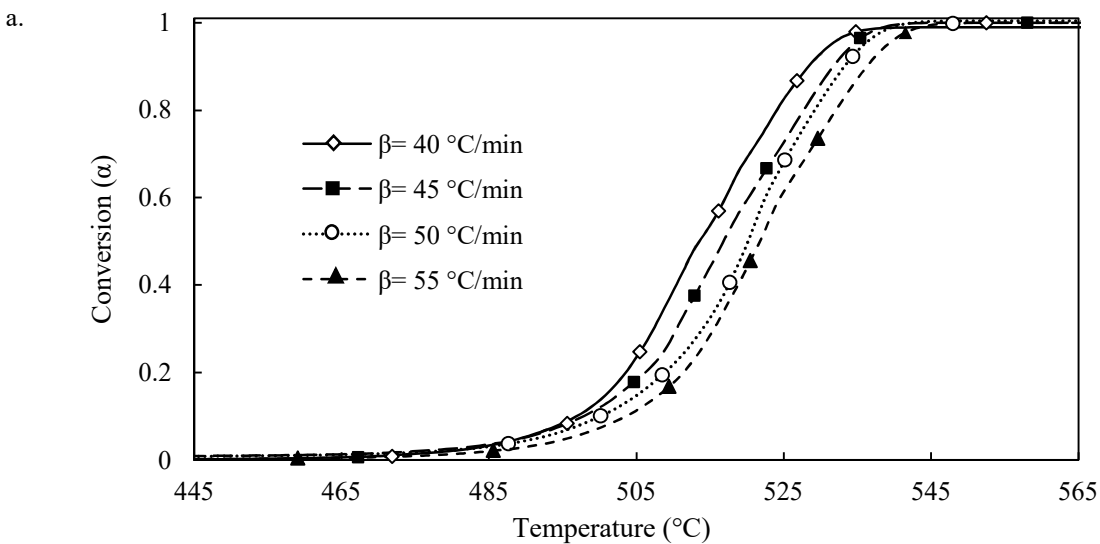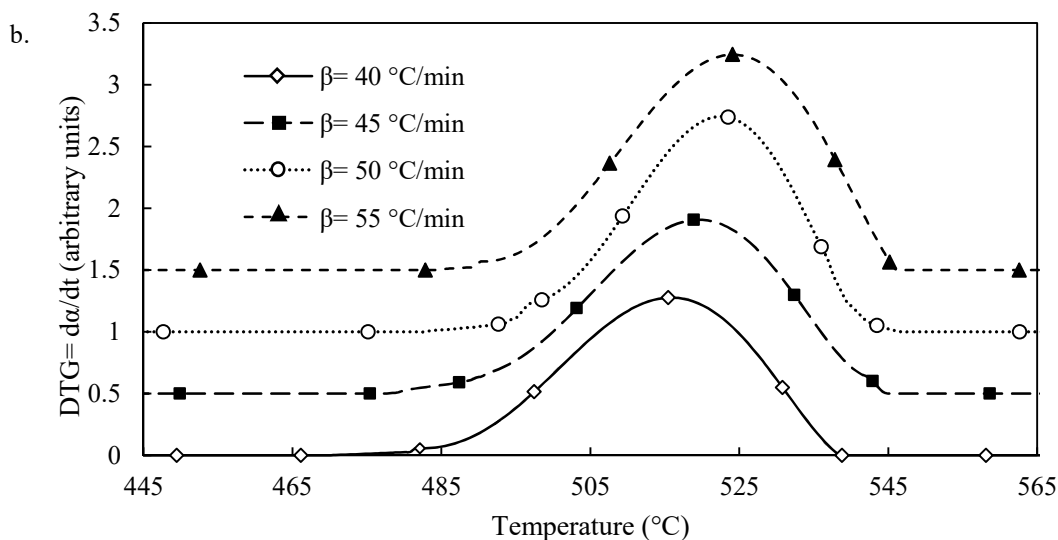
Figure 3.1. (a) TG curves of the HDPE at different heating rates. (b) Corresponding DTG curves. (N_2 flow rate=30 mL.min^{-1})

Table 3.2. Starting (T_i), maximum degradation rate (T_p) and completion (T_f) temperatures of decomposition reactions at 40, 45, 50 and 55 °C.min^{-1}, (N_2 flow rate=30 mL.min^{-1}).

Heating rate (°C.min^{-1})	T_i (°C)	T_p (°C)	T_f(°C)
40	476.47	516.15	535.47
45	479.42	519.67	536.92
50	481.68	522.67	538.5
55	484.7	524.12	542.45

Figure 3.1a and Table 3.2 indicate that higher heating rates delay weight loss, and that the reaction takes place at higher temperatures. This temperature lag might be an error caused by inaccuracies in the temperature measurements, as the TGA thermocouple cannot record the sample temperature accurately. In the best conditions, the TGA thermocouple measures the furnace temperature near to the sample pan; in the other words, the recorded reaction temperature is not the sample temperature. This error is more problematic in non-isothermal measurements, especially for endothermic reactions, since the furnace temperature increases much faster than the sample temperature.

The temperature lag might also partly be caused by the heat of the reaction. The cracking of waste plastic is an endothermic reaction. When the reaction starts, the sample needs more heat to maintain the required reaction temperature; however, regardless of the sample temperature, the furnace temperature increases at a constant rate. As the temperature lag increases with higher heating rates, the error in the temperature measurement is expected to increase with higher heating rates. For this reason, the employment of high heating rates is not recommended for kinetic study. Newkirk [27] investigated the effects of heating rates and enthalpy of the reaction on the temperature measurement.

The DTG curves in Figure 3.1b, which are representative of the reaction rate, indicate that the reaction rate is higher at a higher heating rate. As the increasing the heating rate increases the reaction temperature, it is expected to see a bigger decomposition rate ($d\alpha/dt$) at higher heating rates as well.

3.4.2. Isothermal TGAs of HDPE

Figure 3.2 shows the isothermal TGA results at five different temperatures of 390, 400, 410, 420 and 430 °C (pre-heating rate was 50 and 25 °C.min^{-1} respectively). According to Figure 3.2a, the TG curves at two different pre-heating rate of 50 and 25 °C.min^{-1} are closely matched. It demonstrates that the pre-heating rate before the target temperature has no detectable impact on the decomposition rate and it may not have impact on the reaction mechanism too. DTG curves were calculated from the TG curves in Figure 3.2a and shown in Figure 3.2b. The variation of conversion (TG) and reaction rate (DTG) with time and temperature demonstrate that the decomposition rate is extremely affected by the operating temperature. As it can be seen in Figure 3.2b, the decomposition rate ($d\alpha/dt$) is higher at higher temperatures. As a result, the required

time to complete the decomposition reactions could be significantly decreased by increasing temperature.

a.

b.
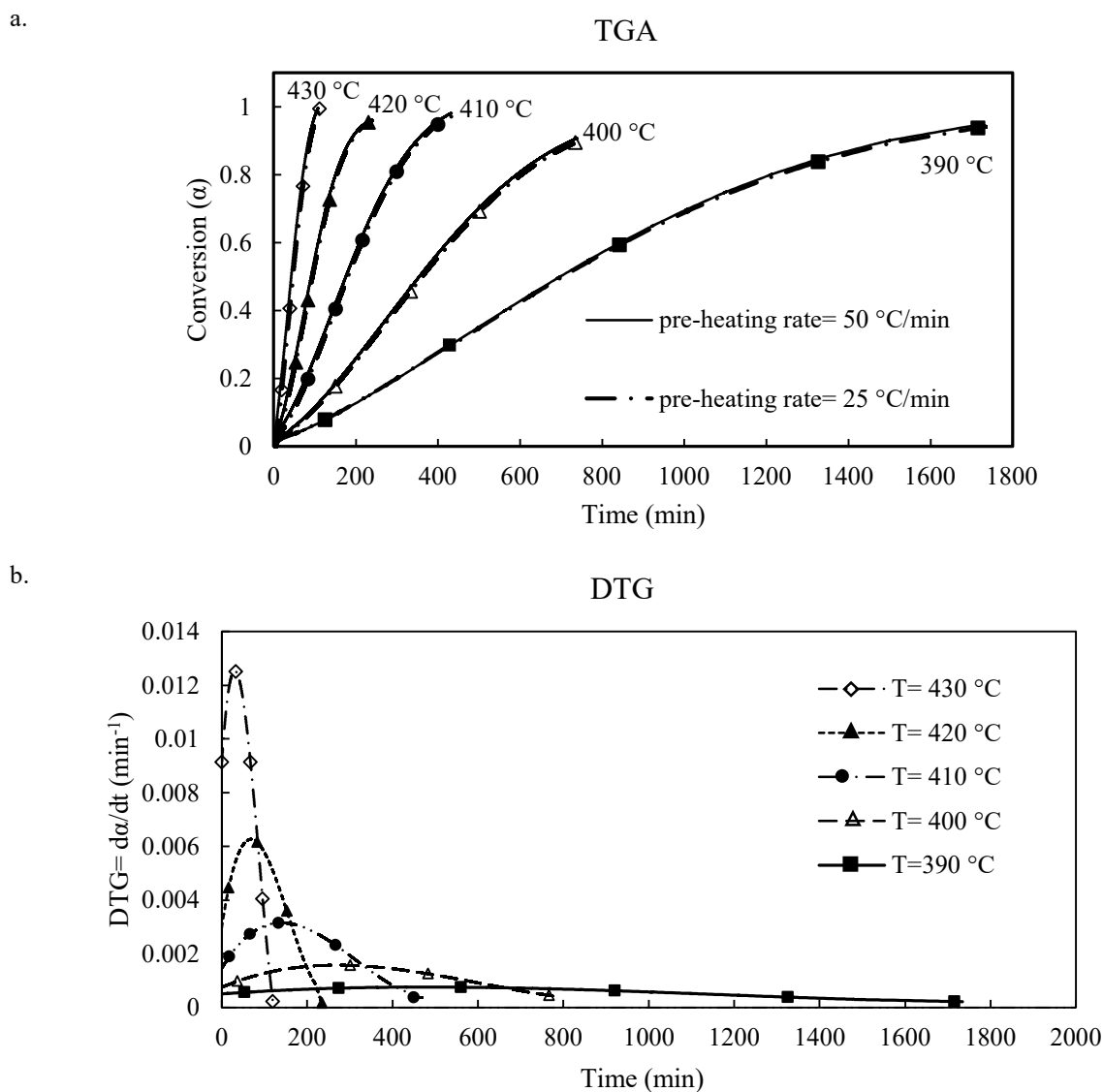
Figure 3.2. (a) TG curves of HDPE at different constant temperatures (b) Corresponding DTG curves. (N_2 flow rate=30 mL.min^{-1})

3.4.3. Isoconversional methods

Figure 3.3 shows the DSC curves of the mixtures of the unreacted/reacted HDPE at different conversions. The melting point and fusion heat of the samples were determined by measuring the temperature at the top of the peak and the area of the peak for each DSC curve, respectively, as

44

shown in Figure 3.4 and Table 3.A.1. According to Figures 3.3 and 3.4, the collected samples from the TGA have different chemical identities compared to the HDPE; and based on their DSC trends, melting points and fusion heats, the nature of the reacted HDPE at different conversions should be different. The results verify that the cracking reactions are dynamic and generate different chemicals during the lifetime of the reaction. It can thus be concluded that cracking of waste plastic involves multiple simultaneous and sequential reactions, and the chemical identity of the reactants is continuously changing.

Consequently, as the cracking of waste plastic is not a reaction of a single pure chemical component, the kinetic parameters cannot be considered constant during this process. Due to the production of several intermediates, isoconversional methods should be used to define the kinetic parameters as a function of the reacted fraction or conversion.
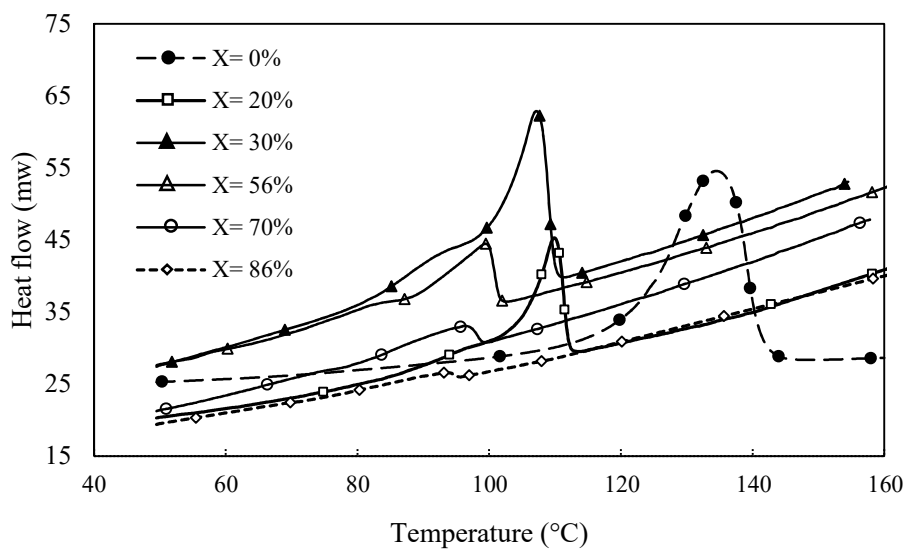
Figure 3.3. DSC curves for the collected samples from TGA. Each graph shows after X% conversion.
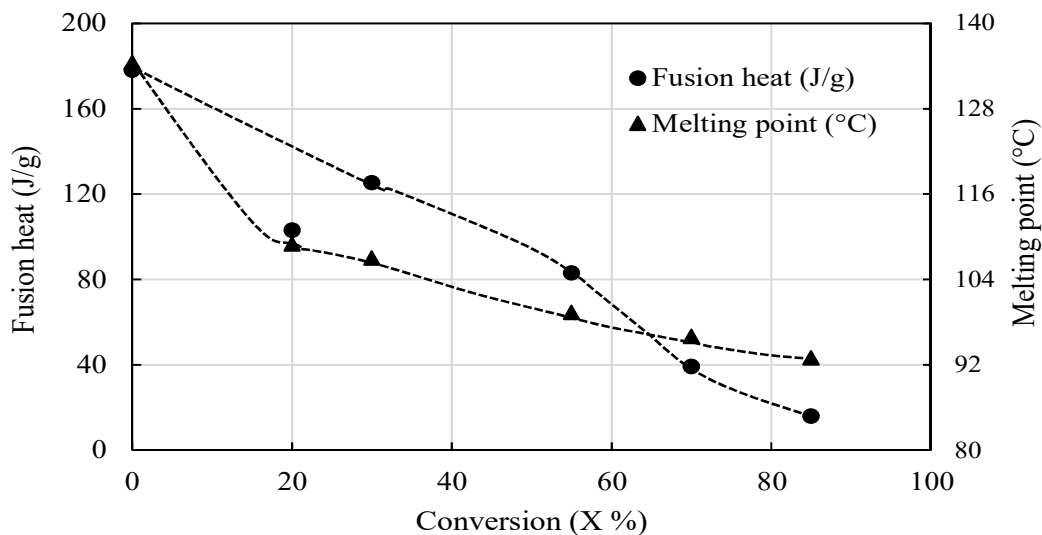
Figure 3.4. Fusion heats and melting points retrieved from the DSC curves for the collected samples from TGA after X% conversion.

3.4.4. Estimation of kinetic parameters

Traditionally, for a first-order reaction, the rate of reaction combined with Arrhenius equation can be presented by Eq. (2).

$$\frac{d\alpha}{dt} = A_0 . exp\left(-\frac{E_a}{RT}\right).(1-\alpha) \tag{2}$$

where α is the conversion of reactants and can be expressed by $(m_0 - m)/m_0$, m_0 is the initial weight of sample (mg), m is the weight of the sample at any time (mg), t is the time (min), A_0 is the pre-exponential factor (K^{-1}), E_a is the apparent activation energy (kJ.mol^{-1}), R is the gas constant (kJ.mol^{-1}.K^{-1}) and T is the reaction temperature (K).

3.4.4.1. Non-isothermal study

Under non-isothermal conditions, when the temperature increases at a constant heating rate, $\beta = dT/dt$, Eq. (2) can be rearranged as Eq. (3).

$$\beta \frac{d\alpha}{dT} = A_0. \, exp\left(-\frac{E}{RT}\right).(1-\alpha) \tag{3}$$

The non-isothermal TGAs presented in Figure 3.1 could be used in the isoconversional methods described by Friedman, Ozawa, FWO and KSO. Table 3.3 presents a summary of all of the methods.

Table 3.3. Mathematical equations of Friedman, Ozawa, FWO and KAS methods.

Method	Expression	Eq.	Ref	Linearization plot
Friedman	$ln\left(\beta \frac{d\alpha}{dT}\right) = ln(A_0) + ln(1-\alpha) - \frac{E_a}{R}\frac{1}{T}$	(4)	[21]	$ln(\beta.d\alpha/dT)$ against $1/T$
Ozawa	$ln(\beta) = -ln\left(\frac{d\alpha}{dT}\right) + ln(A_0) + ln(1-\alpha) - \frac{E_a}{R}\frac{1}{T}$	(5)	[32]	$ln(\beta)$ against $1/T$
FWO	$ln(\beta) = ln\left(-\frac{A_0 E_a}{R \, ln(1-\alpha)}\right) - 5.331 - 1.052\frac{E_a}{R}\frac{1}{T}$	(6)	[21]	$ln(\beta)$ against $1/T$
KAS	$ln\left(\frac{\beta}{T^2}\right) = ln\left(-\frac{A_0 R}{E_a \, ln(1-\alpha)}\right) - \frac{E_a}{R}\frac{1}{T}$	(7)	[21]	$ln(\beta/T^2)$ against $1/T$

The activation energy and frequency factor of decomposition of the HDPE were determined by plotting the left-hand sides of Eqs. (4-7) against temperature inverse for constant conversions in the range of 0.05–0.95. The outcome of this calculation is the activation energy and pre-exponential factor that were summarized in Figures 3.5 and 3.6 and Table 3.A.2 for all the methods. Figure 3.A.1 shows the sample calculation for the Ozawa method.

Figures 3.5 and 3.6 highlight the dependency of the determined activation energy and pre-exponential factor on the conversion. While the calculated kinetic parameters from the Ozawa, FWO, and KAS methods increase gradually, the results from the Friedman method, especially before the 25% conversion, are different. In the Friedman method, the reactions starts at a higher level of activation energy and frequency factor; thus, when the reactions exceeds to 25% conversion, a sharp drop is observed in the obtained kinetic parameters, followed by a moderate

increase by E_a and *ln(A_0)*. It is important to note that as the reaction exceeds, both E_a and *ln(A_0)* are associated with fluctuation.
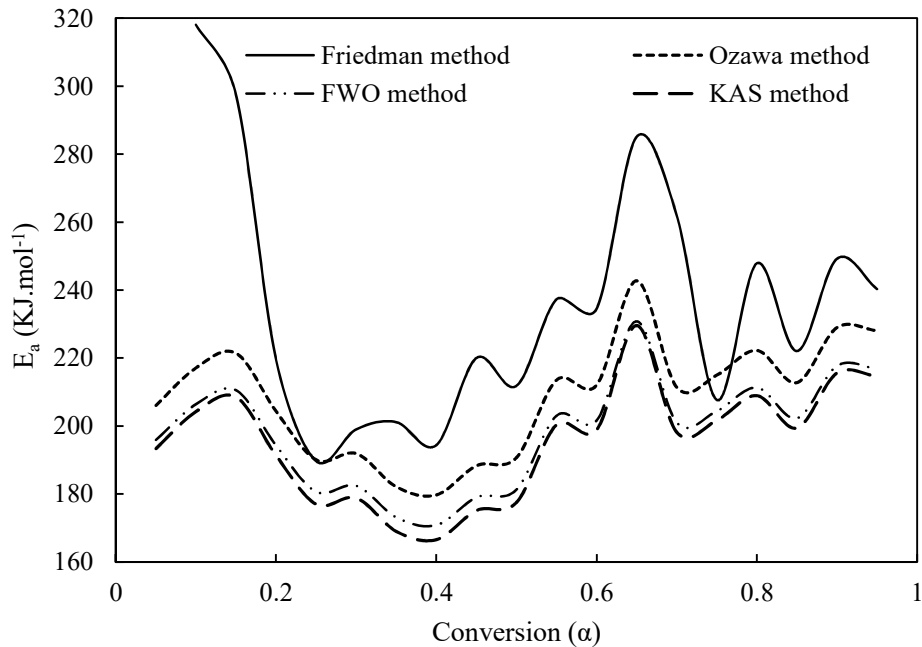
Figure 3.5. Estimated E_a from Friedman, Ozawa, FWO and KAS methods using non-isothermal data.
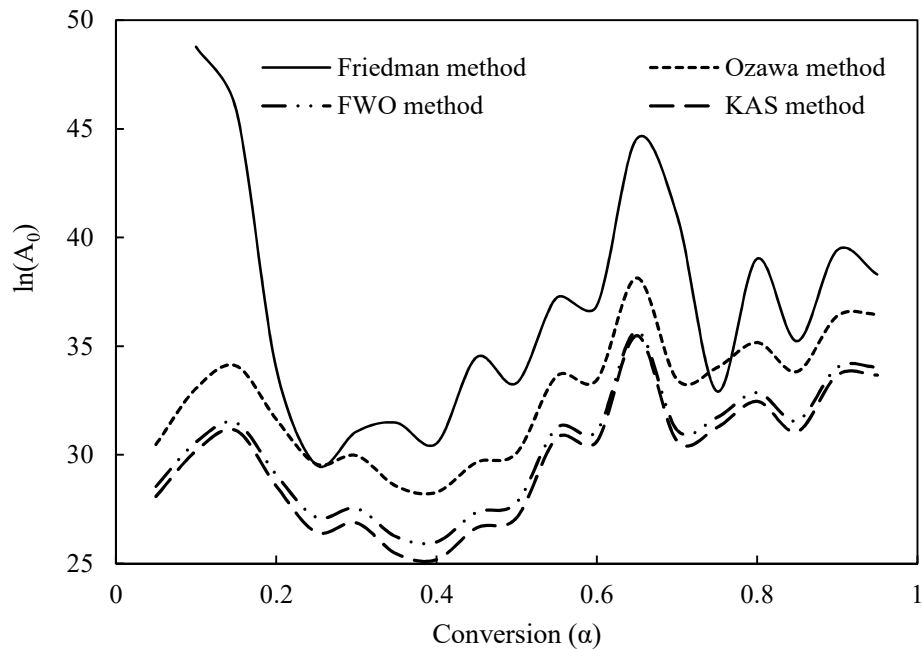
Figure 3.6. Estimated *ln(A₀)* from Friedman, Ozawa, FWO and KAS methods using non-isothermal data.

To examine the reliability of the estimated kinetic parameters from the employed techniques, the DTG curves were presented in Figure 3.7, using the determined kinetic parameters, and evaluated against the experimental data under non-isothermal conditions with a heating rate of 50 °C.min^{-1}. Figure 3.7 demonstrates that the FWO and KAS methods failed to generate an acceptable match with the experimental DTG curve at 50 °C.min^{-1}. Conversely, the Friedman and Ozawa methods showed good agreements, generating reliable kinetic parameters for the pyrolysis of the HDPE.
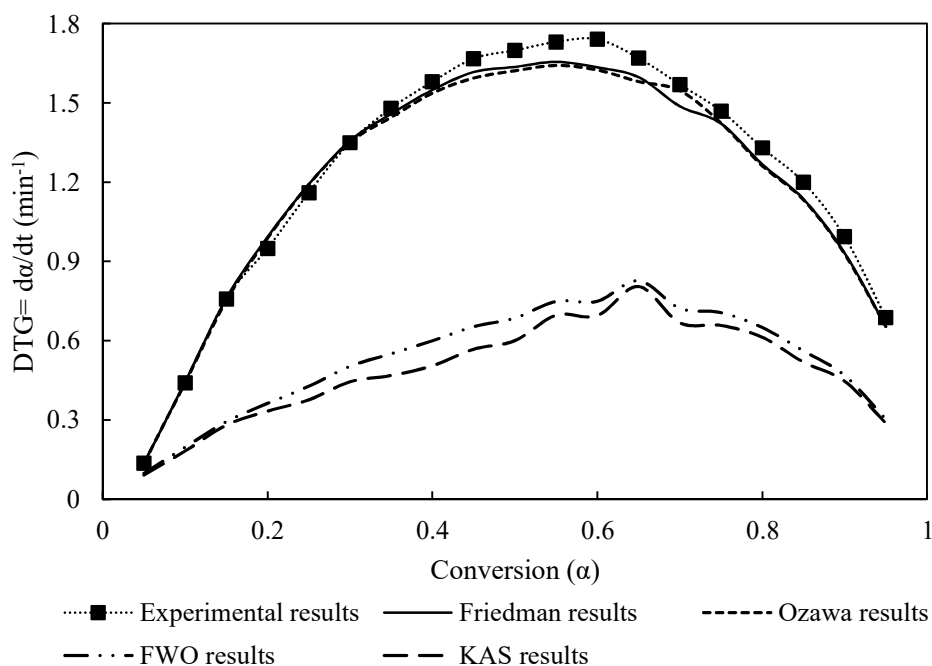
Figure 3.7. Non-isothermal DTG curves from the Friedman, Ozawa, FWO, KAS methods against the experimental data (β=50 °C.min^{-1} and N$_2$ flow rate=30 mL.min^{-1}).

The majority of researchers have used non-isothermal methods, mostly Friedman and Ozawa, for the kinetic study of polymer decompositions. However, we believe that using isothermal

measurements is a better and more reliable technique for finding the kinetic parameters. In non-isothermal measurements, the decomposition mechanism defers from one temperature to another. In Figures 3.5 and 3.6, the fluctuations associated with E_a and $ln(A_0)$ are the obvious evidences of diverse reaction mechanisms in non-isothermal pyrolysis of HDPE. However, by keeping the temperatures constant, we decrease the number of variables and restrict the reactions to follow a narrower pathway. As a result, the kinetic parameters, calculated from isothermal measurements, are better representatives of the polymer decompositions. Moreover, since most pyrolysis reactors work under isothermal conditions, it is necessary to find the isothermal kinetic parameters.

3.4.4.2. Isothermal study

In the first attempt the well-known isoconversional model-free method was applied to determine the kinetic parameters from the isothermal datasets presented in Figure 3.2a at different temperatures: 390, 400, 410, 420 and 430 °C. This method is isoconversional since it finds kinetic parameters at different extents of the reaction. The model-free method is an integral method and starts with the integration of Eq. (2) as follows.

$$\int \frac{d\alpha}{(1-\alpha)} = A_0.exp\left(-\frac{E_a}{RT}\right)\int dt \rightarrow -\ln(1-\alpha) = A_0.exp\left(-\frac{E_a}{RT}\right).t \tag{8}$$

Applying natural logarithm operator converts Eq. 8 to a linear format as:

$$\ln(-\ln(1-\alpha)) = \ln(A0) - \frac{E_a}{RT} + \ln(t) \quad or \quad -\ln t = \ln(A_0) - \ln(-\ln(1-\alpha)) - \frac{E_a}{RT} \tag{9}$$

where E_a and A_0 are determined from the slope and the intercept of the plotting of $–ln(t)$ against T^{-1} for constant conversions in the range of 0.05 to 0.95. Figure 3.A.2 shows the model-free method linear regression. Figure 3.8 and Table 3.A.3 present the determined activation energy and pre-exponential factor from the model-free method for the isothermal datasets. As shown in Figure

3.8, up to 25 % conversion, the obtained kinetic parameters decrease to the minimum values, and

beyond 25 % weight loss, both activation energy and frequency factor increase gradually.
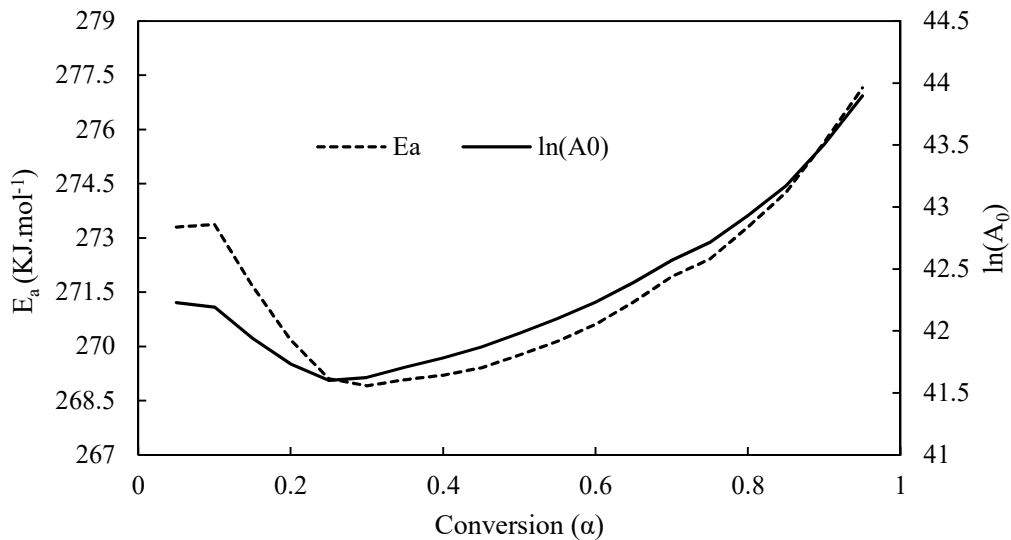
Figure 3.8. Estimated E_a and $ln(A_0)$ from the model- free method using isothermal data presented in
Figure 3.2.

Figure 3.9 shows the evaluation of the estimated DTG curves from the model-free method at

420 °C against the experimental data presented in Figure 3.2b. Despite the recommended use of

the model-free method in the kinetic study of polymer decomposition, in this work, it could not

lead to a good match with the experimental data.
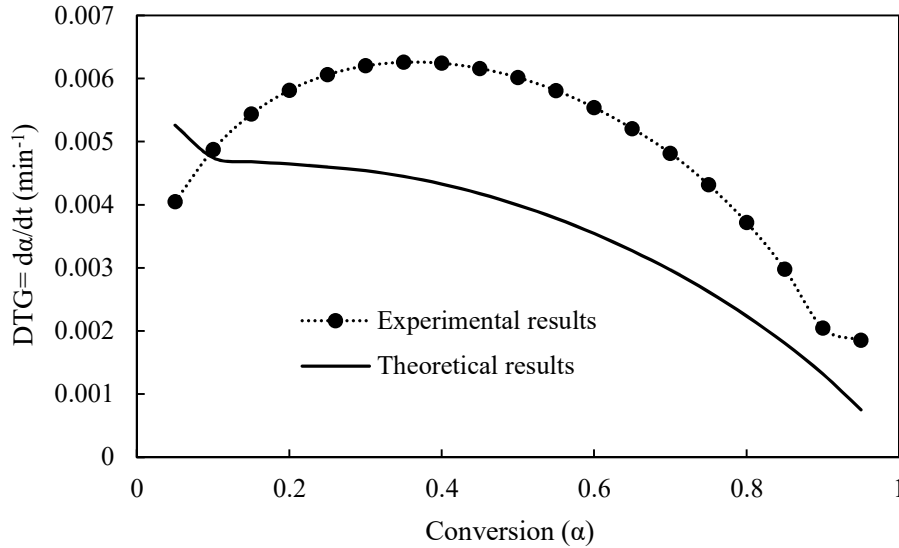
Figure 3.9. Isothermal DTG curves from the model-free method and experimental data (T=420 °C and N$_2$ flow rate=30 mL.min^{-1}).

The problem with the model-free method might be the employed integration in Eq. (8). To solve the equation using this method, it should be assumed that E_a and A_0 are constant. However, these parameters are not constant and they change with the progress of reactions. Therefore, to overcome this problem, we use Eq. (2) directly without converting it to the integral form. Notably, Eq. (2) is the differential form of the reaction rate for a batch reactor. Considering that TGA is also a batch reactor, Eq. (2) can be directly used with no further treatment. Thus, the integration step can be omitted and logarithm operator can be applied to Eq. (2) directly. Using this method, there is no need to assume that E_a and A_0 are constant. Consequently, it reduces the uncertainty associated with the aforementioned assumption.

$$ln\left(\frac{1}{1-\alpha}\cdot\frac{d\alpha}{dt}\right) = ln(A_0) - \frac{E_a}{RT} \tag{10}$$

In Eq. 10, $d\alpha/dt$ can be determined at any conversion factor using Figure 3.2. Applying a linear regression and plotting the left-hand side of Eq. (10) against the temperature inverse leads

to a frequency factor and apparent activation energy at different conversions. Figure 3.A.3 and shows the sample calculation of the linear regression employed in this method.

Figure 3.10 and Table 3.A.3 present the calculated activation energy and frequency factor from the proposed method for the isothermal datasets. According to Figure 3.10, in the beginning of the decomposition reactions, activation energy drops, and after 20 % conversion, it increases moderately. On the other hand, $ln(A_0)$ grows steadily till end of the reactions.

In Figure 3.11, using the obtained kinetic parameters DTG curves at 420 °C were generated and compared with the experimental DTG curves under the same conditions. As shown in Figure 3.11, the comparison of the theoretical and experimental data led to an acceptable agreement.
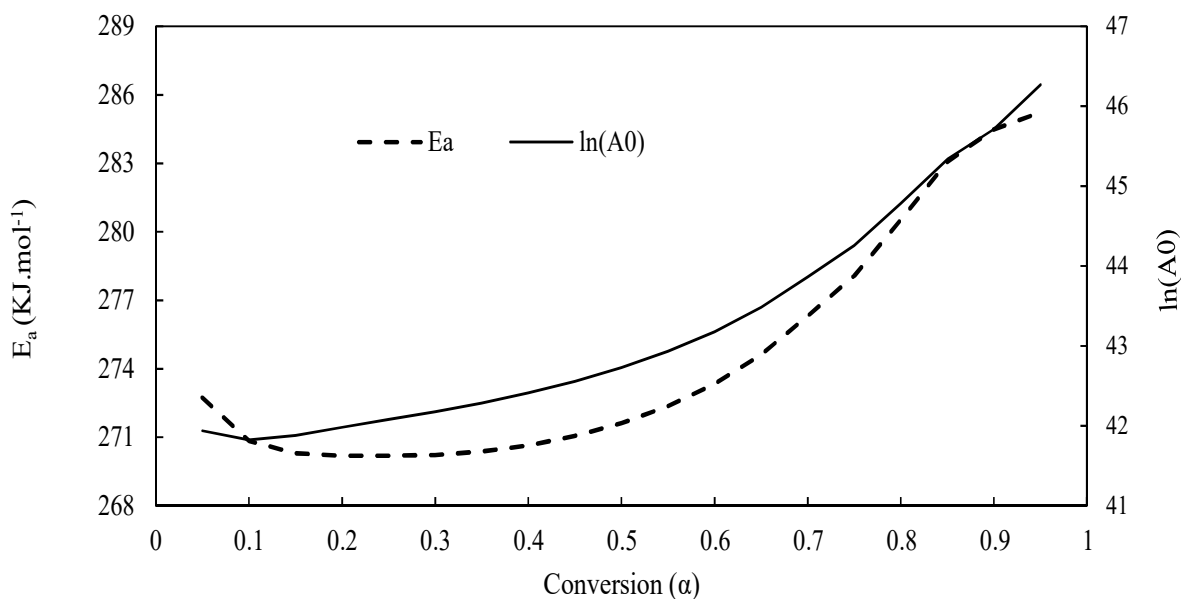
Figure 3.10. Estimated E_a and $ln(A_0)$ from the proposed method in this work using isothermal data presented in Figure 3.2.
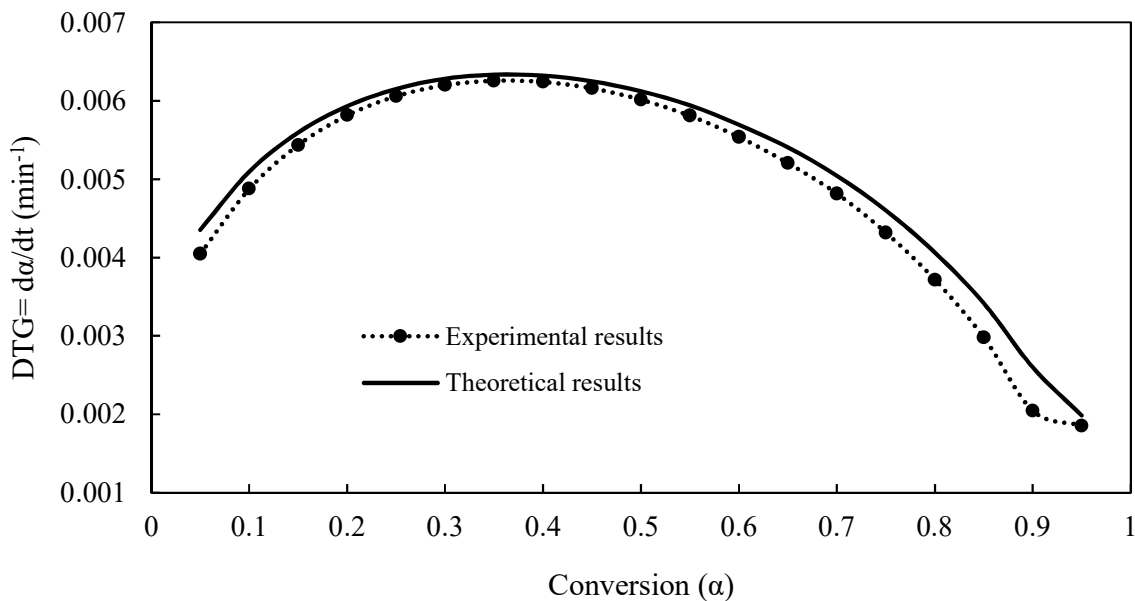
Figure 3.11. Isothermal DTG curves from the proposed method in this work and experimental data (T=420 °C and N_2 flow rate=30 mL.min^{-1}).

As it can be seen in Figures 3.8 and 3.10, the calculated kinetic parameters from isothermal datasets have smoother trends with almost no fluctuations. It seems that in isothermal measurements as in each run the temperature maintains constant, reactions mechanisms are homogenous through the whole decomposition range.

3.5. Conclusion

TGA was confirmed to be a valuable tool for determining the kinetic parameters for the cracking of plastics. This paper employed different methods for use in kinetic studies and tested their consistency with the experimental data.

The use of DSC and TGA proved the necessity of using isoconversional methods. Using the isoconversional Friedman, Ozawa, FWO, and KAS methods, we analyzed the non-isothermal data. The estimated kinetic parameters from the Friedman and Ozawa methods matched the experimental data.

In addition, we studied isothermal datasets using an integral method called model-free; however, this failed to lead to a proper agreement with the experimental data. This work proposed a new differential isoconversional method to analyze isothermal TGAs. Reliability of this new approach was investigated, and the evaluation of the results against the experimental data indicated an acceptable match.

Besides them, it was observed that isothermal approach could limit the involved reaction mechanisms in pyrolysis of HDPE and generate more reliable data.

Acknowledgment

References

[1] Innovation, Science and Economic Development Canada, 2012. Industry Profile for the Canadian Plastic Products Industry. Retrieved from http://www.ic.gc.ca/eic/site/plastics-plastiques.nsf/eng/pl01383.html

[2] The statistical portal, 2014. Production of plastics worldwide from 1950 to 2014. Retrieved from http://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/

[3] Miskolczi N, Bartha L, Deak G. Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks. Polymer Degradation and Stability 2006; 91(3): 517-526

[4] El-Fadel M, Findikakis AN, Leckie JO. Environmental Impacts of Solid Waste Landfilling. Journal of Environmental Management 1997; 50: 1-25

[5] Al-Salem SM, Lettieri P, Baeyens J. Recycling and recovery routes of plastic solid waste (PSW): A review. Waste Management 2009; 29(10): 2625-2643

[6] Aguado J, Serrano DP, San Miguel G, Escola JM, Rodríguez JM. Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins. Journal of Analytical and Applied Pyrolysis 2007; 78(1): 153-161

[7] Rasul Jan M, Shah J, Gulab H. Catalytic conversion of waste high-density polyethylene into useful hydrocarbons. Fuel 2013; 105: 595-602

[8] Rasul Jan M, Shah J, Gulab H. Degradation of waste High-density polyethylene into fuel oil using basic catalyst. Fuel 2010; 89(2): 474-480

[9] Angyal A, Miskolczi N, Bartha L. Petrochemical feedstock by thermal cracking of plastic waste. Journal of analytical and applied pyrolysis 2007; 79(1-2): 409-414

[10] Miskolczi N, Bartha L, Deák G, Jóver B. Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons. Polymer Degradation and Stability 2004; 86(2): 57-366

[11] Muhammad C, Onwudili JA, Williams PT. Thermal Degradation of Real-World Waste Plastics and Simulated Mixed Plastics in a Two-Stage Pyrolysis–Catalysis Reactor for Fuel Production., Energy and Fuels 2015; 29(4): 2601-2609

[12] Mastral JF, Berrueco C, Gea M, Ceamanos J. Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite. Polymer Degradation and Stability 2006; 91(12): 3330-3338

[13] Miskolczi N, Bartha L, Deák G, Jóver B, Kalló D. Thermal and thermo-catalytic degradation of high-density polyethylene waste. Journal of Analytical and Applied Pyrolysis 2004; 72(2): 235-242

[14] Schirmer J, Kim JS, Klemm E. Catalytic degradation of polyethylene using thermal gravimetric analysis and a cycled-spheres-reactor. Journal of Analytical and Applied Pyrolysis 2001; 60(2): 205-217

[15] Ding W, Liang J, Anderson LL. Thermal and catalytic degradation of high density polyethylene and commingled post-consumer plastic waste. Fuel Processing Technology 1997; 51(1-2): 47-62

[16] Neves IC, Botelho G, Machado AV, Rebelo P. Catalytic degradation of polyethylene: An evaluation of the effect of dealuminated Y zeolites using thermal analysis. Materials Chemistry and Physics 2007; 104(1): 5-9

[17] Yan G, Jing X, Wen H, Xiang S. Thermal Cracking of Virgin and Waste Plastics of PP and LDPE in a Semibatch Reactor under Atmospheric. Energy and Fuel 2015; 29(4): 2289-2298

[18] Yang J, Miranda R, Roy C. Using the DTG curve fitting method to determine the apparent kinetic parameters of thermal decomposition of polymers. Polymer Degradation and Stability 2001; 73(3): 455-461

[19] Lee SY, Yoon JH, Kim JR, Park DW. Catalytic degradation of polystyrene over natural clinoptilolite zeolite. Polymer Degradation and Stability 2001; 74(2): 297-305

[20] Saha B, Maiti AK, Ghoshal AK. Model-free method for isothermal and non-isothermal decomposition kinetics analysis of PET sample. Thermochimica Acta 2006; 444(1): 46-52

[21] Aboulkas A, El harfi K, El Bouadili A. Thermal degradation behaviors of polyethylene and polypropylene. Part I: Pyrolysis kinetics and mechanisms. Energy Conversion and Management 2010; 51: 1363–1369

[22] Vyazovkin1 S, Sbirrazzuoli N. Isoconversional Kinetic Analysis of Thermally Stimulated Processes in Polymers. Macromolecular Rapid Communications 2006; 27(18): 1515-1532

[23] Kong Y, Hay JN. The enthalpy of fusion and degree of crystallinity of polymers as measured by DSC. European Polymer Journal 2003; 39(8): 1721-1727

[24] Kong Y, Hay JN. The measurement of the crystallinity of polymers by DSC. Polymer 2002; 73(14): 3873-3878

[25] Powel DA. An apparatus giving thermogravimetric and differential thermal curves simultaneously from one sample. Journal of Scientific Instruments 1957; 34: 225-227

[26] TA instruments, 1994. Decomposition kinetics using TGA. Retrieved from http://www.tainstruments.co.jp/application/pdf/Thermal_Library/Applications_Briefs/TA075.PDF

[27] Newkirk AE. Thermogravimetric Measurements. Analytical Chemistry 1960; 32(12): 1558-1563

[28] Waters DN, Paddy JL. Equations for Isothermal Differential Scanning Calorimetric Curves. Analytical Chemistry 1988; 60(1): 53-57

[29] Vyazovkin S, Wight CA. Kinetics of Thermal Decomposition of Cubic Ammonium Perchlorate. Chemistry of Materials 1999; 11: 3386-3393

[30] Vyazovkin S, Wight CA. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. Thermochimica Aceta 1999; 340-341: 53-68

[31] Fischer PE, Jou CS, Gokalgandhi SS. Obtaining the Kinetic Parameters from Thermogravimetry Using a Modified Coats and Redfern Technique. Industrial and Engineering Chemistry Research 1987; 26(5): 1037-1040

[32] Ozawa K. A New Method of Analyzing Thermogravimetric Data. Bulletin of the chemical society of Japan 1965; 38(11): 1881-1886

Appendix 3.A

(a)

(b)
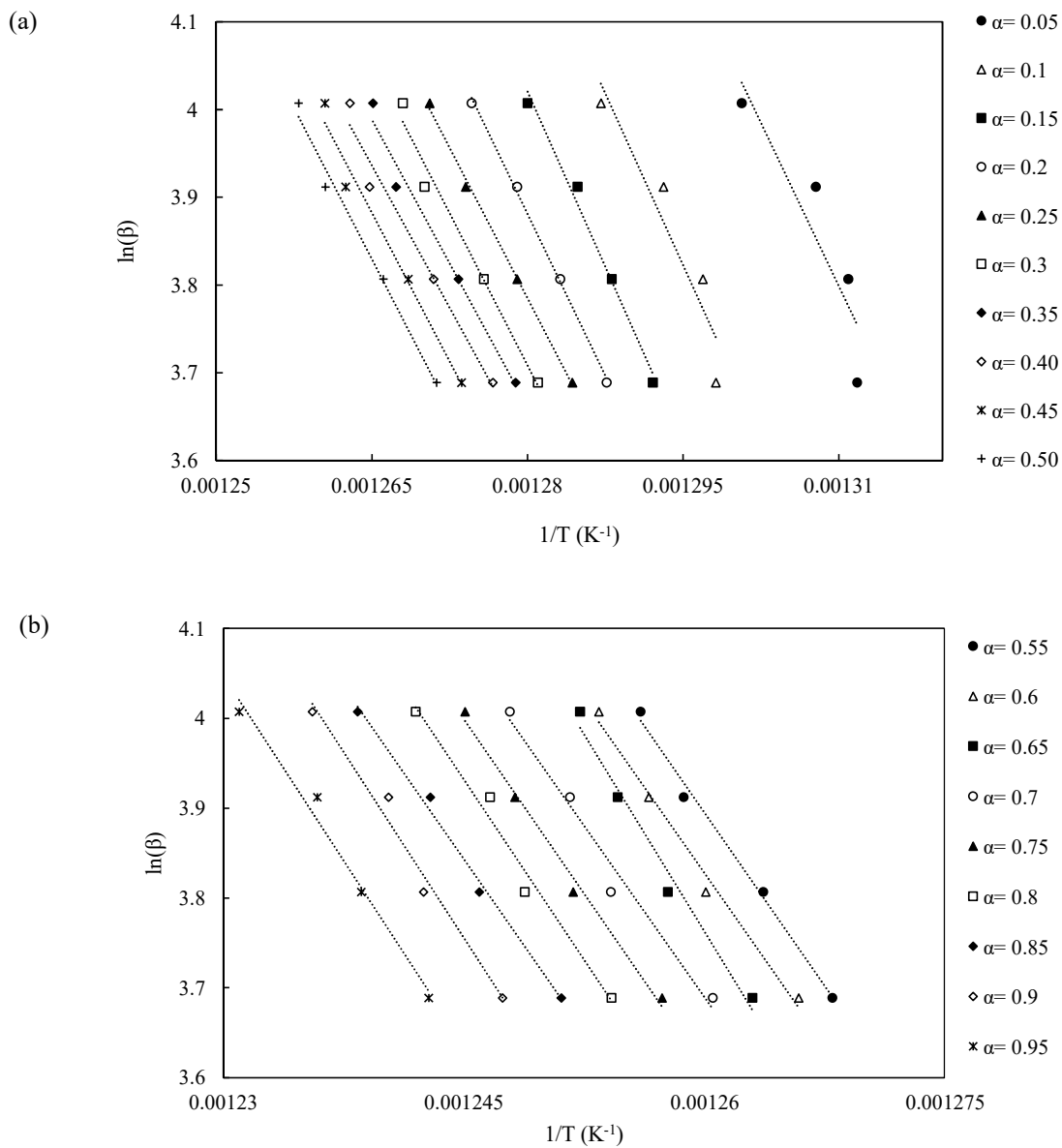
Figure 3.A.1. Ozawa plots for HDPE. **(a)** conversion range: 0.05-0.5, **(b)** conversion range: 0.55-0.95.

(a)
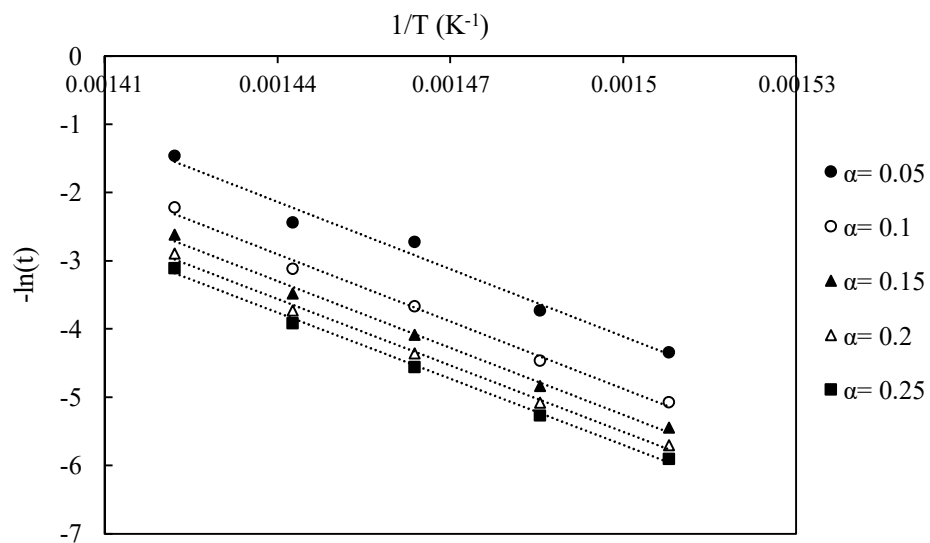
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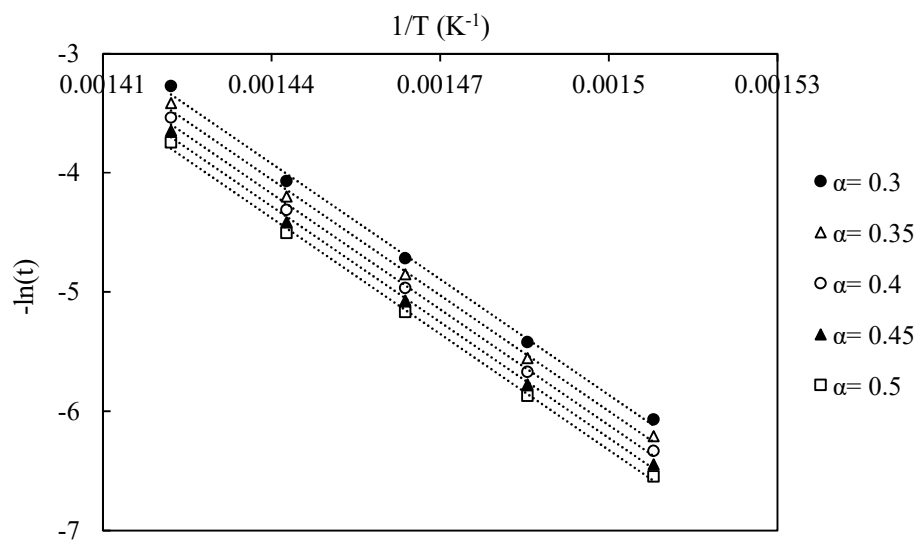
(c)
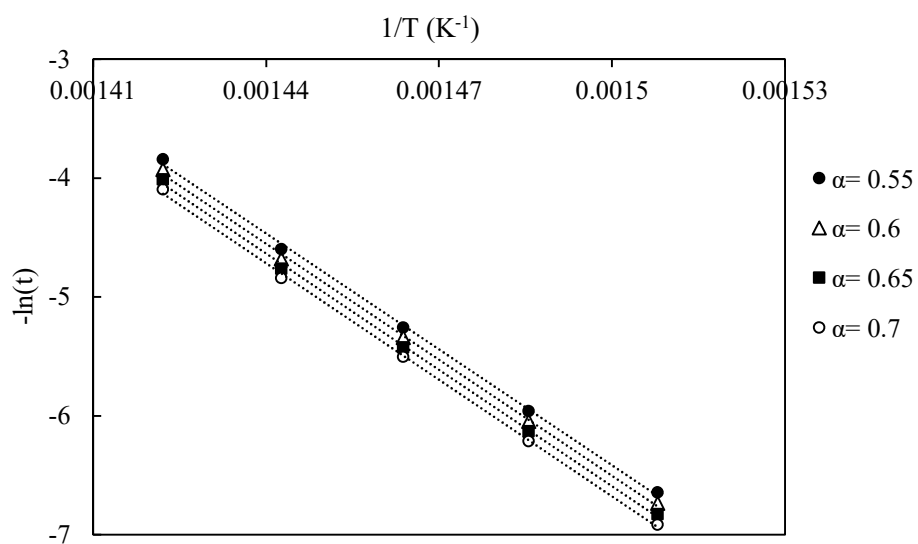
(d)
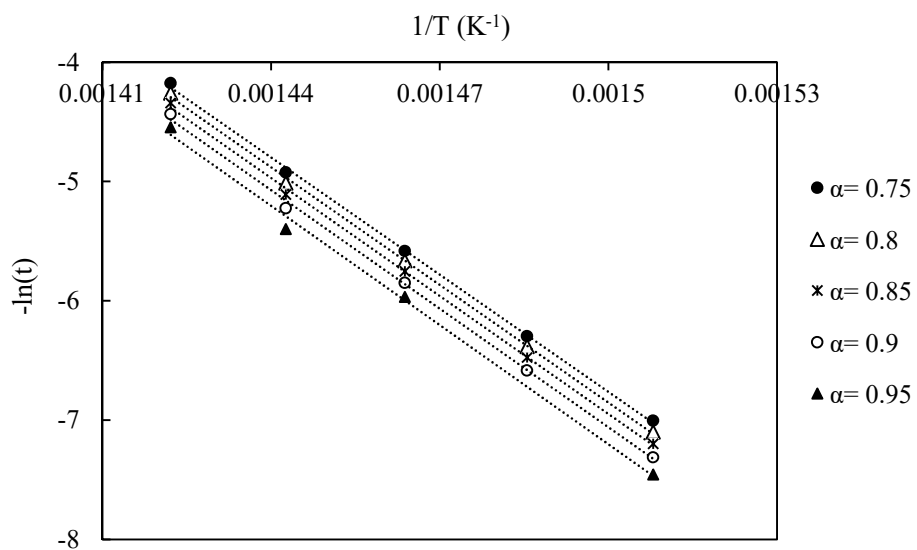
Figure 3.A.2. Linear regression for the model-free method **(a)** conversion range: 0.05-0.25, **(b)** conversion range: 0.3-0.5 and **(c)** conversion range: 0.55-0.7, **(d)** conversion range: 0.75-0.95.

(a)

1/T (K⁻¹)

(b)

1/T (K⁻¹)

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(c)

1/T (K⁻¹)

(d)

1/T (K⁻¹)
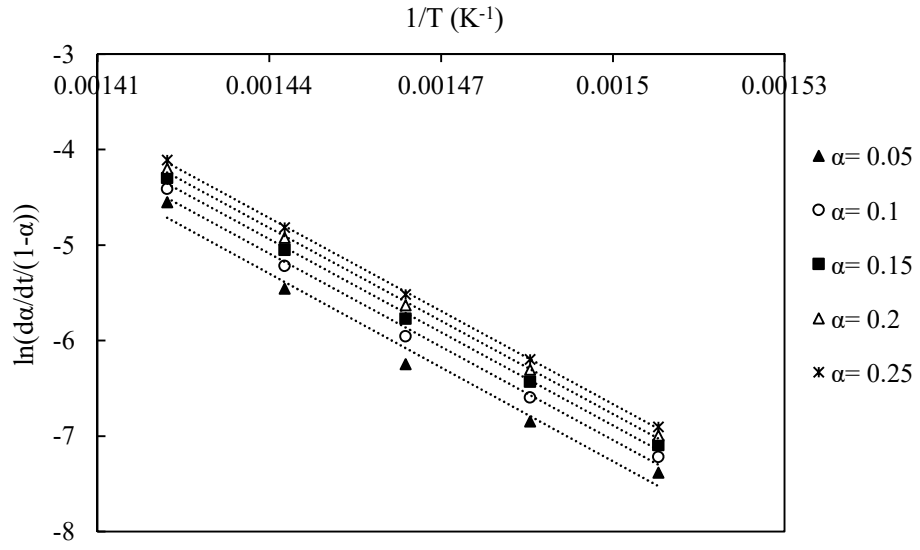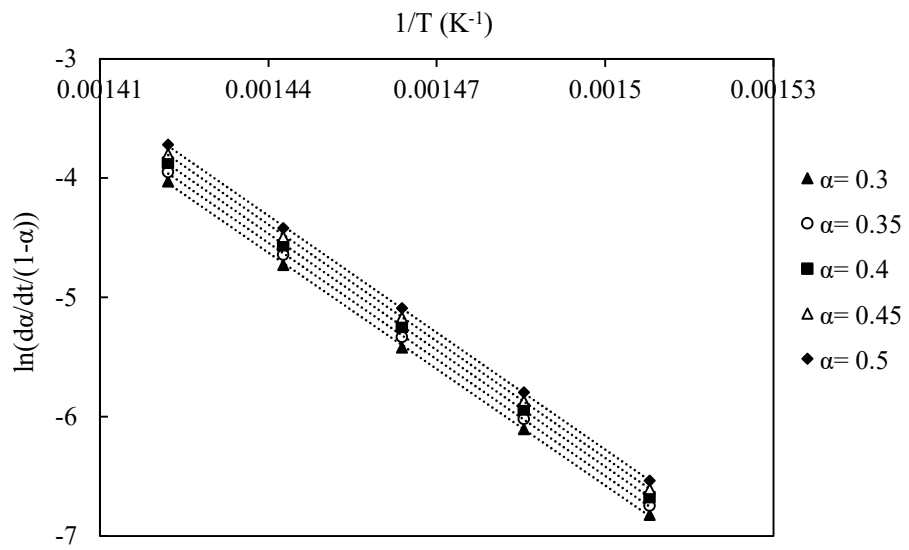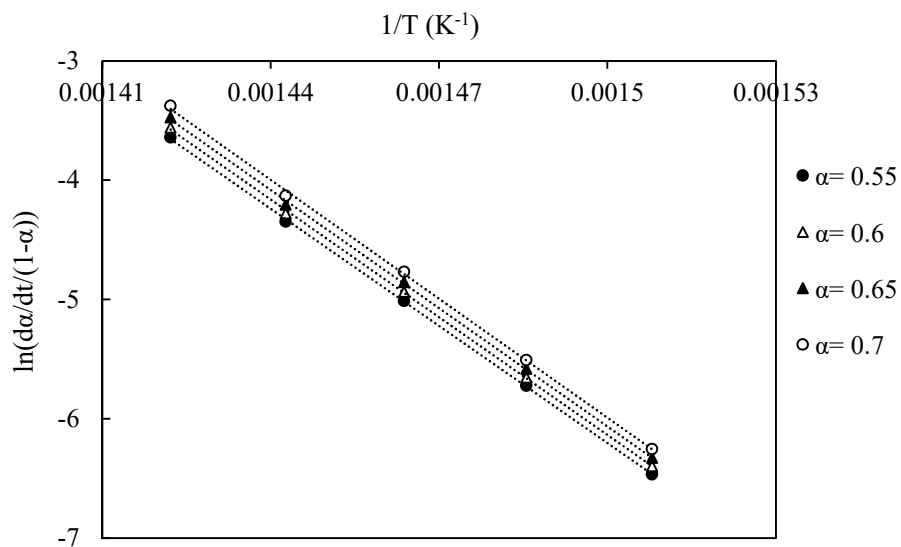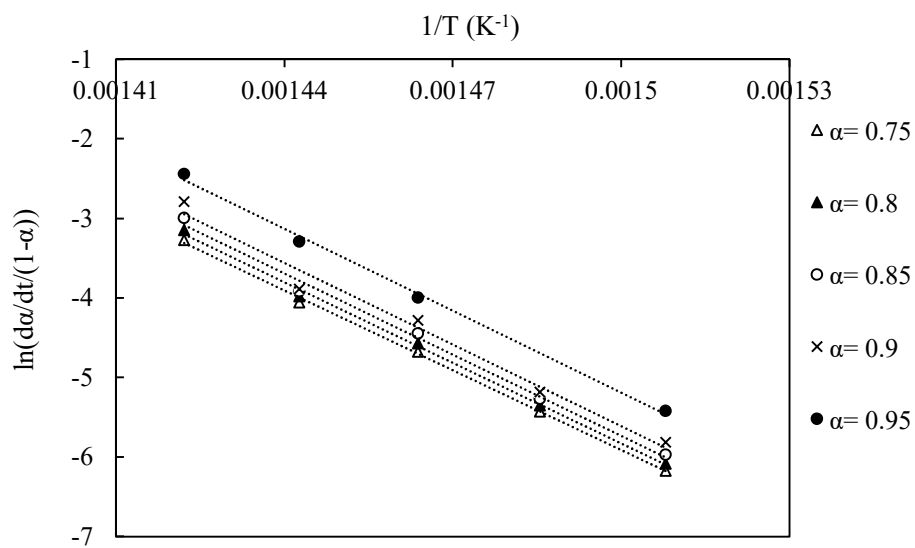
Figure 3.A.3. Linear regression for the proposed method **(a)** conversion range: 0.05-0.25, **(b)** conversion range: 0.3-0.5, **(c)** conversion range: 0.55-0.7 and **(d)** conversion range: 0.75-0.95.

Table 3.A.1. Determined melting points and fusion heats from DSC curves presented in Figure 3.4.

Conversion (X%)	0	20	30	56	70	85
Melting point (°C)	134.5	109	107	99.33	96	93
Fusion heat (J/g)	178	103.04	125.34	83	39.27	15.93

Table 3.A.2. Calculated E_a and $ln(A_0)$ using the Friedman, Ozawa, FWO and KAS methods.

	Friedman method			Ozawa method		
α	E_a (kJ.mol^{-1})	$ln(A_0)$	R^2	E_a (kJ.mol^{-1})	$ln(A_0)$	R^2
0.05	115.61	16.242	0.98	206.09	30.477	0.84
0.10	318.08	48.765	0.99	217.13	33.059	0.90
0.15	297.57	45.874	0.99	221.44	34.097	0.99
0.20	219.53	33.988	0.95	204.31	31.642	1.00
0.25	189.69	29.532	0.94	190.02	29.582	1.00
0.30	199.01	31.064	0.97	191.89	29.971	0.98
0.35	201.16	31.472	0.98	182.09	28.557	0.98
0.40	194.38	30.519	0.96	179.70	28.278	0.97
0.45	220.01	34.487	0.97	188.30	29.658	0.98
0.50	211.83	33.302	0.96	190.71	30.090	0.99
0.55	237.28	37.227	0.95	213.55	33.626	0.99
0.60	234.52	36.852	0.90	212.06	33.452	0.99
0.65	285.10	44.542	0.97	242.77	38.143	0.98
0.70	262.00	41.044	0.98	211.45	33.473	0.98
0.75	207.68	32.918	0.97	214.99	34.017	0.99
0.80	247.88	39.015	0.89	222.27	35.171	0.98
0.85	222.06	35.222	0.93	212.78	33.833	0.99
0.90	249.22	39.412	0.92	229.00	36.392	0.98
0.95	240.31	38.293	0.88	228.09	36.475	0.98
	FWO method			KAS method		
α	E_a (kJ.mol^{-1})	$ln(A_0)$	R^2	E_a (kJ.mol^{-1})	$ln(A_0)$	R^2
0.05	195.90	28.543	0.85	193.36	28.074	0.82
0.10	206.40	30.583	0.90	204.27	30.173	0.88
0.15	210.49	31.466	0.99	208.51	31.113	0.99
0.20	194.21	29.086	1.00	191.33	28.559	1.00
0.25	180.63	27.118	1.00	177.01	26.434	1.00
0.30	182.40	27.534	0.98	178.84	26.866	0.98
0.35	173.09	26.219	0.98	169.02	25.438	0.98
0.40	170.82	25.985	0.97	166.60	25.173	0.97
0.45	179.00	27.351	0.98	175.18	26.632	0.97

0.50	181.28	27.800	0.99	177.55	27.103	0.99
0.55	203.00	31.242	0.99	200.38	30.775	0.99
0.60	201.57	31.093	0.99	198.85	30.607	0.99
0.65	230.77	35.683	0.98	229.55	35.474	0.98
0.70	201.00	31.139	0.98	198.20	30.639	0.97
0.75	204.36	31.720	0.99	201.70	31.249	0.99
0.80	211.28	32.859	0.98	208.95	32.452	0.98
0.85	202.26	31.558	0.99	199.42	31.055	0.99
0.90	217.68	34.019	0.98	215.61	33.662	0.98
0.95	216.81	34.030	0.98	214.64	33.657	0.98

Table 3.A.3. Calculated E_a and $ln(A_0)$ using the Friedman, Ozawa, FWO and KAS methods.

	model-free method			The proposed method		
α	E_a (kJ.mol^{-1})	$ln(A_0)$	R^2	E_a (kJ.mol^{-1})	$ln(A_0)$	R^2
0.05	273.30	42.228	0.98	272.72	41.939	0.98
0.10	273.37	42.192	0.99	270.84	41.823	0.99
0.15	271.66	41.938	0.99	270.30	41.880	1.00
0.20	270.17	41.733	1.00	270.19	41.980	1.00
0.25	269.10	41.601	1.00	270.19	42.081	1.00
0.30	268.91	41.624	1.00	270.22	42.177	1.00
0.35	269.07	41.707	1.00	270.37	42.285	1.00
0.40	269.20	41.781	1.00	270.65	42.411	1.00
0.45	269.41	41.869	1.00	271.05	42.557	1.00
0.50	269.76	41.979	1.00	271.62	42.730	1.00
0.55	270.14	42.098	1.00	272.36	42.934	1.00
0.60	270.61	42.232	1.00	273.33	43.178	1.00
0.65	271.23	42.392	1.00	274.62	43.483	1.00
0.70	271.93	42.570	1.00	276.31	43.861	1.00
0.75	272.42	42.714	1.00	278.07	44.257	1.00
0.80	273.30	42.931	1.00	280.54	44.785	1.00
0.85	274.25	43.170	1.00	283.06	45.336	0.99
0.90	273.30	42.228	0.98	272.72	41.939	0.98
0.95	273.37	42.192	0.99	270.84	41.823	0.99

Chapter 4: Kinetic Parameters of Catalytic Cracking of High-density Polyethylene in The Presence of ZSM-5 Zeolites Using Isothermal TGA Tests

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4.1. Abstract

Using Thermogravimetric Analysis, catalytic cracking of high-density polyethylene was studied over three ZSM-5 catalysts with different Si/Al ratios of 25, 38 and 80. TGA measurements were employed to evaluate catalytic activity of the catalysts. ZSM-5 catalysts with Si/Al ratios of 25 and 38 revealed the highest catalytic activity. The effect of cat/HDPE ratio on the activity of the catalysts was studied. The inflection temperature decreased considerably when cat/HDPE was increased to 15%. The presence of the efficient amount of the catalysts shortened the reaction time dramatically, and allowed to conduct isothermal TGA tests at low temperatures of 330 to 370 °C. The kinetic parameters of catalytic cracking of HDPE were determined using the isothermal TGA datasets and a differential isoconversional kinetic study method. The obtained kinetic parameters at different conversion factors were compared with those of thermal cracking. The kinetic study results revealed considerable reductions in both apparent activation energy and frequency factor in the presence of the zeolites. All the results were evaluated against the experimental data and good agreement was observed. Using the Arrhenius equation, the rate coefficients of thermal and catalytic cracking were calculated. Comparing the rate coefficients of catalytic cracking against pure thermal cracking clearly elucidated the high activity of the zeolites.

Keywords:

Kinetic parameters, Catalytic cracking, TGA, Isothermal approach, HDPE, ZSM-5

4.2. Introduction

Nowadays, waste plastic management is a controversial and important issue. Most waste plastics are disposed in landfills and incineration plants that cause environmental problems such as air and soil pollution, underground water resources contamination and global warming [1].

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Nevertheless, waste plastics are highly calorific and have the potential to be converted into fuels or high value chemicals. Treatment of waste plastics by thermal cracking is a promising method to convert them into valuable hydrocarbons, and also preserve the virgin petroleum resources [1,2].

However, thermal cracking only works under high temperatures, and its main disadvantage is the wide range of products. Therefore, further processes are required to enhance the quality and commercial value of the products [2,3]. The employment of appropriate catalysts can control the product distribution, enhance the quality of the products, decrease the required operating temperature, accelerate the reaction rate, and reduce the activation energy of the involved reactions [1,4-18].

Activity of catalysts in cracking of polymers is mainly a result of their acidic properties, such as Si/Al ratio, strength and number of the acidic sites [1,5,11,17,19]; other specifications such as particle size, surface area, pore size distribution and access to the active sites also control the catalytic activity [1,17,19]. Owing to the high catalytic activity of zeolites, they are the most commonly used catalysts in this field [4,5-8,10-13,19-22]. The more acidic zeolites like HZSM-5 are more effective in the production of gasoline range hydrocarbons and encounter a very low coke decomposition.

This study is an experimental work conducted on catalytic cracking of HDPE in the presence of ZSM-5 catalysts. The main focus of this work is set on the kinetic parameters of the process. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) are the common methods to find kinetic parameters and characteristics of cracking of polymers [5,13,14,19,22-24]. Among all the kinetic models available in the literature, we employ a differential isoconversional method, which works with high certainty isothermal TGA curves. This method was previously used to describe kinetic parameters of thermal cracking of HDPE and

showed good agreement with experimental results [23]. In the current research, prior to any kinetic study, catalytic activity of the catalysts in relation to their strength to shorten the reaction time and reduce the required operating temperature would be assessed. In this regard, TGA is a reliable technique to compare activity of the catalysts. Using quick, time efficient non-isothermal TGA measurements, catalytic activity of the catalysts would be evaluated against each other. Furthermore, the efficient amount of those catalysts with the highest activity would be determined. Afterward, with the aid of precise, high certainty isothermal TGA measurements and the recommended kinetic study method in [23], kinetic parameters of catalytic cracking of HDPE would be calculated.

4.3. Materials and methods

4.3.1. Raw material

Pure HDPE with a specific gravity of 0.93-0.94 and average particle size of 2 mm has been used in this study. Using differential scanning calorimetry (DSC), melting point, heat of fusion and crystallinity were measured at 134.5 °C, 178 J/g and 64.23%, respectively. HDPE has a low degree of branching, giving it favourable properties to have a broad range of applications in different industries such as packaging, automobile, electronics and construction. In this respect, it constitutes one third of the produced waste polymers around the world [1].

The catalysts used in this study were three ZSM-5 catalysts with different Si/Al ratio of 25, 38 and 80. Before any use, the catalysts were calcined at 500 °C for 5 h under dry air to eliminate any undesirable components. The relevant properties of the catalysts are listed in Table 4.1.

Table 4.1. Typical properties of the catalysts employed in this study.

Catalyst	Sample name	Si/Al	Average grain size (µm)	BET area (m^2/g)
ZSM-5	ZSM-5 (25)	25	9.2	425
ZSM-5	ZSM-5 (38)	38	6.1	425
ZSM-5	ZSM-5 (80)	80	7.6	425

4.3.2. Thermogravimetric experiments

Thermal decomposition of HDPE in the absence and presence of the catalysts was carried out in Perkin-Elmer TGA7 Thermogravimetric Analyzer. TGA measurements were conducted into non-isothermal and isothermal modes under nitrogen flow rate of 30 mL/min in disposable aluminum pans. Before each measurement, TGA was purged for 2 h to avoid any oxidation. Any trace of oxygen in the chamber can have a significant effect on the results. If the TGA instrument was interrupted to stop, the nitrogen purging process was set 24 h before testing a new sample. This method guarantees that the reaction zone contains no oxygen. TGA was calibrated according to the manufacturer's specifications (operating manual) for weight and temperature.

In the non-isothermal TGA measurements, mixtures of HDPE and a catalyst were heated up from 40 °C to 520 °C at a moderate heating rate of 25 °C/min. In all the tests, 13 mg of the HDPE was used. Two types of non-isothermal cracking were performed:

1- When the cat/HDPE ratio was 20%, activity of the catalysts were compared by evaluating their degradation temperatures.

2- The cat/HDPE ratios of 5, 10, 15, 20 and 25% were employed to find the proper amounts of the catalysts. This step was conducted only for the catalysts with the highest activity. The efficient cat/HDPE ratio was determined when adding more catalyst did not induce any noteworthy drop in the degradation temperature.

In the isothermal TGA measurements, precisely 13 mg HDPE mixed with the optimum amount of a catalyst was subjected to different constant temperatures of 330, 340, 350, 360 and 370 °C to reach complete decomposition reactions. The pre-heating rate up to the target temperatures was 50 °C/min. With the aid of the isothermal datasets and the kinetic study method developed by Khedri et al. [23], the activation energy and frequency factor of the reactions were determined at different extent of the reactions.

It is worth mentioning that the data recorded by TGA shows an overall weight loss of the mixture of the polymer and catalysts. Assuming a constant weight of the catalyst during the reaction, the weight loss of the plastic can be calculated. All the reported decomposition curves in this study are already corrected by initial mass of catalysts and also baseline measurements for empty sample pans. All the measurements were performed 3 times to ensure reproducibility of the results.

4.4. Results and discussions

4.4.1. Catalytic activity

Figure 4.1 shows the non-isothermal TG (conversion or weight loss) and DTG (conversion rate) curves for decomposition of HDPE in the absence and presence of the catalysts. The catalyst to plastic ratio and the employed heating rate were 20 % and 25 °C/min, respectively. The starting (T_i) and completion (T_f) temperatures and inflection temperature (the temperature at the maximum degradation rate) (T_c) were retrieved from the TG and DTG curves and shown in Table 4.A.1.

In Figure 4.1, if compared with thermal cracking, it can be clearly seen that all the zeolites shifted the TG and DTG curves towards lower temperatures. ZSM-5 (25) and (38) showed similar degradation temperatures, which demonstrates their similar activities in cracking of HDPE. In

relation to the catalysts performance in decreasing the degradation temperature, ZSM-5 (25) and (38) showed higher activity than ZSM-5 (80). This fact might be due to the lower acidity of ZSM-5 (80). The acidity of the zeolites are due to the Lewis and Brønsted acid parts. Increasing the Si/Al ratio by dealumination of zeolites reduces the content of Al in the catalyst, and strengthens the acidity of Brønsted acidic sites; however, it also decreases the number of acidic sites, and therefore, lesser acidic spots would be available to conduct catalytic reactions. For these reasons, ZSM-5 (80) with Si/Al ratio of 80 showed the minimum activity among the employed ZSM-5 catalysts in this study. Similar results were obtained in [12,20,25] where increasing Si/Al ratio of ZSM-5 catalysts reduced acidity and activity of the catalysts and dropped the rate of catalytic reactions. Therefore, ZSM-5 (25) and (38) were chosen for further experiments in the following sections of this study.

The catalyst residue in the sample pan was light brown and it was a sign of coke deposition on the catalyst. Besides that, according to the TG curves, the final conversion of HDPE in all the tests was above 98%. After each TGA measurement, the amount of coke deposited on the catalyst was measured by reheating the catalyst residue under air flow in TGA. The temperature ramped to 500 °C at 25 °C/min and maintained constant for 5h. After burning all the deposited coke, the catalyst was white. In all the cases, the coke deposition was measured to be lesser than 1.5 wt% of the initial weight of HDPE.
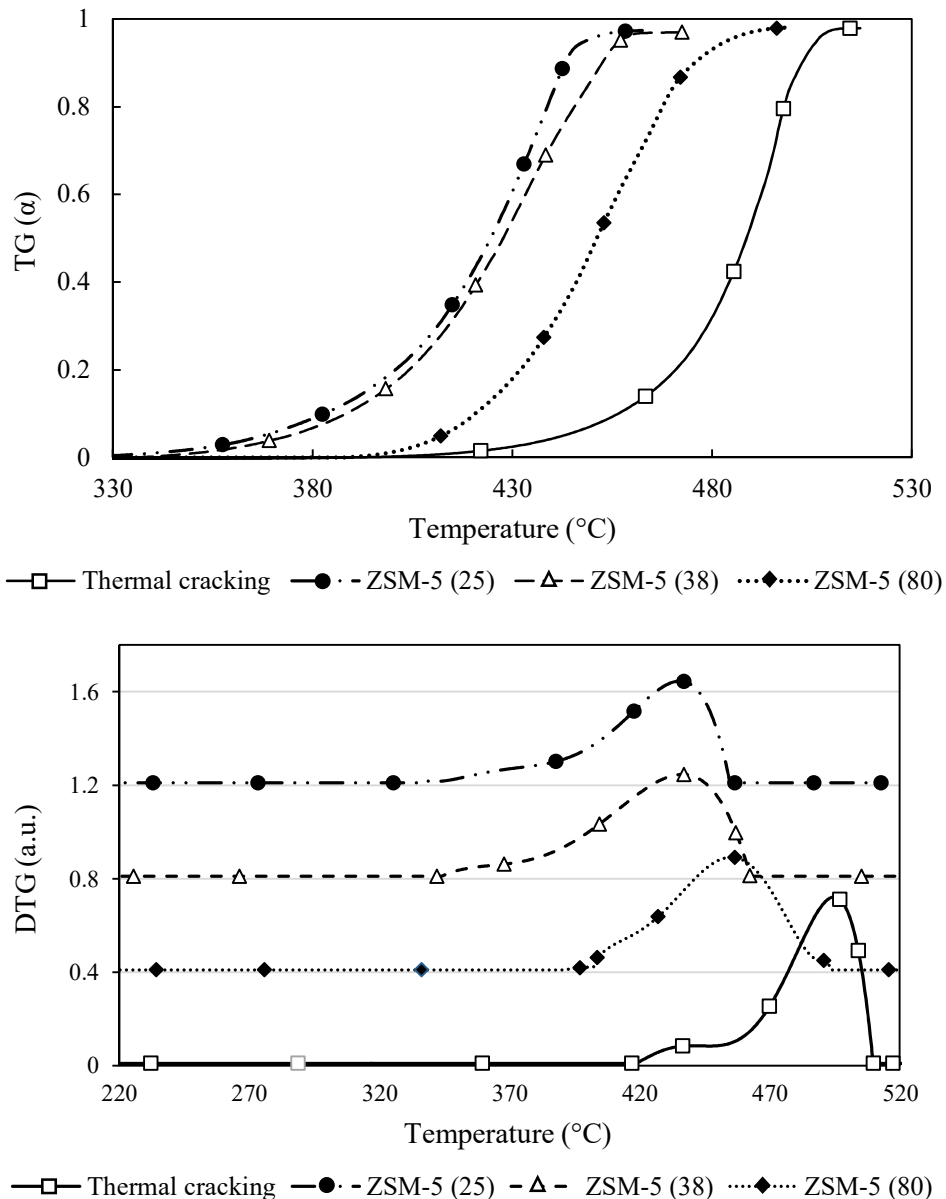
Figure 4.1. TG-DTG curves of the HDPE in the absence and presence of the zeolites (cat/HDPE= 20%, heating rate=25 °C/min and N$_2$ flow rate=30 mL.min^{-1}).

4.4.2. Cat/HDPE ratio

In order to find the required amount of catalysts, non-isothermal TGA measurements were performed from 50 °C to 520 °C at 25 °C/min. In TGA, 13 mg of HDPE was introduced to ZSM-5 (25) and ZSM-5 (38) with different cat/HDPE ratios of 5% to 25%. Figure 4.2 shows the inflection temperatures retrieved from the conducted non-isothermal TGAs. From Figure 4.2, for

the both catalysts, it can be observed that increasing the cat/HDPE ratios to 15% decreased the inflection temperatures considerably. It is because at constant weight of HDPE, adding more catalysts provided more active acidic sites per unit of weight of HDPE to conduct catalytic reactions, and lowered the inflection temperatures. However, no notable reduction was observed beyond the cat/ HDPE of 15%. This can be attributed to the high catalytic activity of the zeolites and enough acidic spots to conduct catalytic reactions. Likewise Mastral et al. [10] Schrimer et al. [12] and Rasul Jan et al. [15] observed no further improvement in the results by increasing the cat/polymer ratio beyond a specific amount. Therefore, in relation to the activity of the catalysts, the efficient cat/HDPE ratio was considered to be 15%.
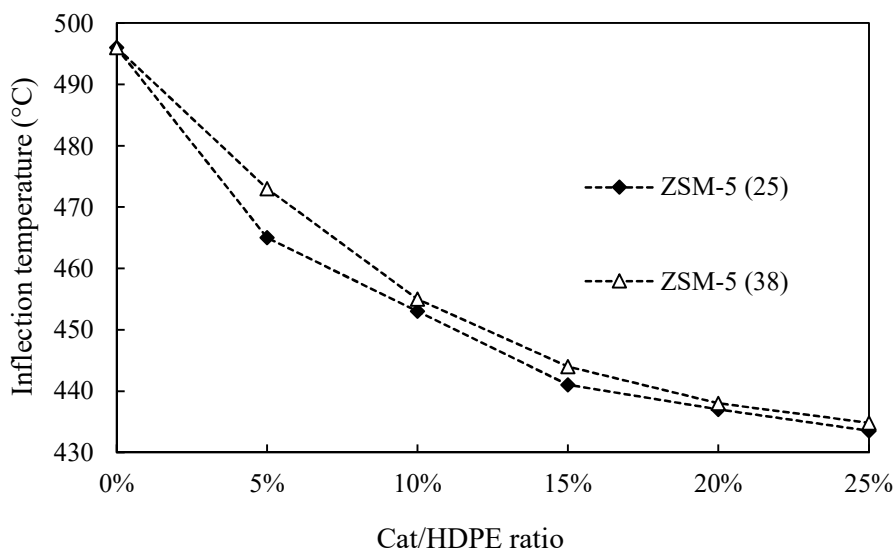
Figure 4.2. Inflection temperatures describing the effect of catalyst fraction (heating rate= 25 °C/min and N_2 flow rate=30 mL.min^{-1}).

4.4.3. Isothermal TGA measurements

Isothermal TGA tests in the presence of ZSM-5 (25) and (38) with cat/HDPE ratio of 15% were conducted at low temperatures of 330, 340, 350, 360 and 370 °C. The TG and DTG curves at the aforementioned temperatures are plotted in Figure 4.3. If compared with the results of thermal

cracking in [23], it is evident that employing the catalysts induced a considerable reduction in the reaction time. At 370 °C, while in the absence of catalysts, after 1 hour, the weight loss of HDPE was lesser than 4 % (not shown in here), in the presence of the zeolites, completion reaction time dropped to lesser than 10 min. Based on all these comparisons and observations, ZSM-5 (25) and (38) were quite successful to conduct fast cracking reactions at low temperatures.
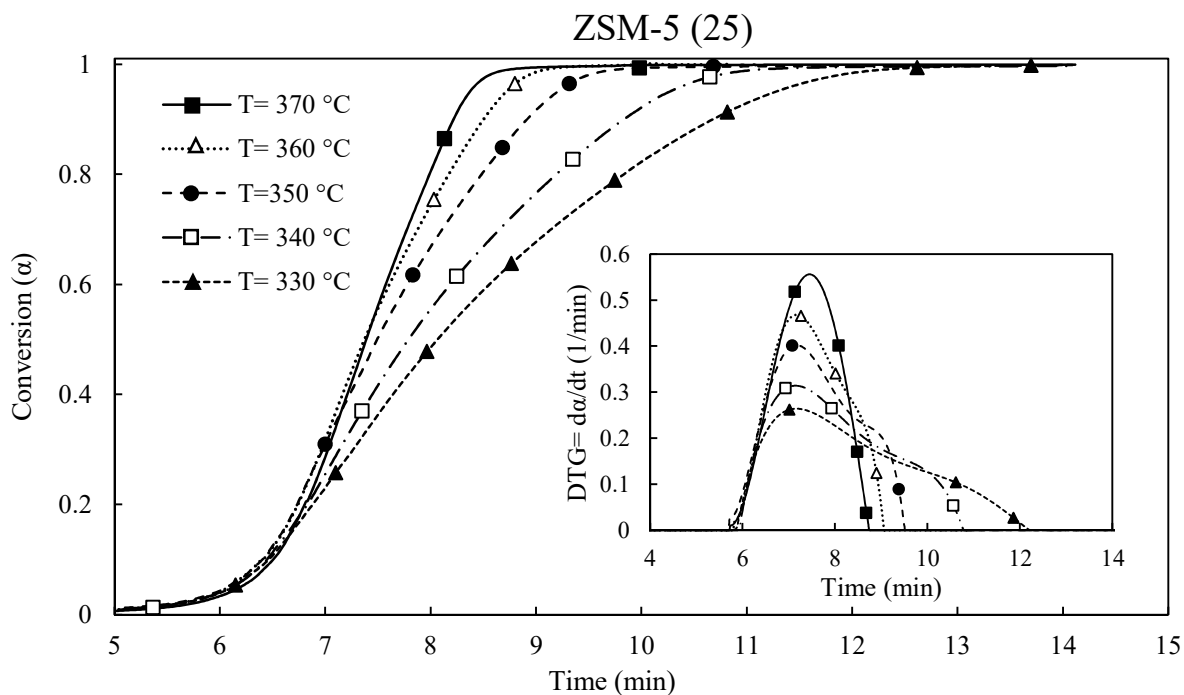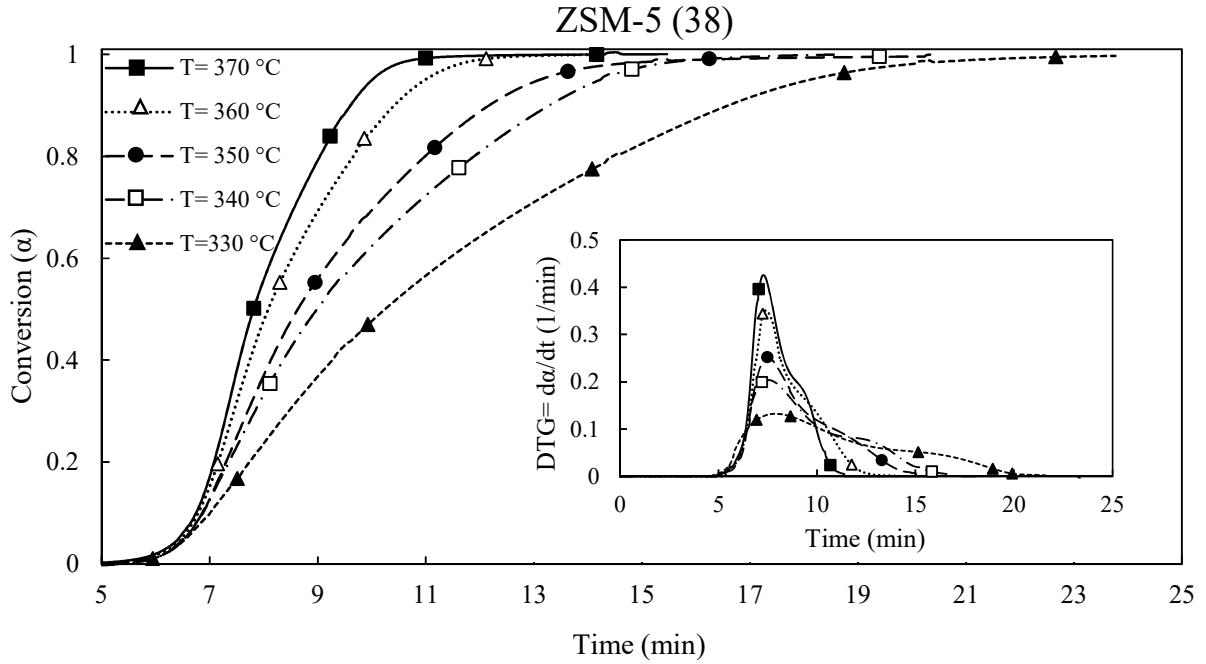
Figure 4.3. Isothermal TG-DTG curves at constant temperatures in the presence of ZSM-5 (25) and (38) (cat/HDPE=15% and N_2 flow rate=30 mL.min^{-1}).

4.4.4. Kinetic study using isothermal TGAs

The kinetic parameters of catalytic cracking of the HDPE over ZSM-5 (25) and (38) were calculated using the kinetic study method developed by Khedri et al [23]. This method works under isothermal conditions and for a first order reaction is expressed by equation (1). This equation is the logarithmic form of the equation of rate of reaction combined with the Arrhenius equation

$$ln\left(\frac{1}{1-\alpha}\cdot\frac{d\alpha}{dt}\right) = ln(A_0) - \frac{E_a}{RT} \tag{1}$$

Where α is the conversion factor and can be calculated by $(m_0 - m)/m_0$, m_0 is the initial weight of sample (mg), m is the weight of the sample at any time (mg), t is the time (min), A_0 is the frequency factor, E_a is the apparent activation energy (kJ/mol), T is the temperature (K), and R is the universal gas constant (kJ/mol.K).

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According to equation (1), the plot of $ln\left(\frac{1}{1-\alpha} \cdot \frac{d\alpha}{dt}\right)$ against $1/T$ leads to a straight line with a negative slope. The activation energy and frequency factor are obtained from the slope $(-E_a/R)$ and the intercept $(ln(A_0))$ of the line, respectively. The same calculation should be computed at different conversion factors to obtain the kinetic parameters at different extent of reaction. Figures 4.A.1 and 4.A.2 demonstrate the linear regression employed in this method.

Figure 4.4 and Table 4.A.2 show the calculated activation energy and frequency factor at different conversion factors in the presence of ZSM-5 (25) and (38). For comparison purposes, Figure 4.4 contains the results of pure thermal cracking of HDPE determined elsewhere [23]. Both ZSM-5 (25) and (38) demonstrated high activity to decrease the kinetic parameters of cracking of HDPE.

The profiles of kinetic parameters over the whole decomposition range show that the cracking reactions are governed by multiple steps. As the reactions exceed, an overall increase in the obtained kinetic parameters can be observed. However, according to Figure 4.4, in catalytic cracking, the dependency of E_a and $ln(A_0)$ on the conversion factor is lesser considerable than thermal cracking. In the presence of ZSM-5 (25) and (38), after 70% and 30% conversions, respectively, the kinetic parameters remained fairly constant and weakly dependent on the extent of the reactions. On the other hand, in case of pure thermal cracking, up to 75% conversion factor, E_a and $ln(A_0)$ continuously increase.

From Figure 4.4, a similar trend can be observed between the E_a and $ln(A_0)$ profiles of each catalyst, and as shown in Figure 4.A.3, the graph of $ln(A_0)$ against E_a is straight line.
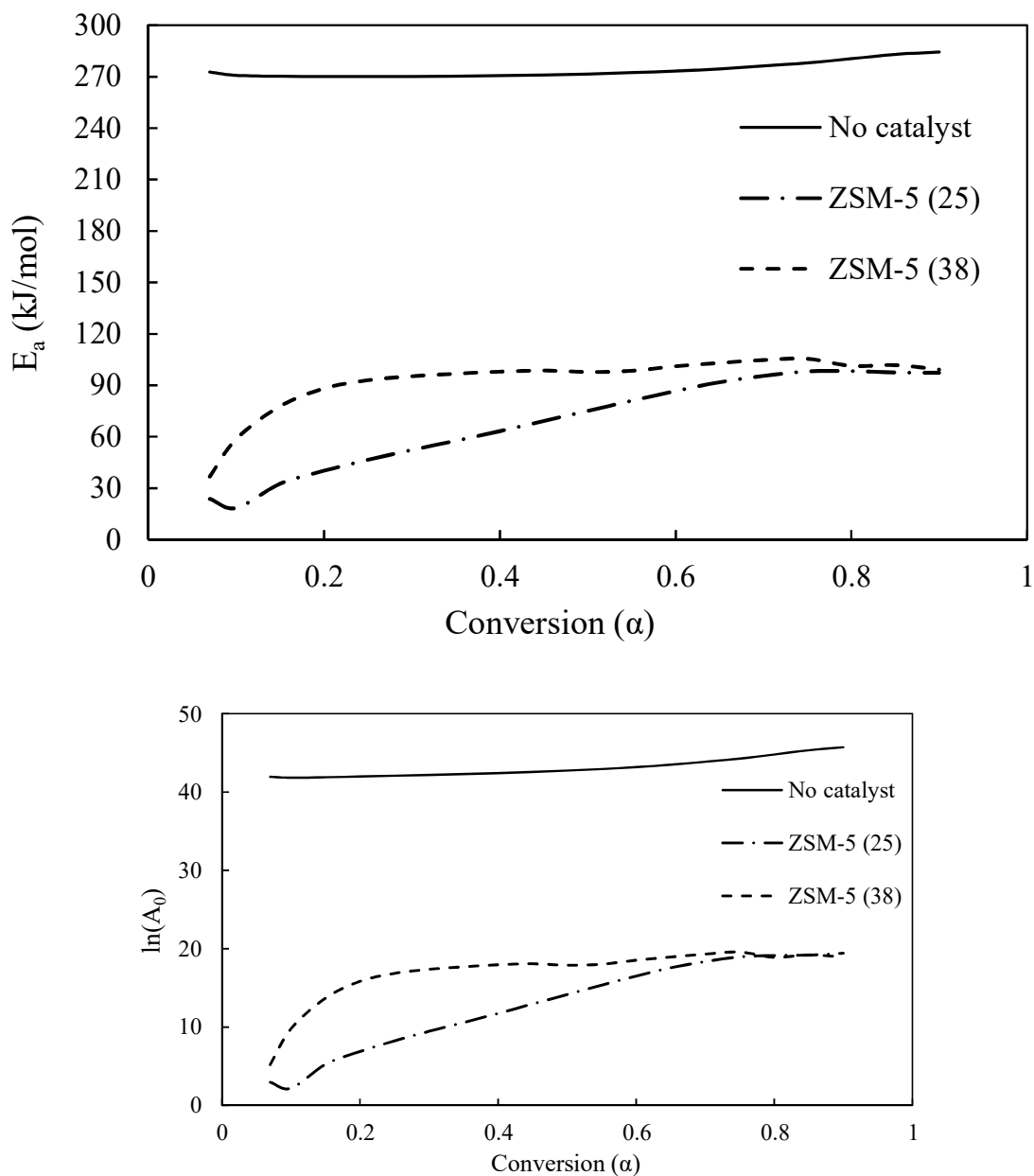
Figure 4.4. E_a and $ln(A_0)$ calculated from equation (1) and isothermal TG datasets presented in Figure 4.3.

The reliability of the calculated kinetic parameters were evaluated against the experimental results. The obtained activation energy and frequency factor values were employed in the equation (1) to predict the DTG ($d\alpha/dt$) curves at different temperatures of 330, 340, 350, 360 and 370 °C as shown in Figures 4.5 and 4.6. The comparison of the theoretical and experimental results (the

original DTG curves recorded by TGA) leads to an acceptable agreement. These results prove the employed kinetic study method is precisely applicable for catalytic cracking of HDPE.

T= 330 °C

T= 340 °C

T= 350 °C

T= 360 °C
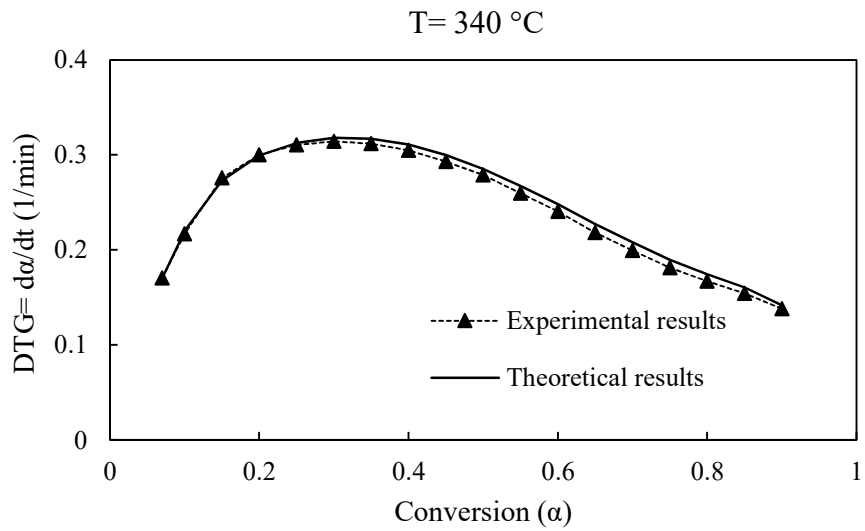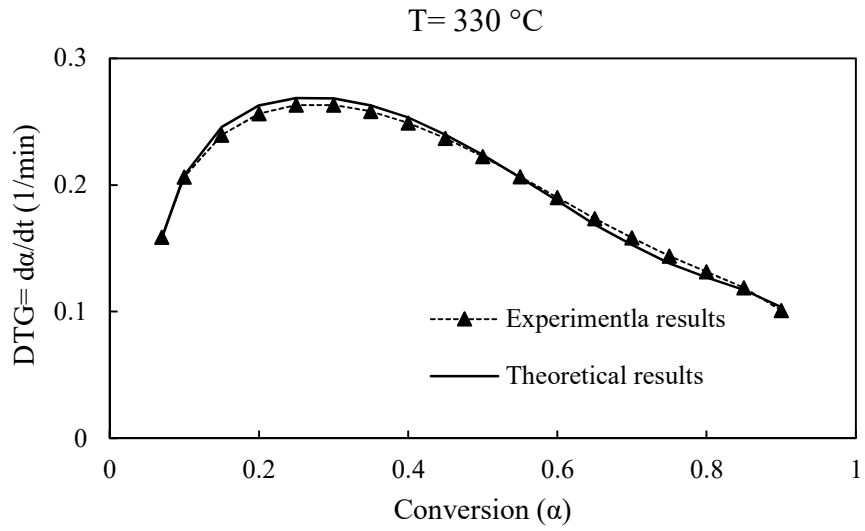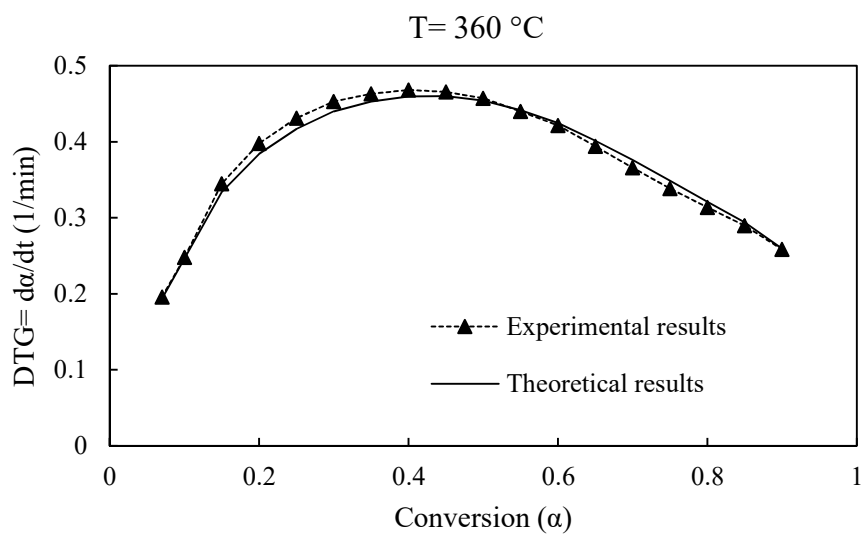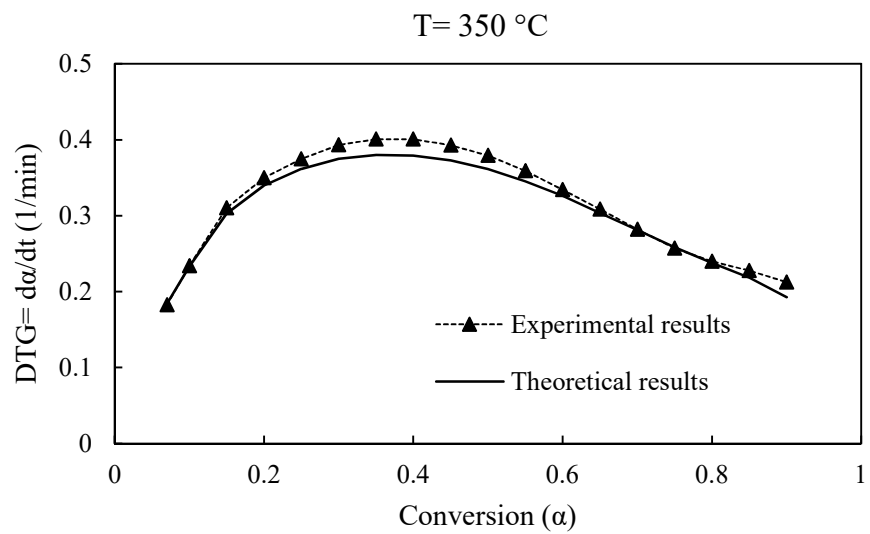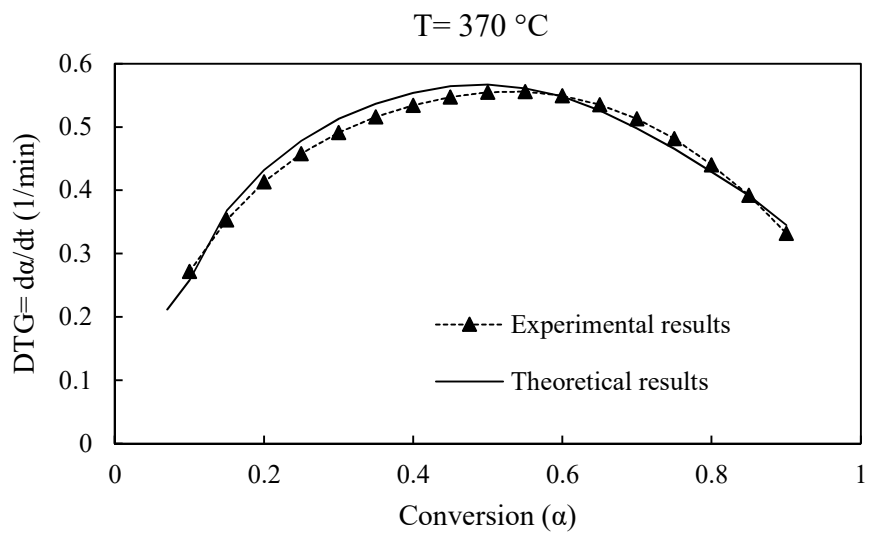
Figure 4.5. Theoretical and experimental isothermal DTG ($d\alpha/dt$) curves in the presence of ZSM-5(25) (cat/HDPE=15% and N_2 flow rate=30 mL.min^{-1}).
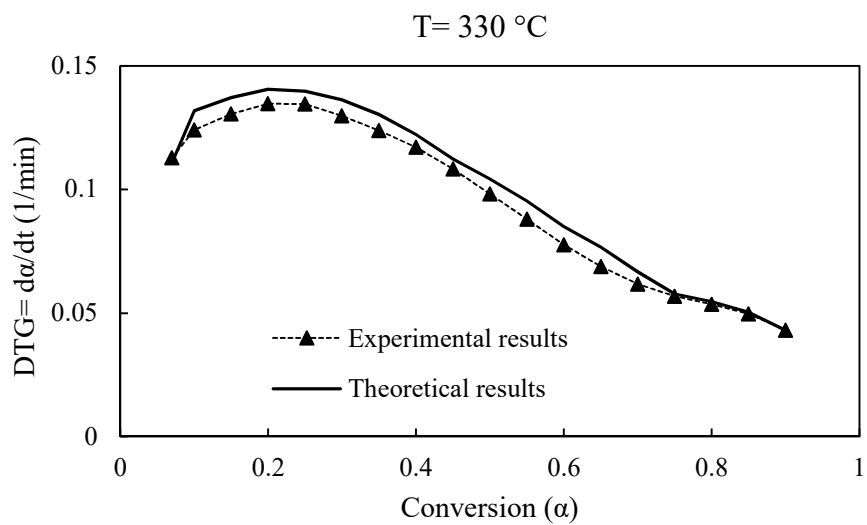
T= 340 °C
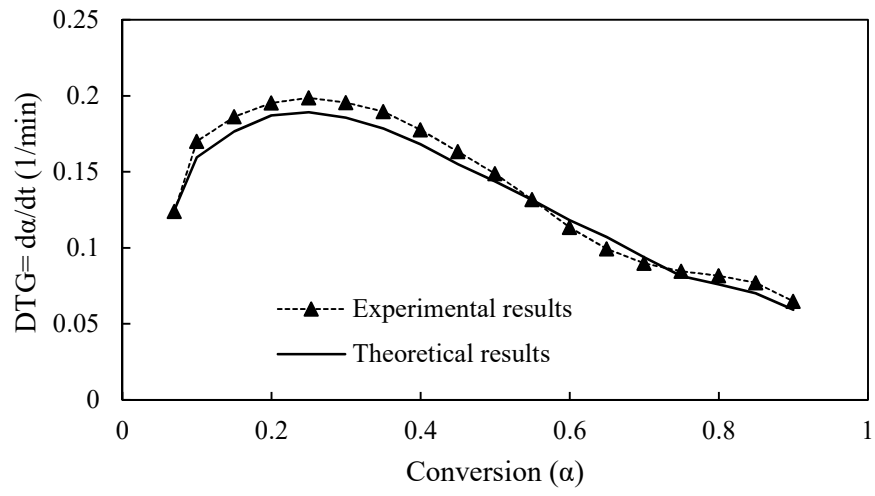
T= 350 °C
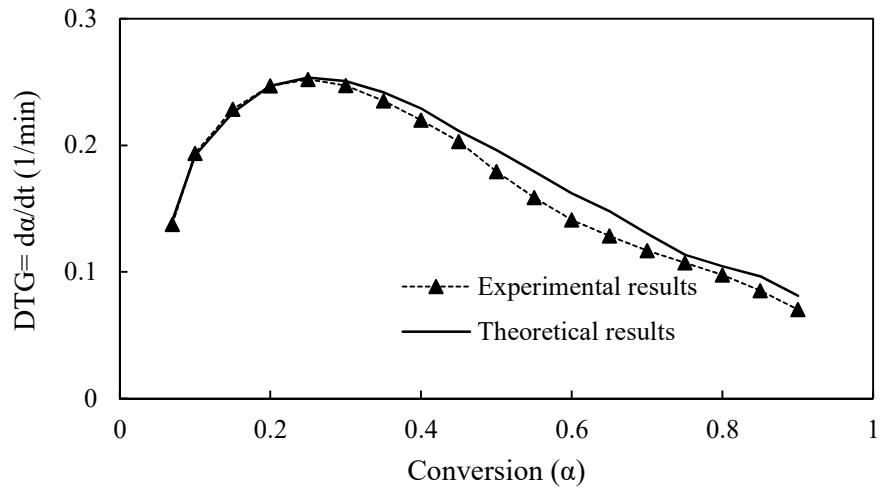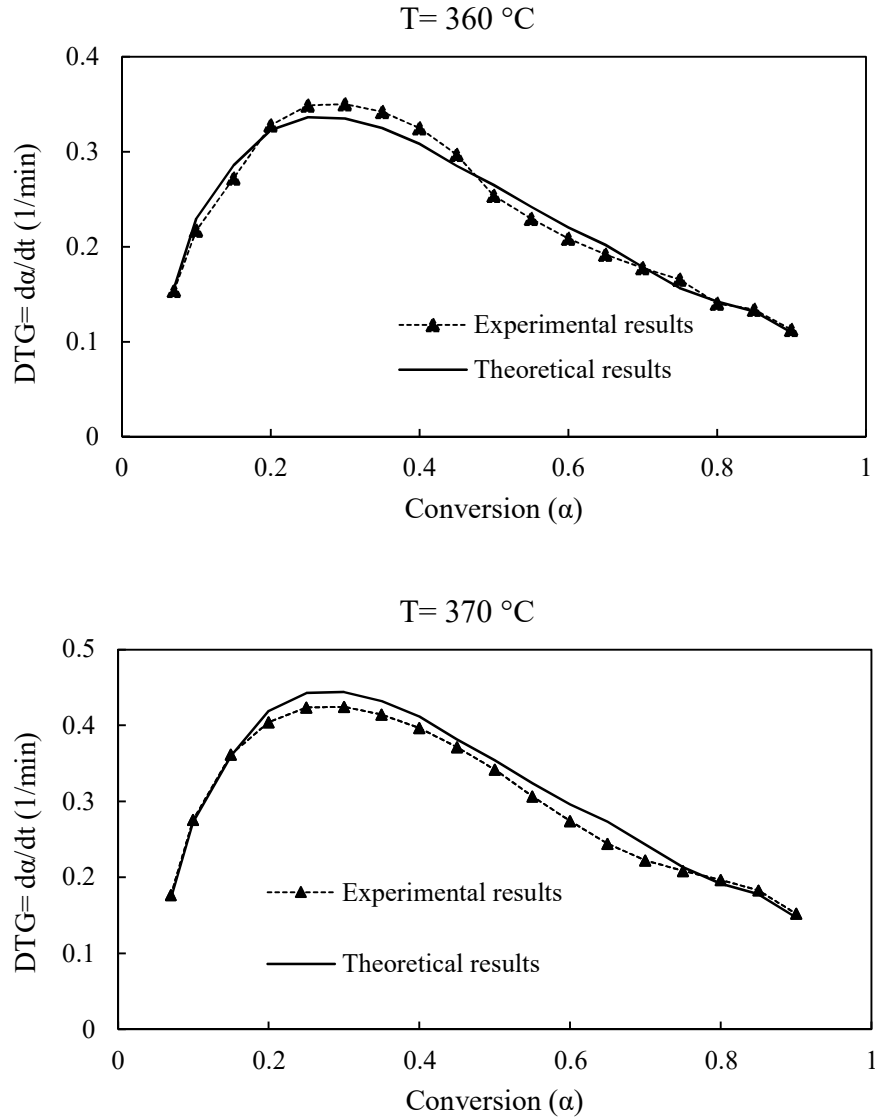
Figure 4.6. Theoretical and experimental isothermal DTG ($d\alpha/dt$) curves in the presence of ZSM-5(38) (cat/HDPE=15% and N_2 flow rate=30 mL.min^{-1}).

The determined activation energy and frequency factors were employed to find the rate coefficient using the Arrhenius equation expressed by equation (2).

$$k = A_0 e^{-\frac{E_a}{RT}}$$

(2)

where k is the rate coefficient and for a first order reaction its unit is *min^{-1}*. When E_a and A_0 are constant, k is only temperature dependent; however, in the pyrolysis of polymers, as kinetic

parameters are functions of conversion factor, therefore the rate coefficient varies at different extent of the reactions. The obtained rate coefficients for thermal and catalytic cracking of HDPE in the presence of ZSM-5 (25) and (38) were named k_{th}, k_{25} and k_{38}, respectively. Figure 4.7 shows the rate coefficients at different conversions and temperatures. It can be observed that the rate coefficients were increased significantly by using a catalyst or increasing the temperature. The highest values were found with ZSM-5 (25) at 370 °C.
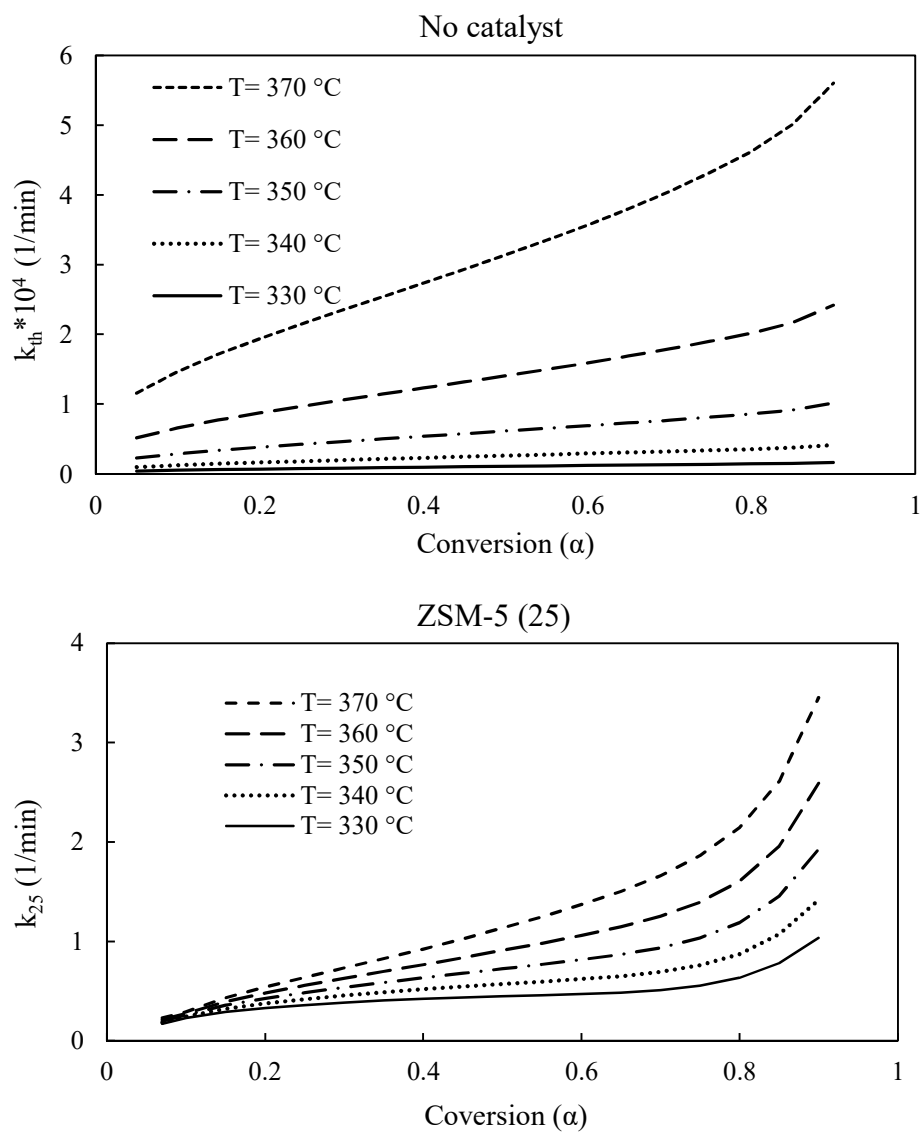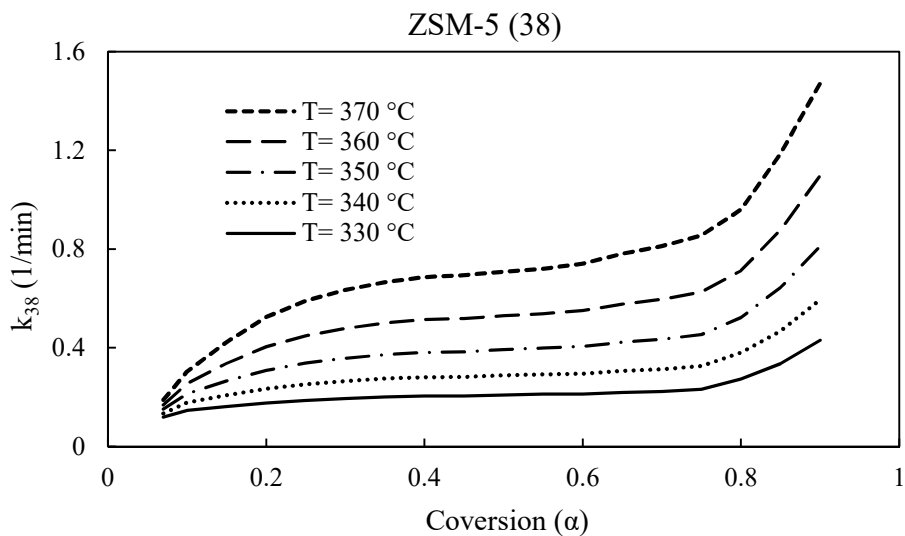
Figure 4.7. Reaction rate coefficient determined by the Arrhenius equation (cat/HDPE=15%).

Since all the kinetic parameters were determined for the first order reactions, comparing the rate constants might illuminate a better evaluation of activity of the catalysts in the cracking of HDPE. Figure 4.8 demonstrates the ratios of rate coefficients of catalytic and thermal cracking. At any constant conversion, the difference between thermal and catalytic cracking is more considerable at lower temperatures. From Figure 4.8 it can be seen that in case of ZSM-5 (25), catalytic activity at 330 °C is 20 times more than that of at 370 °C. It might be attributed to this fact that higher temperatures are more favorable for coke formation on the active surface area of the catalysts. Similar results were observed in [13], where coke formation at higher temperatures decreased activity of the catalysts, and consequently reduced the difference between thermal and catalytic cracking.
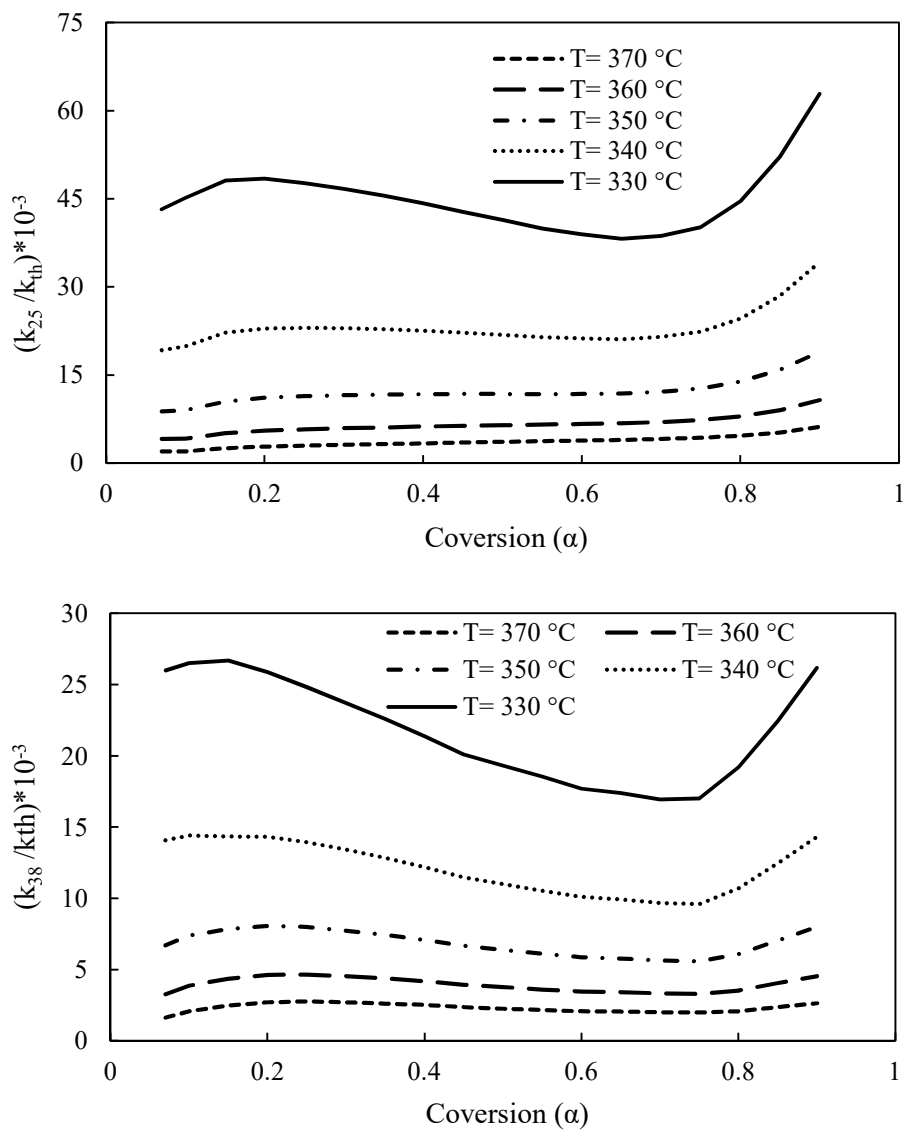
Figure 4.8. Ratios of rate coefficients of catalytic and thermal cracking (cat/HDPE=15%).

4.5. Conclusion

In this work, catalytic cracking of HDPE was investigated in the presence of ZSM-5 zeolites. The TGA instrument recorded decomposition curves at different conditions. Non-isothermal measurements were employed to compare activity of the catalysts. One of the main purposes of using catalysts in cracking of polymers is to reduce the required operating temperature and

consequently the operational costs. In relation to the degradation temperature range, ZSM-5 with Si/Al ratios of 25 and 38 demonstrated higher activity than ZSM-5 with Si/Al ratio of 80. Acidity of a zeolite has significant effect on the catalytic activity, and it is a function of strength and number of acidic sites in the zeolite. Therefore, the week performance of ZSM-5#3 might be due to the dealumination of the catalyst.

By increasing cat/HDPE ratio of ZSM-5 (25) and (38), reaction rate increased dramatically, but no further enhancement was observed beyond 15%. As a result, the efficient cat/HDPE ratio was estimated to be 15% for the both catalysts.

In the presence of the efficient amount of the catalysts, isothermal TGA tests were performed at different temperatures and analyzed using a differential isoconversional kinetic study method. Assuming a first order reaction, apparent activation energy and frequency factor of catalytic cracking were determined at different conversion factors. In the presence of the ZSM-5 catalysts, a significant drop was observed in the kinetic parameters of cracking of HDPE.

With the aid of the Arrhenius equation and the calculated activation energy and frequency factor, rate coefficients were determined for thermal and catalytic cracking. In the presence of the catalysts, the rate coefficients increased dramatically; the increase was more significant at lower temperatures than that of higher temperatures, and it was explained by the greater possibility of coke formation and catalyst deactivation at higher temperatures.

References

[1] Kumar, S; Panda, A.K; Singh, R.K. (2011) A review on tertiary recycling of high-density polyethylene to fuel, Resour Conserv Recy, 55, 893-910.

[2] Garforth, A.A; Lin, Y.-H; Sharratt, P.N; Dwyer, J. (1998) Production of hydrocarbons by catalytic degradation of high density polyethylene in a laboratory fluidised-bed reactor, J. Appl Catalysis A, 169, 331-342.

[3] Gobin, K; Manos, G. (2004) Polymer degradation to fuels over microporous catalysts as a novel tertiary plastic recycling method. Polym Degrad Stab, 83(2), 267-279.

[4] Manos, G; Garforth, A; Dwyer, J. Catalytic degradation of high-density polyethylene on an ultrastable-y zeolite. nature of Initial polymer reactions, pattern of formation of gas and liquid products, and temperature effects. Ind Eng Chem Res 2000, 39, 1198.

[5] Gobin, K; Manos, G. (2004) Thermogravimetric study of polymer catalytic degradation over microporous materials. Polym Degrad Stab, 86, 225-231.

[6] Seo, Y.-H; Lee, K.-H; Shin, D.-H. (2003) Investigation of catalytic degradation of high density polyethylene by hydrocarbon group type analysis. J Anal Appl Pyrolysis, 70(2), 383-398.

[7] Muhammad, C; Onwudili, J.A; Williams, P.T. (2015) Thermal Degradation of Real-World Waste Plastics and Simulated Mixed Plastics in a Two-Stage Pyrolysis−Catalysis Reactor for Fuel Production. Energy Fuels, 29, 2601-2609.

[8] Miskolczi, N; Bartha, L; Deák, G; Jóver, B; Kalló, D. (2004) Thermal and thermo-catalytic degradation of high-density polyethylene waste. J. Anal Appl Pyrolysis, 72(2), 235-242.

[9] Jan, M.R; Shah, J; Gulab, H. (2013) Catalytic conversion of waste high-density polyethylene into useful hydrocarbon. Fuel, 105, 595-602.

[10] Mastral, J.F; Berrueco, C; Gea, M; Ceamanos, J. (2006) Catalytic degradation of high density polyethylene over nanocrystalline HZSM-5 zeolite. Polym Degrad Stab, 91, 3330-3338.

[11] Neves, I.C; Botelho, G; Machado, A.V; Rebelo, P. (2007) Catalytic degradation of polyethylene: An evaluation of the effect of dealuminated Y zeolites using thermal analysis. Mater Chem Phys, 104(1), 5-9.

[12] Schirmer, J; Kim, J.S; Klemm, E. (2001) Catalytic degradation of polyethylene using thermal gravimetric analysis and a cycled-spheres-reactor. J. Anal Appl Pyrolysis, 60(2), 205-217.

[13] Miskolczi, N; Bartha, L; Deak, G. (2006) Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks. Polym Degrad Stab, 91(3), 517-526.

[14] Lee, S.Y; Yoon, J.H; Kim, J.R; Park, D.W. (2001) Catalytic degradation of polystyrene over natural clinoptilolite zeolite. Polym Degrad Stab, 74(2), 297-305.

[15] Jan, M.R; Shah, J; Gulab, H. (2010) Degradation of waste High-density polyethylene into fuel oil using basic catalyst. Fuel, 89(2), 474-480.

[16] Huang, W.-C; Huang, M.-S.; Huang, C.-F; Chen, C.-C; Ou, K.-L.(2010) Thermochemical conversion of polymer wastes into hydrocarbon fuels over various fluidizing cracking catalysts. Fuel, 89(9), 2305-2316.

[17] Aguado, J; Serrano, D.P; San Miguel, G; Escola, J.M; Rodríguez, J.M. (2007) Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins, Journal of Analytical and Applied Pyrolysis. J Anal Appl Pyrolysis, 78(1), 153-161.

[18] Serrano, D.P; Aguado, J; Escola, J.M; Garagorri, E; Rodriguez, J.M; Morselli, L; Palazzi, G; Orsi, R. (2004) Feedstock recycling of agriculture plastic film wastes by catalytic cracking. Appl. Catal. B: Environ, 49, 257–265.

[19] Durmuş, A; Koç, S.N; Pozan, G.S; Kaşgöz, A. (2005) Thermal-catalytic degradation kinetics of polypropylene over BEA, ZSM-5 and MOR zeolites. Appl Catal B: Environ, 61(3–4), 316-322.

[20] Ali, S; Garforth, A.A; Harris, D.H; Rawlence, D.J; Uemichi, Y. (2002) Polymer waste recycling over "used" catalysts. Catal Today, 75, 247-255.

[21] Elordi, G; Olazar, M; Lopez, G; Amutio, M; Artetxe, M; Aguado, R; Bilbao, J. (2009) Catalytic pyrolysis of HDPE in continuous mode over zeolite catalysts in a conical spouted bed reactor. J. Anal. Appl. Pyrolysis, 85, 345–351.

[22] Carmo, N; Afonso, D; Santos, E; Fonseca, I; Lemos, F; Lemos, M. A. N. D. A. (2016) Coprocessing of Waste Plastic and Hydrocarbons over MFI (HZSM-5). Int. J Chem Kinet, 48, 329-336.

[23] Khedri, S; Elyasi, S. (2016) Corrigendum to "Kinetic analysis for thermal cracking of HDPE: A new isoconversional approach". Polym Degrad Stab, 133, 330-342.

[24] Coelho, A; Costa, L; Marques, M.M; Fonseca, I.M; Lemos, M.A.N.D.A; Lemos, F. (2012) The effect of ZSM-5 zeolite acidity on the catalytic degradation of high-density polyethylene using simultaneous DSC/TG analysis. J. Appl Catalysis A, 413-414, 183-191.

[25] Garforth, A; Fiddy, S; Lin, Y.-H; Ghanbari-Siakhali, A; Sharratt, R.N; Dwye, J. (1997) Catalytic degradation of high density polyethylene: An evaluation of mesoporous and microporous catalysts using thermal analysis. Thermochimica Acta, 294, 65-69.

Appendix 4.A

Table 4.A.1. Characteristic temperatures of decomposition of the HDPE over different catalysts (cat/HDPE=20%).

	No catalyst	ZSM-5 (25)	ZSM-5 (38)	ZSM-5 (80)
T_i(K)	421	340	343	393
T_c(K)	496	435	436	457
T_f(K)	511	456	462	495

Table 4.A.2. Calculated E_a and $\ln(A_0)$ from the isothermal data sets for ZSM-5 (25) and (38).

	ZSM-5 (25)			ZSM-5 (38)		
Conversion (α)	E_a (kJ/mol)	$\ln(A_0)$	R^2	E_a (kJ/mol)	$\ln(A_0)$	R^2
0.07	23.72	2.957	0.99	36.66	5.1841	0.98
0.10	18.38	2.197	0.98	58.58	9.7611	0.95
0.15	32.51	5.242	0.96	77.73	13.677	0.97
0.20	40.07	6.878	0.97	88.08	15.825	0.98
0.25	46.46	8.238	0.98	92.93	16.851	0.99
0.30	52.21	9.454	0.98	95.24	17.355	0.99
0.35	57.54	10.570	0.98	96.71	17.678	0.99
0.40	63.15	11.731	0.99	97.94	17.94	0.99
0.45	69.09	12.947	0.99	98.56	18.067	0.99
0.50	74.99	14.150	0.99	97.74	17.89	0.99
0.55	80.89	15.348	1.00	98.40	18.01	0.99
0.60	86.56	16.503	1.00	101.06	18.523	0.99
0.65	91.71	17.559	1.00	103.02	18.926	1.00
0.70	95.38	18.344	0.99	104.70	19.309	0.99
0.75	98.01	18.950	0.99	105.45	19.563	0.99
0.80	98.18	19.124	1.00	101.27	18.898	0.99
0.85	97.37	19.170	1.00	101.74	19.197	0.98
0.90	97.18	19.414	0.99	99.12	18.923	0.97
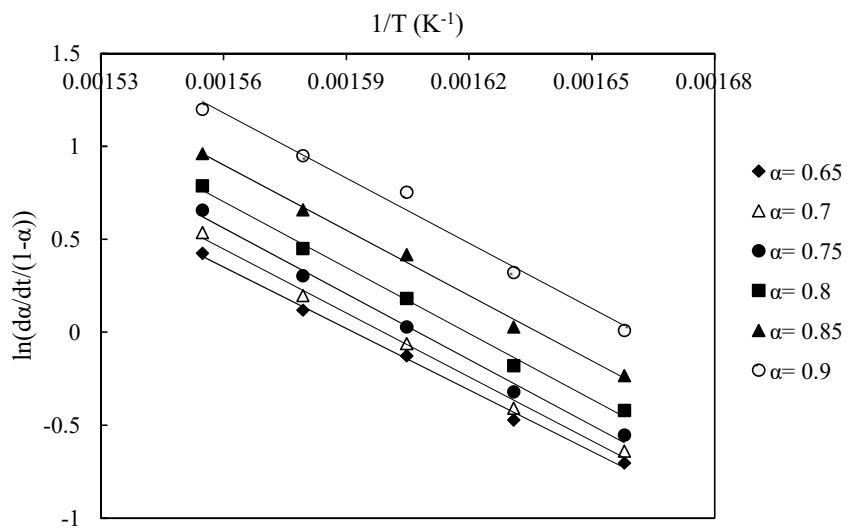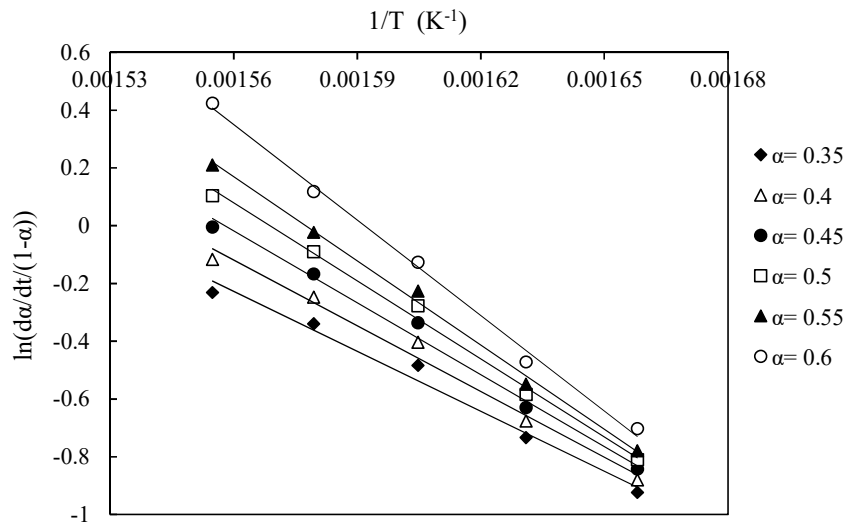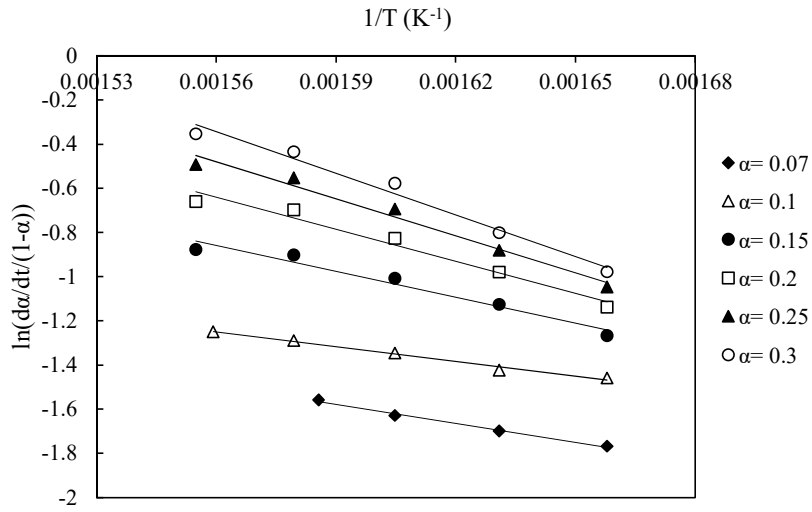
Figure 4.A.1. Linear regression for the employed isoconversional-isothermal method in the presence of the ZSM-5 (25).
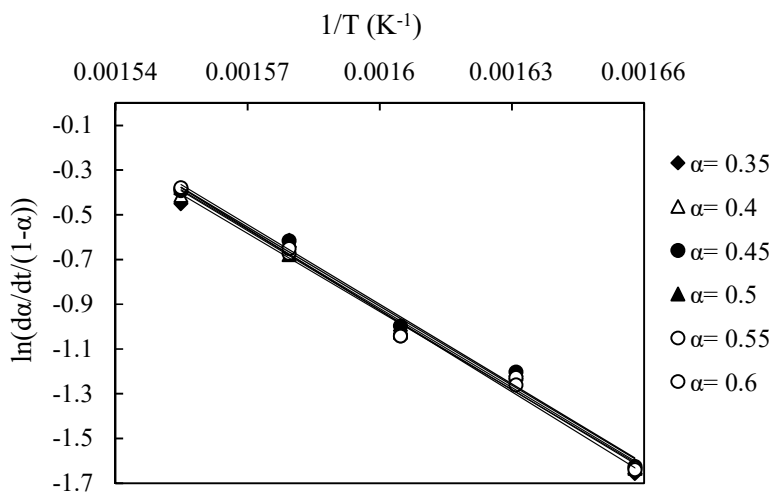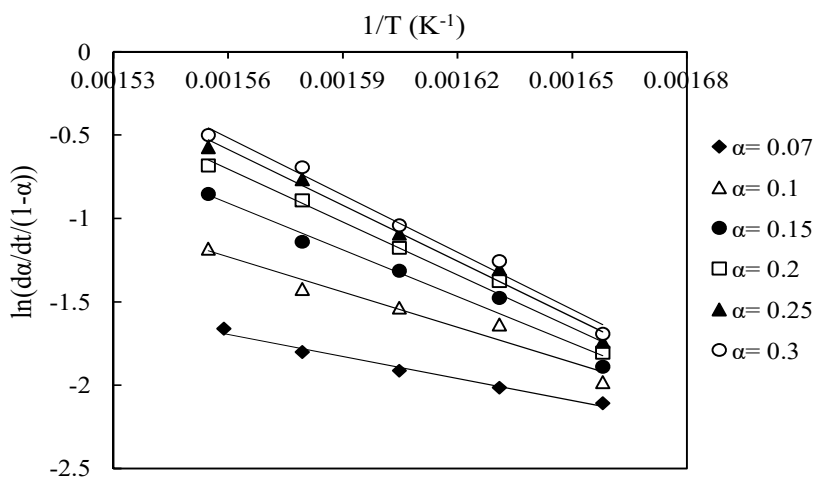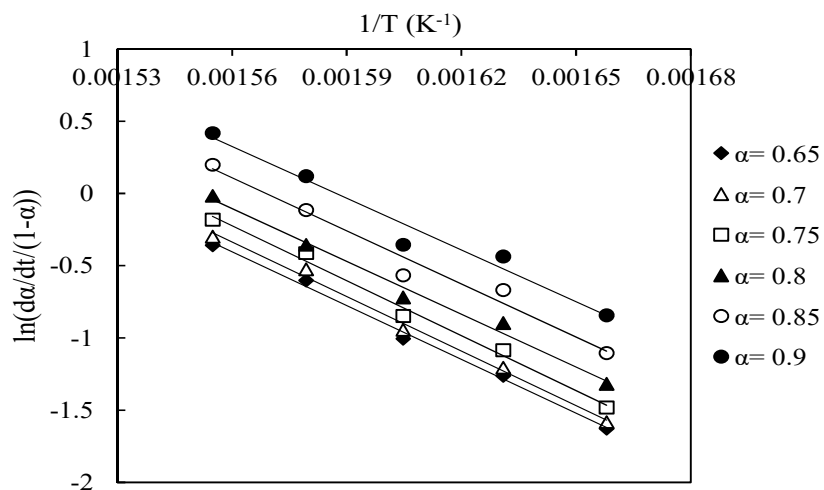
Figure 4.A.2. Linear regression for the employed isoconversional-isothermal method in the presence of the ZSM-5 (38).
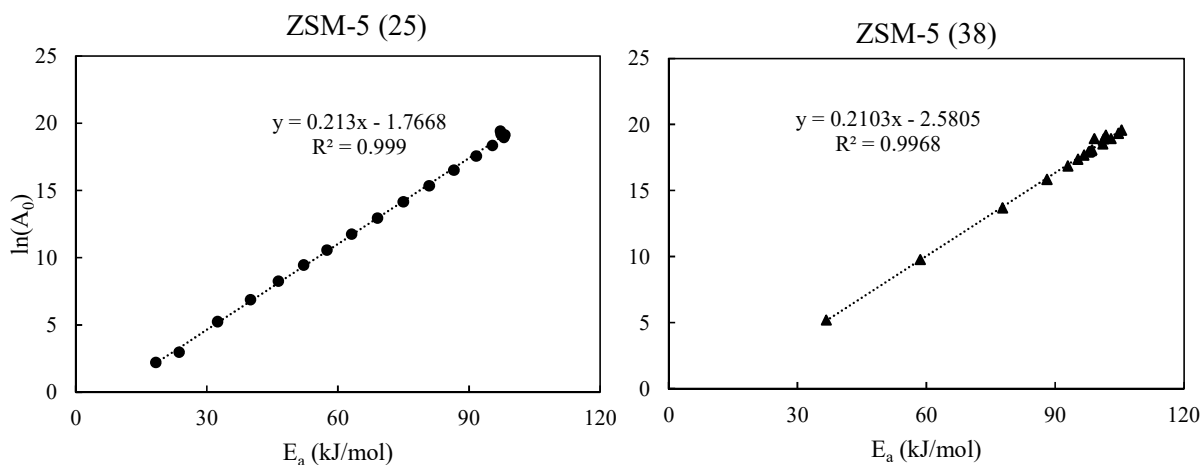
Figure 4.A.3. Estimated $\ln(A_0)$ versus E_a from the isoconversional- isothermal method.

Chapter 5: A Study on The Deactivation, Regeneration and Reuse of ZSM-5 in Pyrolysis of High-density Polyethylene

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5.1. Abstract

Using a Thermogravimetric Analyzer, catalytic cracking of high-density polyethylene was conducted in the presence of a ZSM-5 zeolite at 370 °C and a catalyst to polymer ratio of 15 %. The objective of this work was to evaluate deactivation, regenerability and reuse of ZSM-5 in consecutive cracking tests. When catalyst activity decreased by 80 %, catalyst was regenerated in a Differential Scanning Calorimetry at 480 °C for 5 h. After catalyst regeneration, ZSM-5 was reused in the same cracking tests. The TGA results were compared with those that were determined with fresh catalyst and in pure thermal cracking. Catalyst deactivation was caused by coke deposition and loss of acidity of the ZSM-5. After catalyst regeneration, due to catalyst dealumination, the initial activity of the catalyst was never recovered. The effect of calcination temperature (500, 600 and 700 °C) on the activity of ZSM-5 in cracking of high-density polyethylene was explored. Emission Scanning Electron Microscope and Fourier Transform Infrared Spectrophotometer were employed to explain the changes in catalytic activity after catalyst calcination. Calcination at 500 °C did not change activity of the catalyst, but at 600 and 700 °C acidity and activity of the ZSM-5 samples dropped.

Keywords:

Pyrolysis; HDPE; ZSM-5; TGA; Deactivation; Regeneration

5.2. Introduction

Although landfilling and incineration are the most conventional approaches in waste plastic management, they cause environmental problems by realising chemicals into soil, water resources and air [1,2]. One of the alternative methods in waste plastic management is thermal pyrolysis, which converts waste polymers into hydrocarbons, and when optimized, it can be an efficient,

environmentally-friendly approach [3,4]. However, this method has some disadvantages. For example, it requires high operating temperatures and leads to a wide range of products; therefore, further processes are required to separate the products and enhance their quality. On the other hand, employment of catalysts has attracted the attention of many researchers in order to solve the aforementioned drawbacks of thermal cracking [5-7].

Zeolites have exhibited to be striking catalysts in converting waste polymers into light and valuable hydrocarbons. The popularity of this catalyst family has been ascribed to their strong acidity, significant activity, high selectivity and favorable structures to produce light hydrocarbons with higher commercial value in the range of C_5 to C_{12} [8-10]. Of the several zeolites employed, ZSM-5 is the most commonly used catalyst in this field [3,4,8,10,11].

One of the main problems in using of ZSM-5 for cracking of polymers is the quick deactivation, which mainly occurs due to coke deposition on the active sites of catalysts and pore blocking [12,13]. Although working at lower temperatures can relatively lower amount of coke deposition, it cannot be fully prevented [14,15]. The deposited coke can be burnt partially or fully in the presence of oxygen at high temperatures in a regeneration process. While regeneration aims to recover the initial activity of the catalyst, its performance depends on different factors such as place of coke and type of catalyst [16]. In fact, from industrial point of view, catalyst deactivation rate and its regenerability are two important factors to choose a catalyst; otherwise catalytic pyrolysis of polymers would not have any economic justification [17].

In addition to coke deposition, catalyst deactivation might be caused by catalyst dealumination and aggregation after a number of conversion- regeneration cycles [18,19]. In this case, due to loss of acidic sites of the catalyst and mechanical deactivation, catalyst deactivation is no longer reversible; therefore, the initial activity of the catalyst cannot be recovered [18].

This work investigated activity, deactivation and reuse of a ZSM-5 zeolite in cracking of HDPE. Consecutive catalytic cracking tests were conducted. When the catalytic activity dropped to a certain extent, catalyst was regenerated and reused in the same decomposition tests. The advantage of this approach was to have a better understating of activity and deactivation behavior of the catalyst in a series of cracking-regeneration experiments. Using this approach, catalyst regeneration was employed only when catalytic activity was no longer satisfactory; therefore, unnecessary regeneration steps could have been avoided. In addition, the effect of calcination temperature on activity of catalyst in cracking of HDPE was studied.

5.3. Experimental

5.3.1. Materials

The polymer used was pure high-density polyethylene (HDPE) with the characteristics listed in Table 5.1. Specific gravity was measured at room temperature. Melting point, fusion heat and crystallinity were determined using a Differential Scanning Calorimetry (DSC).

Table 5.1. Characterization of the employed HDPE.

Specific gravity	Fusion heat (kJ.kg^{-1})	Melting point (°C)	Crystallinity (%)
0.93-0.94	178	134.5	64.23

The employed catalyst was a ZSM-5 zeolite with Si/Al of 25, BET area of 425 m^2.g^{-1} and average grain size of 9.2 μm.

5.3.2. TGA

Polymer decomposition reactions were conducted in TGA7 Perkin Elmer Thermogravimetric Analyzer. Prior to the use for cracking reactions, the TGA calibration procedure was performed for the furnace thermocouple and the balance according to the manufacture instructions. In TGA experiments, 13 mg of HDPE and 1.95 mg of the catalyst were loaded in a disposable aluminum

crucible (cat/HDPE= 15 %). During all the TGA experiments, nitrogen was running through the system with a flow rate of 35 mL.min^{-1}. TGA was programmed to stay at 30 °C for 2 h to purge the chamber fully and eliminate oxygen from the system. Subsequently, temperature increased to 370 °C with a heating rate of 50 °C.min^{-1} and maintained constant to reach complete decomposition reactions. Temperature and sample weight were recorded every 1 s. Before any regeneration, coke deposition was determined with respect to the initial weight of HDPE (13 mg) and catalyst (1.95 mg), and the final decomposition conversion recorded by TGA.

In addition, one TGA test was conducted in the absence of catalyst to evaluate activity of the ZSM-5.

5.3.3. DSC

DSC7 Perkin Elmer Differential Scanning Calorimetry was used for catalyst regeneration. DSC calibration was conducted with melting point and fusion heat of Indium and Tin. In the regeneration process, the coked catalyst (ca. 1.95 mg) was heated in air at a flow rate of 35 mL.min^{-1} at 480 °C for 5 h. Besides catalyst regeneration, DSC instrument was also used to record the heat flow curve of 1.95 mg of Fresh ZSM-5 at 480 °C for 5 h.

5.3.4. Calcination treatment

The effect of calcination temperature of ZSM-5 on cracking of HDPE was investigated. Prior to the use in the plastic degradation, the catalyst samples were calcined in air at 500, 600 and 700°C for 5 h. The calcined catalysts were used in the TGA tests to evaluate their activity.

5.3.5. SEM and FTIR

Hitachi Su-70 Schottky Field Emission Scanning Electron Microscope at 10 kV and Bruker Tensor 37 Fourier Transform Infrared Spectrophotometer were employed to examine the effect of calcination temperature on acidity and catalytic activity of the zeolite in cracking of HDPE.

5.3.6. Conversion-regeneration-conversion cycles

The polymer decomposition experiments (TGA tests) were started using the fresh ZSM-5. After the first TGA run, consecutive cracking tests were conducted with the spent catalyst. Once catalytic activity dropped to 20% of that of the fresh catalyst, the spent catalyst was regenerated, and then reused in the same TGA experiments. This procedure was conducted for 10 regeneration-conversion cycles. All the presented TGA and DSC results were average of two runs.

Deactivation of the used ZSM-5 in consecutive cracking tests was evaluated by defining DOZ as shown in Eq.1. In addition, the efficiency of catalytic cracking was compared with pure thermal cracking by calculating CVT values from Eq. 2.

$$\text{DOZ} = \frac{DTG_{max,HDPE+Catalyst}}{DTG_{max,HDPE+Fres\ catalyst}} \times 100 \tag{1}$$

$$\text{CVT} = \frac{DTG_{max,HDPE+Catalyst}}{DTG_{max,HDPE}} \tag{2}$$

where $DTG_{max,HDPE}$, $DTG_{max,HDPE+Fresh\ Catalyst}$ and $DTG_{max,HDPE+Catalys}$ were the maximum decomposition rates (min^{-1}) in pure thermal cracking, in the presence of the fresh and spent catalyst, respectively. The maximum decomposition rates at different measurements were retrieved from their related TG curves.

5.4. Results and Discussion

5.4.1. Effect of calcination temperature on the activity of ZSM-5 for cracking of HDPE

Figure 5.1 shows the TG (conversion) curves of the plastic at 370 °C over the fresh and the calcined ZSM-5 samples at three different temperatures (500, 600 and 700 °C). The conversion curve of HDPE over ZSM-5 calcined at 500 °C was almost the same as that of the ZSM-5 with no calcination. However, activity of the samples calcined at 600 and 700 °C dropped slightly and their related TG curves prolonged. This loss of activity might be because that the acidity of the catalyst was reduced at the high calcination temperatures.

Figure 5.2 shows the SEM photographs of 500, 600 and 700 °C-calcined ZSM-5 samples. The textural appearance of the catalyst was not affected by calcination and no obvious agglomeration of the catalyst could be detected. The FTIR spectra of the calcined catalysts are shown in Figure 5.3. Catalyst calcination shifted the 1072 and 1219 cm^{-1} signals to 1084 and 1236 cm^{-1}, respectively. A slight shift in the frequency of the 1219 cm^{-1} can be caused by dealumination of zeolite [20]. In this work, it seems that catalyst dealumination was the main reason of loss of activity of the 600 and 700 °C-calcined ZSM-5. Accordingly, ZSM-5 calcination was performed at 500 °C for the rest of this study.
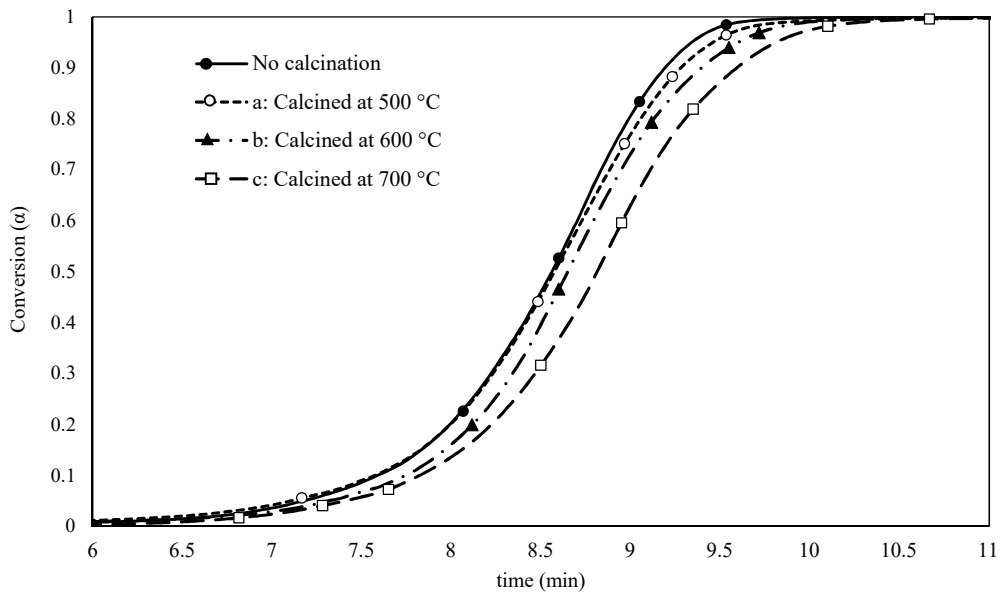
Figure 5.1. Isothermal TGA curves of catalytic cracking of the HDPE at 370°C (cat/HDPE=15%) in the presence of fresh ZSM-5 and calcined ZSM-5 at 500, 600 and 700 °C for 5 h.
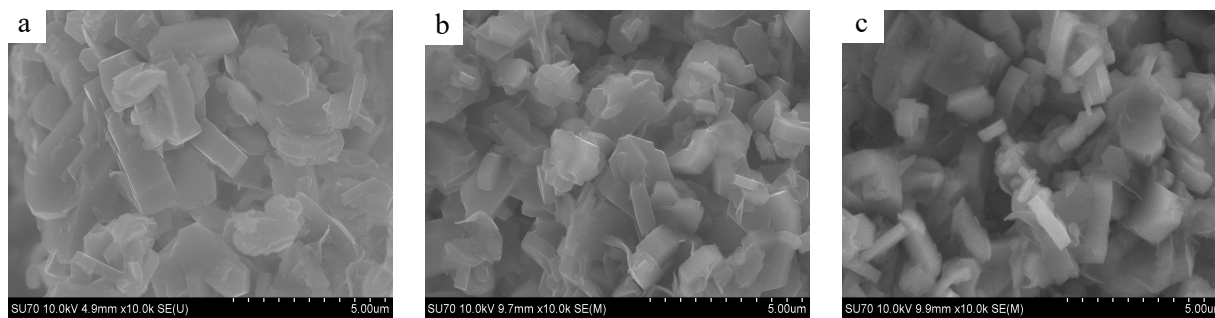
Figure 5.2. SEM of ZSM-5: (a) calcined at 500 °C (b) calcined at 600 °C (c) calcined at 700 °C.
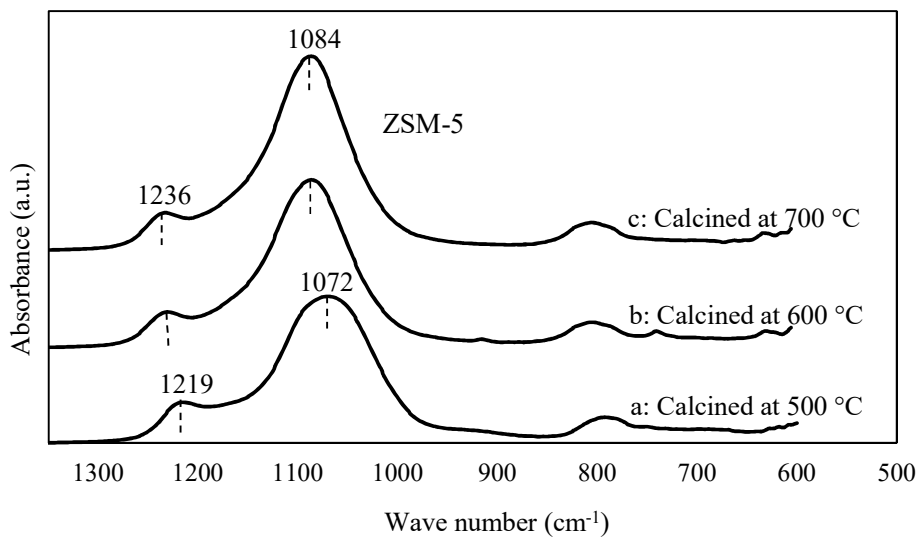
Figure 5.3. FTIR of ZSM-5: (a) calcined at 500 °C (b) calcined at 600 °C (c) calcined at 700 °C for 5 h.

5.4.2. Consecutive catalytic cracking of HDPE

According to Eq. 1, the DOZ determines the ratio of maximum degradation rate in the presence of used catalyst to that corresponding of fresh catalyst at 370 °C. Figure 5.4 presents the DOZ values of cracking of HDPE over fresh, spent and regenerated catalysts at 370 °C. After the first pyrolysis with fresh catalyst, the used catalyst in the crucible was directly employed in a new TGA experiment. The usage of the spent catalysts in TGA continued until the DOZ dropped to lesser than 20%. At this point a regeneration step was carried out.

Overall at the employed conditions and with 10 regeneration steps, the ZSM-5 zeolite could be employed in 54 catalytic cracking tests. Although coke deposition before regeneration steps never exceeded 2 wt. %, it could decrease activity of the catalyst by 5 times. Figure 5.4 also demonstrates the ratio of maximum degradation rate of catalytic cracking to the corresponding of thermal cracking of HDPE (CVT values). These results indicate the significantly high catalytic activity of ZSM-5 in cracking of HDPE. Before the regeneration steps, where catalyst deactivated by almost 80%, activity of the catalyst was still high enough to increase the rate of cracking reactions by at least 1000 times.
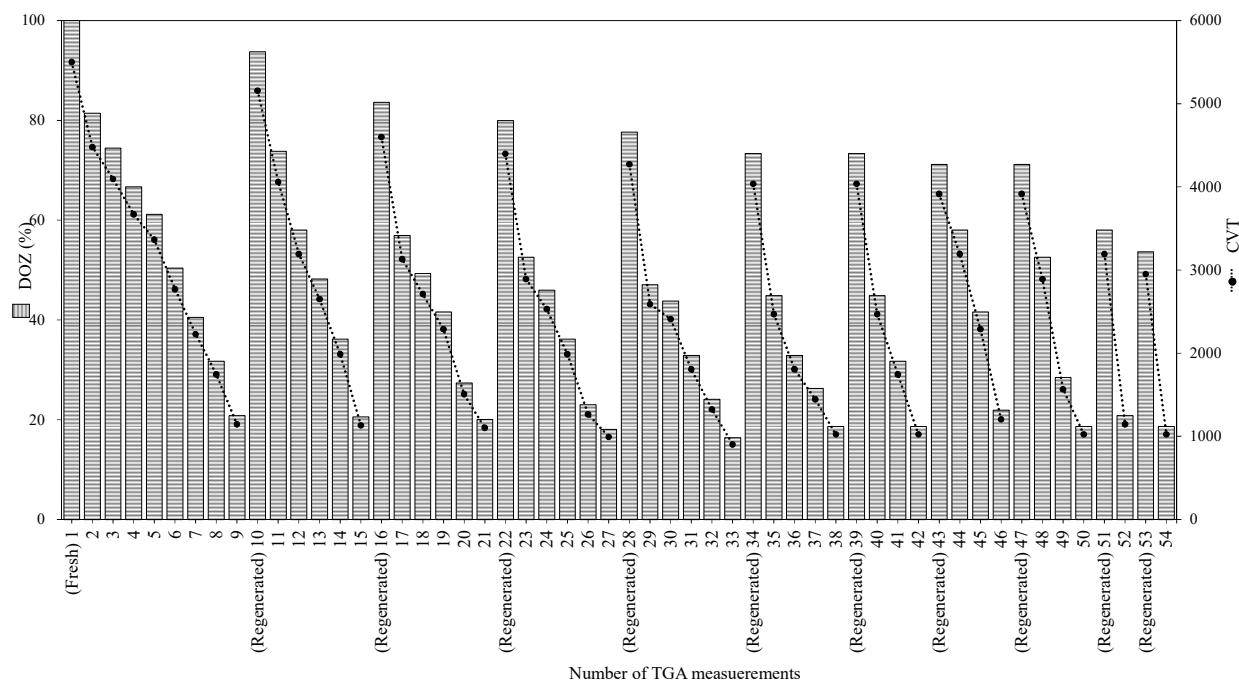
Figure 5.4. DOZ (Eq.1) and CVT (Eq.2) values of the ZSM-5 at different measurements.

5.4.3. Trace of coke in the regenerated catalyst

From Figure 5.4, it can be seen that the regenerations steps failed to recover the initial activity of the catalyst, and therefore, the DOZ could not increase to the initial value of the fresh catalyst. It was possible that the conditions employed in the regeneration steps were not sufficient to burn all the deposited coke, and after regeneration steps the catalyst still contained some coke. This was checked by comparing DSC curves of coked catalyst samples and that of non-coked catalyst.

During regeneration steps, DSC instrument records the heat flow rate absorbed by the catalyst and the deposited coke. As coke burns, the heat flow curve gradually declines. In a successful regeneration, all the deposited coke burns off, and therefore, the DSC curve reaches the DSC curve of the fresh catalyst at the same operating conditions. In other words, the DSC curve of coke burning (the difference of the original DSC curves and the DSC curve of fresh catalyst) drops to zero unless the regenerated catalyst is still contaminated by coke. This approach could help to examine any trace of coke in the regenerated catalyst.

Figure 5.5 shows the DSC curves of the coked catalyst in the 1st, 3rd, 6th, and 10th regeneration steps (ca. 1.95 mg). In addition, Figure 5.5 also contains the DSC curve of non-coked catalyst (fresh) catalyst (1.95 mg) at the regeneration conditions. As the same catalyst weight (1.95 mg) and operating conditions (T= 480 °C, t= 5 h) were employed in all these DSC experiments, the DSC curve of coke burning could be generated by subtracting the DSC of fresh catalyst from the DSC curve of coked catalyst as shown in Figure 5.5.

From Figure 5.5, in case of the 6th and 10th regeneration steps, DSC curves of coke burning did not drop to zero; therefore, the catalyst samples still contained coke residue, and regeneration could not recover initial activity of the ZSM-5. As a result, more severe regeneration conditions were required to burn all the coke either by increasing the temperature or extending the regeneration step time. Nevertheless, more drastic regeneration conditions can cause further mechanical deactivation and dealumination.

In Figure 5.5, no trace of coke was apparent in the 1st and 3rd regenerated catalyst samples; however, Figure 5.4 shows a certain loss of activity for these catalyst samples. Therefore, the observed deactivation could be due to loss of acidity of the catalyst. Although the regeneration temperature was chosen carefully at 480 °C to avoid any damage to the acidic sites and textural properties of the catalysts, due to the involved exothermic coke decomposition reactions, it is possible that the catalyst temperature raised to more than 480 °C. Therefore, the catalyst encountered mechanically failure and more likely dealumination reactions.
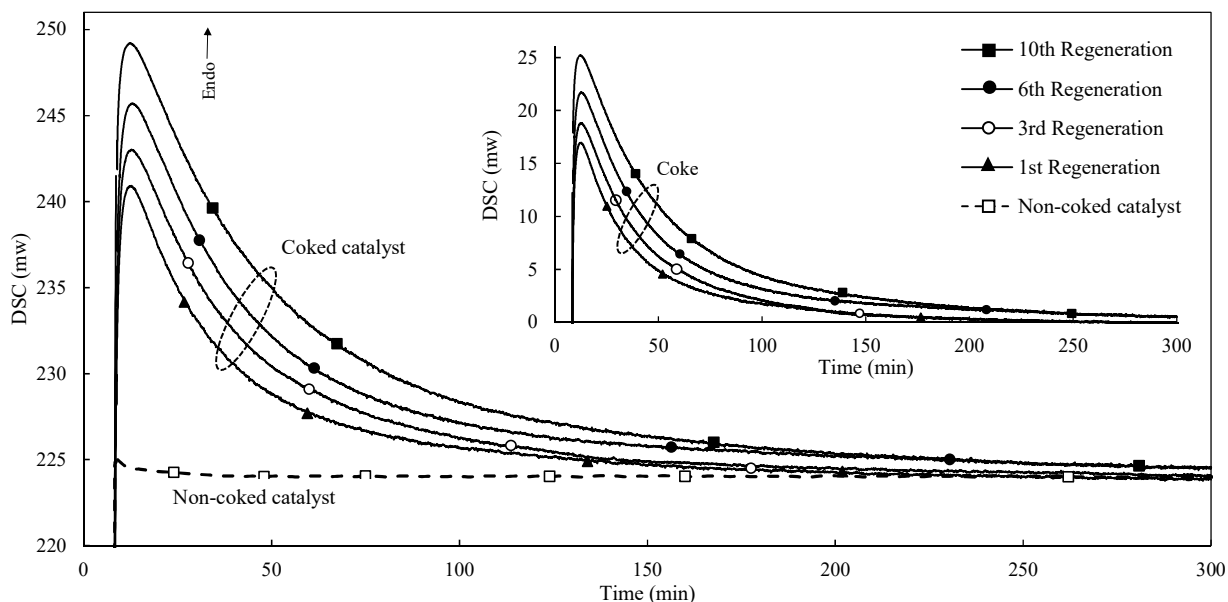
Figure 5.5. DSC curves of the 1st, 3rd, 6th and 10th regeneration steps and the DSC curve of the non-coked catalyst (temperature= 480 °C, time= 5 h).

5.5. Conclusion

Catalytic cracking of HDPE over a ZSM-5 zeolite was studied in a Thermogravimetric Analyzer (TGA). Activity, deactivation behavior and regenerability of the catalyst were examined with respect to the conversion curve of HDPE and the maximum decomposition rate.

Calcination treatment at 600 and 700 °C caused a decrease in catalytic activity of the ZSM-5 for cracking of HDPE. The FTIR and SEM photographs of the calcined samples indicated that dealumination reactions and loss of the acid properties were the main causes of deactivation of the calcined samples.

At a mild operating conditions, 370 °C and cat/HDPE of 15 %, the fresh ZSM-5 showed high activity for cracking of HDPE. After the first run, same TGA experiments repeated with the used catalyst, and quick drop in catalytic activity was detected. It was observed that the presence of 2 wt. % of coke in the catalyst could decrease catalytic activity by 5 times. The regeneration process

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was conducted in air at 480 °C for 5 h to eliminate the deposited coke and recover the initial catalytic activity. However, due to dealumination reactions, initial activity of the catalyst could never be recovered by catalyst regeneration; therefore, some extent of catalyst deactivation was found to be irreversible.

Acknowledgment

References

[1]   Lou X.F, Nair J. The impact of landfilling and composting on greenhouse gas emissions - A review, Bioresource Technology. 100 (2009) 3792–3798

[2]   Johnke B. Emissions From Waste Incineration, Good Practice Guidance and Uncertainty Management (2009) 455–468. http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Emissions+From+Waste+incineration#4.

[3]   Kumar S, Panda A.K, Singh R.K. A review on tertiary recycling of high-density polyethylene to fuel, Resources, Conservation and Recycling. 55 (2011) 893–910

[4]   Marcilla A, Gómez-Siurana A, Berenguer D. Study of the early deactivation in pyrolysis of polymers in the presence of catalysts, Journal of Analytical and Applied Pyrolysis. (2007)

[5]   Takuma K, Uemichi Y, Sugioka M, Ayame A. Production of Aromatic Hydrocarbons by Catalytic Degradation of Polyolefins over H-Gallosilicate, Industrial & Engineering Chemistry Research. 40 (2001) 1076–1082

[6]   Lee K.H, Noh N.S, Shin D.H, Seo Y. Comparison of plastic types for catalytic degradation of waste plastics into liquid product with spent FCC catalyst, Polymer Degradation and Stability. 78 (2002) 539–544

[7]   Pinto F, Costa P, Gulyurtlu I, Cabrita I. Pyrolysis of plastic wastes, Journal of Analytical and Applied Pyrolysis. 51 (1999) 57–71

[8]   Miskolczi N, Bartha L, Deák G, Jóver B, Kalló D. Thermal and thermo-catalytic degradation of high-density polyethylene waste, Journal of Analytical and Applied Pyrolysis. 72 (2004) 235–242

[9]   Serrano D.P, Aguado J, Escola J.M, Rodríguez J.M. Influence of nanocrystalline HZSM-5 external surface on the catalytic cracking of polyolefins, Journal of Analytical and Applied Pyrolysis. 74 (2005) 353–360

[10]   Aguado J, Serrano D.P, Miguel G.S, Escola J.M,. Rodríguez J.M. Catalytic activity of zeolitic and mesostructured catalysts in the cracking of pure and waste polyolefins, Journal of Analytical and Applied Pyrolysis. 78 (2007) 153–161

[11]   Seo Y, Lee K, Shin D. Investigation of catalytic degradation of high- density polyethylene by hydrocarbon group type analysis, Journal of Analytical and Applied Pyrolysis. 70 (2003) 383–398.

[12]   López A, Marco I, Caballero B.M, Adrados A, Laresgoiti M.F. Deactivation and regeneration of ZSM-5 zeolite in catalytic pyrolysis of plastic wastes, Waste Management. 31 (2011) 1852–1858

[13]   Uemichi Y, Hattori M, Itoh T, Nakamura J. Deactivation Behaviors of Zeolite and Silica - Alumina Catalysts in the Degradation of Polyethylene, Industrial & Engineering Chemistry Research. 5885 (1998) 867–872.

[14]   Guisnet M, Magnoux P. Organic chemistry of coke formation, Applied Catalysis A: General. 212 (2001) 83–96

[15]   Miskolczi N, Bartha L, Deák G. Thermal degradation of polyethylene and polystyrene from the packaging industry over different catalysts into fuel-like feed stocks, Polymer Degradation and Stability. 91 (2006) 517–526

[16]   Cerqueira H.S, Ayrault P, Datka J, Magnoux P, Guisnet M. m-Xylene transformation over a USHY zeolite at 523 and 723 K: Influence of coke deposits on activity, acidity, and porosity, Journal of Catalysis. 196 (2000) 149–157

[17]   Ali S, Garforth A.A, Harris D.H, Rawlence D.J, Uemichi Y. Polymer waste recycling over "used" catalysts, Catalysis Today. 75 (2002) 247–255

[18]   Serrano D.P, Aguado J, Escola J.M. Catalytic Cracking of a Polyolefin Mixture over Different Acid Solid Catalysts, Industrial & Engineering Chemistry Research. 39 (2000) 1177–1184

[19]   Nishino J, Itoh M, Ishinomori T, Kubota N, Uemichi Y. Development of a catalytic cracking process for converting waste plastics to petrochemicals, Journal of Material Cycles and Waste Management. 5 (2003) 89–93

[20]   Campbell S.M, Bibby D.M, Coddington J.M, Howe R.F, Meinhold R.H. Dealumination of HZSM-5 Zeolites, Journal of Catalysis. 161 (1996) 338–349

Chapter 6: Determination of the Heat of Pyrolysis of HDPE via Isothermal Differential Scanning Calorimetry: A New Approach for Solid State Reactions

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6.1. Abstract

Due to the complexity of solid state reactions such as cracking of polymers, it is very difficult to find the required heat of the involved reactions. In this study, using a Differential Scanning Calorimetry (DSC) instrument, a new method is proposed to determine the heat of decomposition of polymers at constant temperatures. The integration of an isothermal DSC curve with respect to time gives the overall consumed heat by the process, which consists of two components: net heat of reaction and heat loss. Finding an effective solution to measure heat loss from DSC instrument is an important part of this new approach. The heat loss is determined as function of sample weight and operating temperature. The heat loss is employed to correct the DSC results and produce the net heat of decomposition reactions. This approach is new since, firstly, it uses high-certainty isothermal DSC measurements, and secondly, the heat loss values are calculated in the decomposition range. The procedure was employed to determine the required heat for pyrolysis of high-density polyethylene at constant temperatures of 400, 410, 420 and 430 °C, and the average value was calculated to be 1375±233 kJ/kg.

Keywords:

Heat of Pyrolysis; HDPE; DSC; Isothermal; Heat loss.

6.2. Introduction

Reactors are one of the main pieces of equipment in the chemical industry. In order to design a reactor, kinetic and thermal parameters are required to formulize the mass and heat balances around the reactor. To this aim, one of the important thermal parameters is the heat of reaction. If a reaction is known and all data are available, the heat of reaction could be calculated from thermodynamic reference tables using the enthalpy of all the reactants and products. However, some processes, such as pyrolysis of waste polymers, have a wide range of products, and involve

several serial and parallel reactions. As a result, known thermodynamic data for such processes is very complicated and sometimes impractical. On the other hand, Differential Scanning Calorimetry (DSC) is an alternative method that being used to determine the heat of reaction regardless of unknown details about the involved reactions and products. In fact, DSC is a thermal analysis technique to measure the required heat flows into/from a known amount of sample during a heating or cooling procedure. The obtained results from DSC can provide the heat of reaction, which aids to simulate the heating characterization of a chemical reactor.

There are few studies on the heat of pyrolysis of polymers, and they employ only non-isothermal DSC [1-4]. A literature review in the other fields of solid state reactions, such as pyrolysis of biomass, showed the same trend of using non-isothermal DSC [5-10]. However, non-isothermal DSC datasets are associated with uncertainty and errors, and as the operating temperature is not constant, more variables are uncertain and the sample properties will change more considerably than in isothermal conditions. In contrast, isothermal measurements are shown to be more precise and preferable to produce high certainty results; moreover, the temperature lag (temperature gradient) between sample and furnace is negligible [11-13]. For these reasons, using isothermal DSC is in the best interests of this study.

It is necessary to mention that a DSC apparatus is not an ideal isolated instrument, and therefore, it has heat loss to the environment. There is a need for a procedure to determine the heat loss experimentally, and then subtract it from the original DSC curve to obtain the net required heat for the process. This issue was addressed in one calorific study for measuring the heats of gasification of polymers via non-isothermal DSC measurement [1]; a method was developed to measure amount of heat loss merely as a function of temperature. Prior to decomposition temperature range, heat loss was found at different temperatures when the sample weight was still equal to the initial

value. The obtained heat loss values were extrapolated to the whole temperature range regardless of the loss of sample weight during the reactions. Therefore, the question arises as to what extent this assumption is acceptable.

In the current work, with the aid of a DSC instrument in an isothermal mode, a new methodology is proposed to find heat of solid state reactions. It develops a new procedure to assess the heat loss as function of both temperature and extent of reaction. The difference of the measured heat loss values and the overall consumed heat by DSC instrument gives the net heat of reactions. While this chapter focuses on the heat of decomposition of HDPE, the proposed technique can be employed in other fields such as pyrolysis/gasification of biomass, heavy crude oil, etc.

6.3. Materials and Methods

6.3.1. Polymer (raw material)

The polymer employed in this study was pure HDPE with the specific gravity of 0.935. Using DSC instrument, the melting point and the latent heat of the polymer were determined at 134.5 °C and 178 kJ/kg, respectively.

6.3.2. Thermal Analysis

The heat flow (energetic) measurements were carried out in Perkin Elmer DSC7. Prior to using DSC, it was calibrated by the fusion heats and melting points of tin and indium as the reference materials. For decomposition reactions, like the cracking of polymers, thermogravimetric measurements are required to interpret the obtained DSC results. Since the DSC7 instrument does not measure weight loss during decomposition, TGA tests, using Perkin Elmer TGA7, were conducted separately to produce complementary data. TGA7 was calibrated according to the Perkin Elmer instruction manual.

In both DSC and TGA measurements, HDPE samples were cut into small pieces, and placed in

disposable aluminum crucibles with no lids, heated from the ambient temperature to the target temperatures of 400, 410, 420, and 430 °C, and maintained to complete the reaction. The initial weight of HDPE and the pre-heating rate before the desired temperatures were 13±0.01 mg and 50 °C/min, respectively. Both TG and DSC were purged using pure nitrogen with a flow rate of 60 ml/min to first remove oxygen and prevent any oxidation, and second, to sweep the gaseous products from the system during the decomposition reaction. All the tests were conducted 4 times to ensure reproducibility of the results. In all the DSC and TGA tests, baseline measurements were performed for empty sample pans, and all the reported DSC/TGA curves and values are corrected by baselines.

In the second step of the measurements, the amount of heat loss was determined at the target temperatures and different HDPE weights of 0.2, 1, 2.5, 4.1, 5.5, 7, 8.5, 9.8, 11.5, and the maximum weight of 13 mg. The HDPE sample was heated up to the target temperature and maintained over there prior to starting any reactions. Since temperature is constant and no reaction has stated yet, the recorded heat flow by DSC is the amount of heat loss at the employed temperature and sample weight.

To accomplish the heat loss measurements, it was necessary to find the maximum possible time that HDPE can be kept at the target temperatures with no reactions. Therefore, 0.2 mg of HDPE was placed in an aluminum crucible, temperature ramped to 430 °C and maintained constant for 3 min, and then cooled down to the ambient temperature. As DSC7 has a cooling system working with water at 20 °C, the temperature dropped quickly, in less than 1 min. After the cooling step, the HDPE sample was weighed, and no drop in the sample weight was detected. Besides that, the DSC curve during the 3 min isothermal step remained stable, which explains there was no reaction. This result was verified in TGA instrument as well, and therefore, both TGA and DSC experiments

at 430 °C showed no reaction in the first 3 min.

With the aid of TGA instrument, and matching DSC and TGA results at different reaction times, DSC values were determined at different weights of 0.2, 1, 2.5, 4.1, 5.5, 7, 8.5, 9.8, 11.5, and 13 mg. At any sample weight and temperature, the net heat of reaction was determined by subtracting the values of overall consumed heat and heat loss. Finally, a curve was plotted among the net heat values, and then the area under each curve was calculated to determine the required heat of reaction.

Therefore, regarding the isothermal measurements, the recorded DSC curves contain two components, decomposition heat and heat loss to the environment, which can be expressed by Eq. 1.

$$Q_{DSC} = Q_{dec} + Q_{loss} \tag{1}$$

where Q_{DSC} is the overall consumed heat recorded by DSC, Q_{dec} is the required heat for the decomposition reactions, and Q_{loss} is the amount of heat loss. The aim of this study is to determine the decomposition heat of HDPE (Q_{dec}) using the described methods and procedure.

6.4. Results and Discussion

The isothermal TGA and DSC measurements were performed for 13±0.01 mg of HDPE at the temperatures of 400, 410, 420, and 430 °C. Figure 6.1 shows the DSC and TGA results with the average uncertainty of ±4% and ±1% standard deviation, respectively. All the TGA and DSC curves were corrected by the baseline curves for empty crucibles. The TGA curves showed complete decomposition reactions with no residue left in the crucibles. After each DSC experiment, the used crucible was weighed and no residue or char was detected. Therefore, HDPE, was completely decomposed at the employed temperatures over the reaction time.

The recorded DSC curves in Figure 6.1 are the total heat into the HDPE with the unit of mW,

and according to Eq. 1, contain the heat of decomposition and heat loss to the environment. Table 6.1 lists the integration of each DSC curve with respect to time.
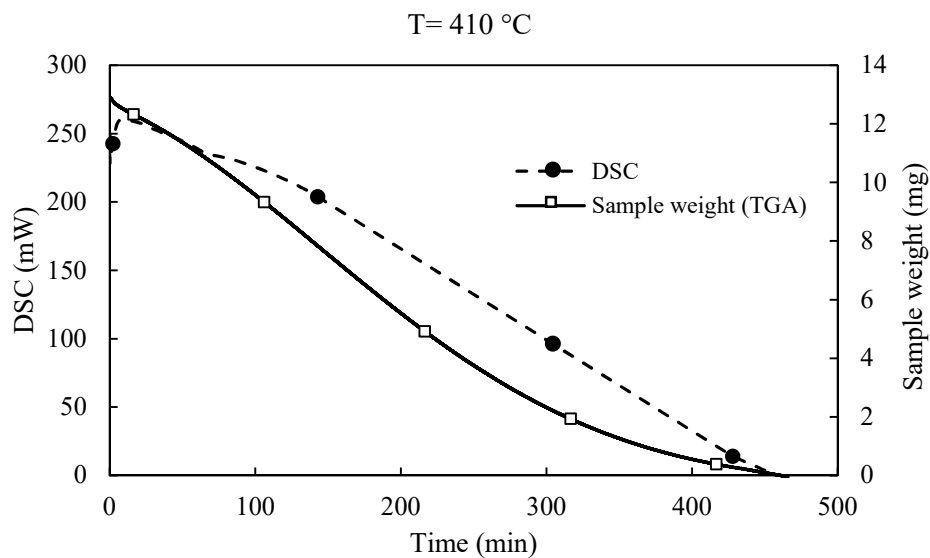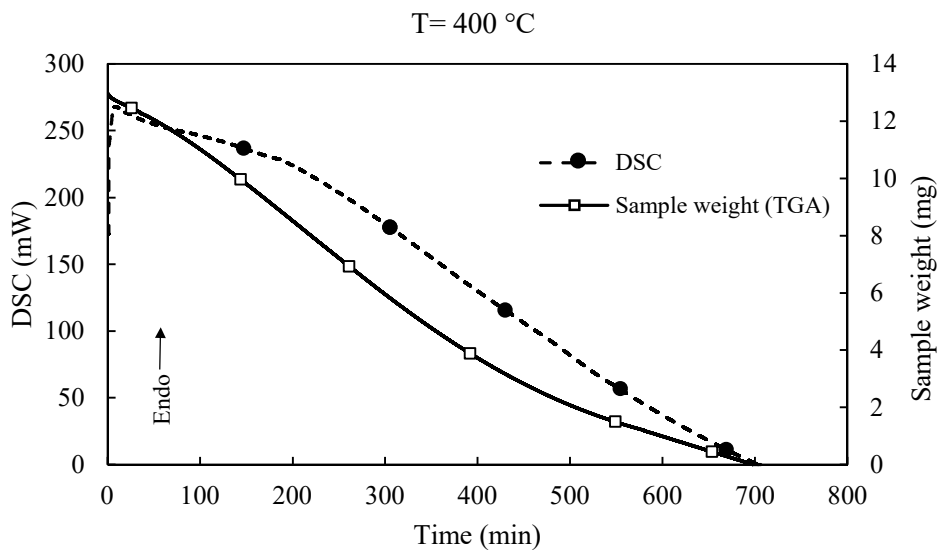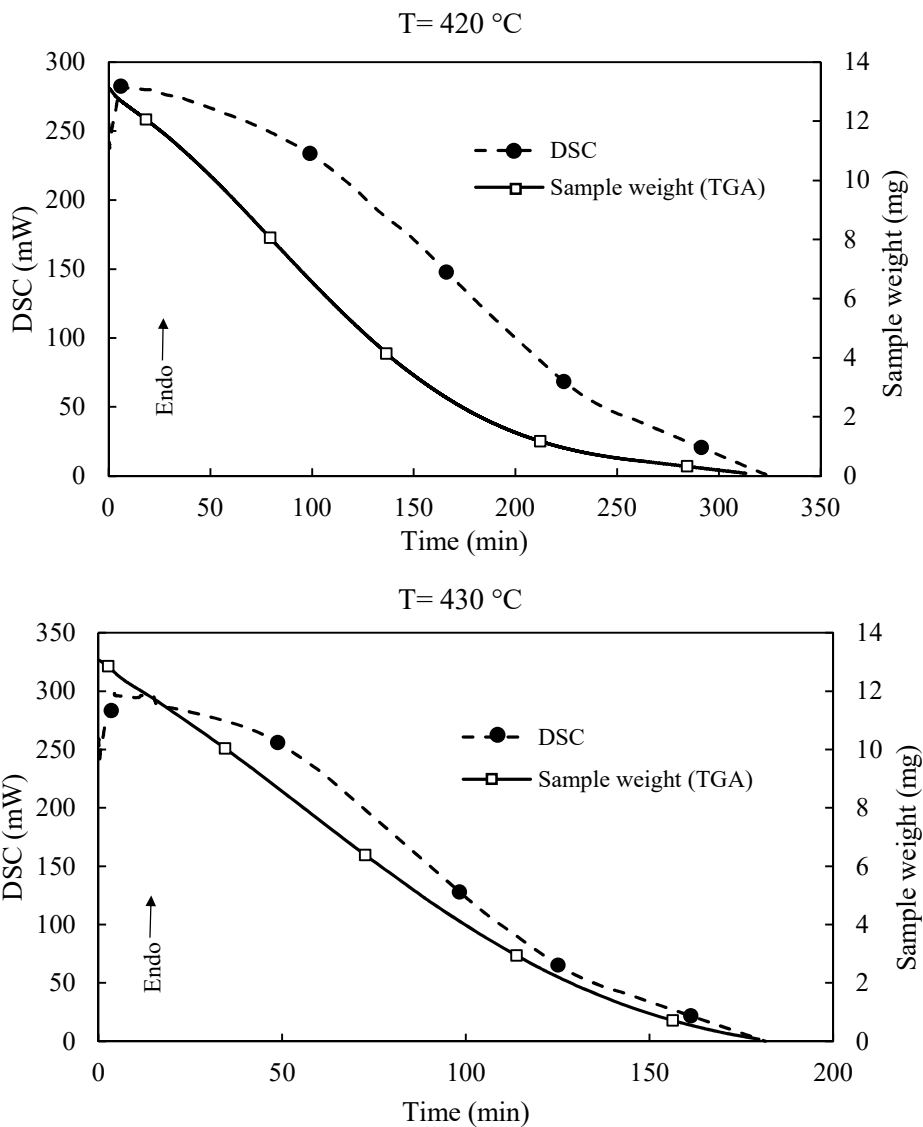
Figure 6.1. Isothermal DSC and TGA results 400, 410, 420 and 430 °C (initial weight= 13±0.01 mg).

Table 6.1. The calculated area under DSC curves in Figure 6.1 in respect to time.

Temperature (°C)	400	410	420	430
Area under DSC curves (Q_{DSC}) (kJ/kg)	7946±318	5145±206	3737±150	2130±85

In order to find the net heat of decomposition reactions, heat loss at different temperatures should be determined and then deducted from the overall heat flow curves in Figure 6.1. Figure 6.2 shows the measured heat loss with an average relative uncertainty of 4.6% standard deviation

at different sample weights and temperatures. At the same sample weight, if compare the heat loss, it increases at higher temperature. At any constant temperature, a prominent feature is that the heat loss value reduces by decreasing amount of the sample, and it could also be due to the drop in the height of the sample in the pan.
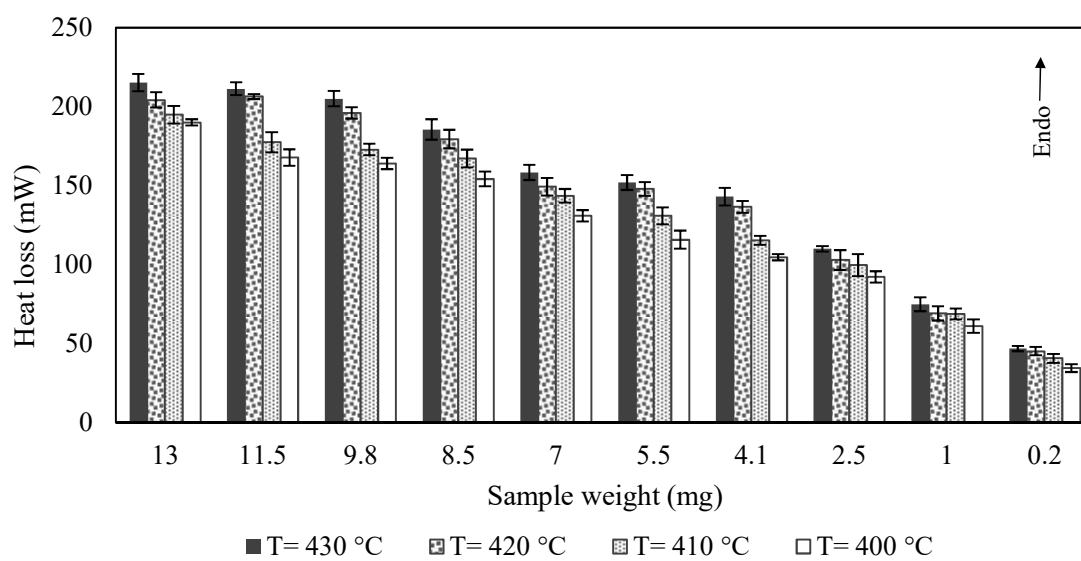

Figure 6.2. Average measured heat loss at different sample weights and temperatures. (4 parallel measurements were taken at each sample weight.)

Calculating the net heat of reactions, DSC values should be determined at the same sample weights employed in the heat loss measurements (0.2, 1, 2.5, 4.1, 5.5, 7, 8.5, 9.8, 11.5, and 13 mg), and then corrected by the determined heat loss values shown in Figure 6.2. However, the DSC curves demonstrate heat flow against time, and cannot specify sample weights. Therefore it is required to combine TGA and DSC results. As an example, Figure 6.3 shows the combined TGA/DSC results at 410 °C. Using the TGA curve for specifying the aforementioned sample weights, DSC values would be obtained, and then treated by the measured heat loss values at the same temperature and sample weights. The same procedure should be conducted at the other sample weights and temperatures.
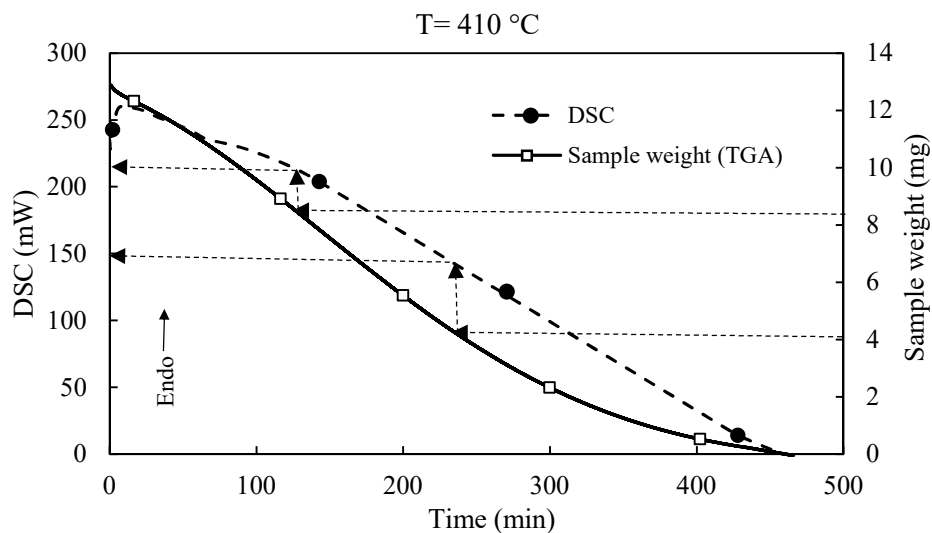
Figure 6.3. Reading DSC values at different sample weights with the aid of TGA curve (T= 410 °C).

At any specific temperature and sample weight, subtracting the heat loss from the corresponding DSC value gives to the net heat of reaction. Accordingly, Figure 6.4 shows overall heat flow, heat loss, and net heat of reactions at different sample weights and temperatures. In order to proceed the calculations and find the net heat of decomposition of HDPE, the net heat values in Figure 6.3 should be plotted against time. Using the TG curves shown in Figure 6.1, the corresponding time to any sample weight was found. Figure 6.5 illustrates the net heat flow curves against time at the target temperatures. The average relative uncertainty of the net heat flow curves was determined to be 17%.

T= 430 °C

Total heat (mW) ---●--- Heat loss (mW) ---△--- Net heat (mW) ---■---

T= 420 °C

Total heat (mW) ---●--- Heat loss (mW) ---△--- Net heat (mW) ---■---

T= 410 °C

Total heat (mW) ---●--- Heat loss (mW) ---△--- Net heat (mW) ---■---
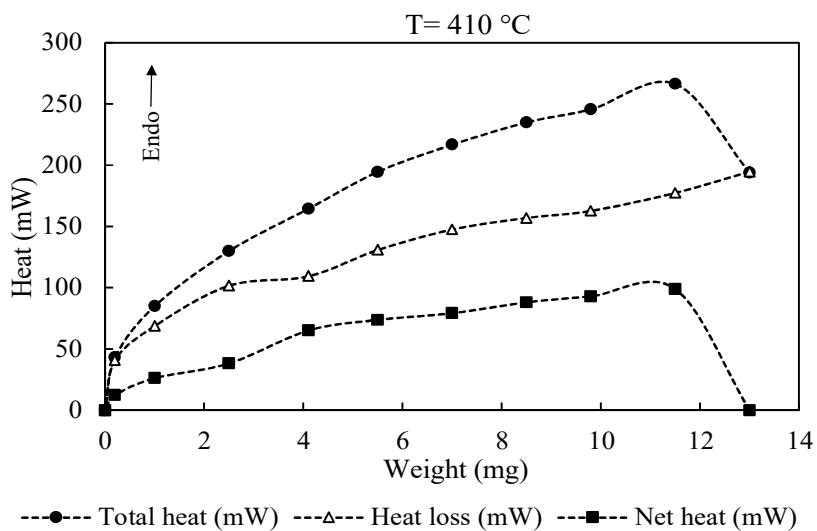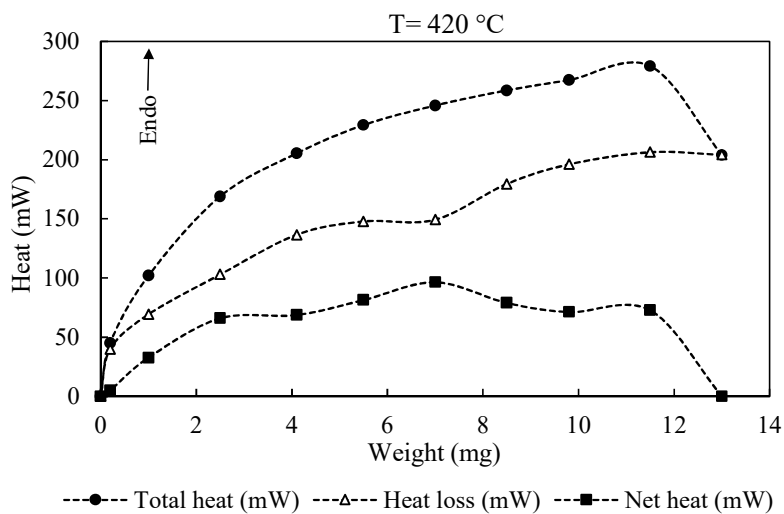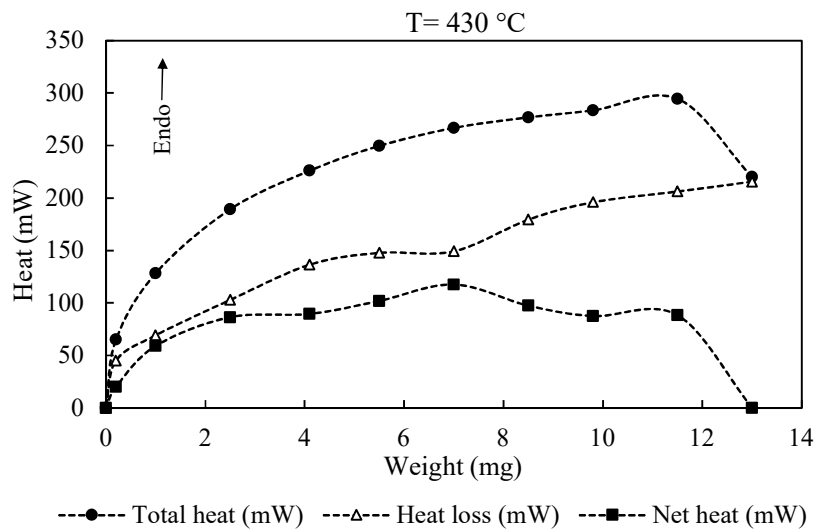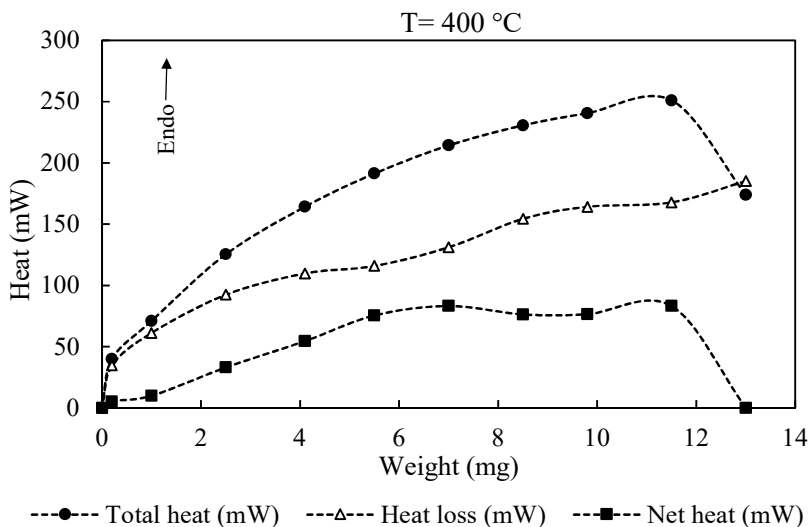
Figure 6.4. Total heat, heat loss and net heat of reaction against different weights of sample.
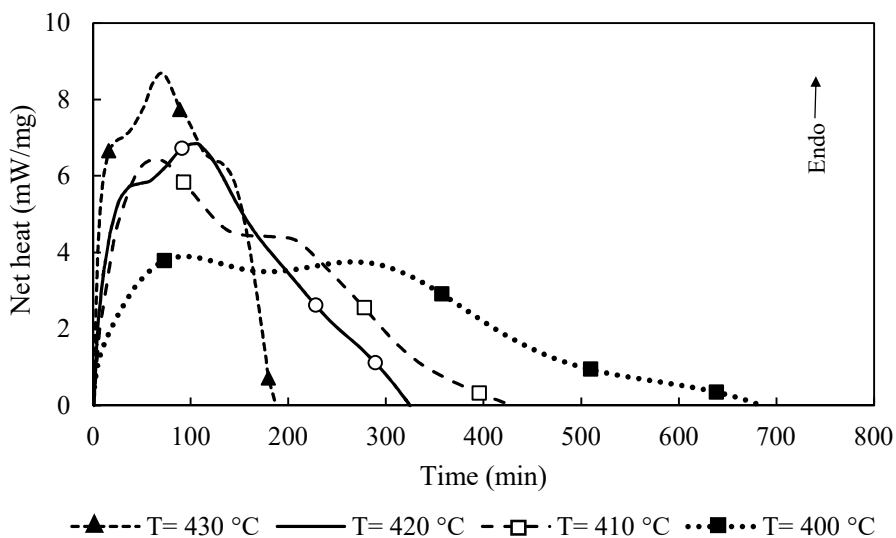
Figure 6.5. Average net required heat for decomposition reactions against time at 400, 410, 420 and 430 °C.

At any constant temperature in Figure 6.5, the heat of reaction is the area under the heat flow curve. Table 6.1 shows the determined heat of decomposition of HDPE at the target temperatures. Considering the variance of the measurements, using numerous measurements at each temperature, the difference in the heat of reactions at different temperatures may be explained. Besides this

uncertainty, it is also known that the products of decomposition of polymers are affected by the operating temperature [14], and considering this fact that the heat of reaction is the difference between the energy of products and reactants, the variation of reaction heat values at different temperatures can be justified.

In addition, a comparison of data in Table 6.2 shows a trend between the operating temperature and the heat of decomposition of HDPE. The results indicate that the heat of reaction increases by decreasing the temperature. It can be justified by this fact that the boiling points of the cracked species might be higher than the operating temperature. Therefore, the produced species have to stay longer in the reaction zone and undergo further pyrolysis reactions to produce smaller products with shorter carbon chain length and lower boiling temperatures. As a result, as decomposition of HDPE at lower temperatures involve further reactions, it requires more heat than higher temperatures. This results can be confirmed by the product distribution of pyrolysis of HDPE at different temperatures available in the literature [14].

Table 6.2. The heat of reaction for pyrolysis of HDPE (The calculated area under each heat flow curve shown in Figure 6.5.)

Temperature (°C)	400	410	420	430
Heat of reaction (Q_{dec}) (kJ/kg)	1581±268	1408±239	1281±217	1231±209

For each of temperature considered, a comparison of data in Tables 6.1 and 6.2 reveals considerable amount of heat loss from the DSC instrument to the environment. The average decomposition heat of HDPE from this study was obtained to be 1375±233 kJ/kg, and in Table 6.3, it was compared with the literature data determined by non-isothermal DSC measurements. The deviation between the results in Table 6.3 is primarily because of employing the isothermal mode in this work versus the non-isothermal mode in the literature.

Another reason could be explained by the employed method to determine amount of heat loss. In the non-isothermal study conducted by Stoliarov and Walters [1], prior to the decomposition range (when sample weight was still equal to its initial value), heat loss was determined at different temperatures, and a linear correlation was obtained between them. Afterwards, the estimated correlation was extended over the whole decomposition temperature range where the sample weight was no longer constant. In fact, it was assumed that heat loss was only temperature dependent. In contrast, our study shows that during the decomposition reactions by decreasing sample weight, the associated heat loss declines as well. Therefore, as the estimated heat loss by Stoliarov and Walters [1] was found regardless of loss of sample in the reaction zone, it was calculated higher than the real value, and according to Eq. 1, it led to a lower net heat of reaction.

Table 6.3. The heat of decomposition of HDPE obtained from this study and previous studies

	Current study	Literature
Q_{dec} (kJ/kg)	1375±233	920±120 [1]
		670 [2]
		649 [3]
		365-556 [4]

While heat loss is a function of temperature and sample weight, it is very important to note that it can be different from various DSC instruments. Furthermore, heat loss strongly depends on the properties of the sample. As a result, the procedure to correct heat loss should be performed for each individual scenario.

6.5. Conclusion

In this study, a new method was proposed to address heat of solid state reactions using DSC instrument. Since DSC instrument is not an isolated system, the recorded heat flow rate in DSC is

associated with heat loss to the environment. This study developed a procedure to find the heat loss as function of both temperature and sample weight. The procedures and methods were employed to find heat of decomposition of HDPE. Using isothermal DSC tests, the heat loss values were measured for different weight of HDPE from 0.2 to 13mg (initial weight was 13mg) at constant temperatures of 400, 410, 420 and 430 °C. It was observed that the lower sample weight and temperatures caused lesser heat loss to the environment. After elimination of heat loss from the heat flow curves, the net heat of pyrolysis of HDPE was determined at the target temperatures. The heat of decomposition decreased by increasing operating temperature; it was explained by this fact that at lower temperatures, the produced hydrocarbons with long carbon chain have lower volatility and require more energy to undergo further cracking reactions. The average heat of reaction among the employed temperatures was calculated to be 1375±233 kJ/kg, and it was evaluated against the literature. The observed deviation from the literature value was attributed to the DSC mode (isothermal in this work versus non-isothermal in the previous studies), and the employed methods in heat loss measurement.

Acknowledgment

References

[1] S.I. Stoliarov, R.N. Walters, Determination of the heats of gasification of polymers using differential scanning calorimetry, Polym. Degrad. Stab. 93 (2008) pp. 422-427

[2] G. Agarwal, B. Lattimer, Method for measuring the standard heat of decomposition of materials, Thermochim. Acta. 545 (2012) pp. 34-47

[3] M.C. Bruns, O.A. Ezekoye, Modeling differential scanning calorimetry of thermally degrading thermoplastics, J. Anal. Appl. Pyrolysis. 105 (2014) pp. 241-251

[4] F. He, W. Yi, J. Zha, Measurement of the heat of smoldering combustion in straws and stalk by means of simultaneous thermal analysis, Biomass. Bioenerg. 33 (2009) pp. 130-136

[5] R. Hoffman, W. Pan, Combining DSC and TG data for measuring heats of reactions, Thermochim. Acta. 166 (1990) pp. 251-265

[6] F. He, W. Yi, X. Bai, Investigation of calorific requirements of biomass pyrolysis using TG-DSC analyzer, Energ. Convers. Manage. 47 (2006) pp. 2461-2469

[7] M.V.D. Velden, J. Baeyns, A. Brems, B. Janssens, R. Dewil, Fundamentals, kinetics and endothermicity of the biomass pyrolysis reactions, Renew. Energ. 35 (2010) pp. 232-242

[8] J. Rath, M.G. Wolfinger, G. Steiner, G. Krammer, F. Barontini, V. Cozzani, Heat of wood pyrolysis, FUEL 82 (2003) pp. 81-91

[9] R. Narayan, M.J. Antal, Thermal lag, fusion, and the compensation effect during biomass pyrolysis, Ind. Eng. Chem. Res. 35 (1996) pp. 1711-1721

[10] M. Stenseng, A. Jensen, K. Dam-Johansen, Investigation of biomass pyrolysis by thermogravimetric analysis and differential scanning calorimetry, J. Anal. Appl. Pyrolysis.58-59 (2001) pp. 765-780

[11] S. Khedri, S. Elyasi, Corrigendum to "Kinetic analysis for thermal cracking of HDPE: A new isoconversional approach", Polym. Degrad.Stab. 133 (2016) pp.330–338

[12] D.N. Waters, J.L. Paddy, Equations for isothermal differential scanning calorimetric curves, Anal. Chem. 60(1) (1988) pp. 53–57

[13] Sima Chervina and Glenn T. Bodman, Mechanism and kinetics of decomposition from isothermal DSC data: development and application, Process. Saf. Prog. 16(2) (1997)

[14] https://en.wikipedia.org/wiki/Differential_scanning_calorimetry

[15] David R. Lide (ed), CRC Handbook of Chemistry and Physics, 84th Edition. CRC Press. Boca Raton, Florida, 2003; Section 6, Fluid Properties; Enthalpy of Fusion

[16] N. Miskolczi, L. Bartha, G. Deak, B. Jover, D. Kallo, Thermal and thermos-catalytic degradation of high-density polyethylene waste, J. Anal. Appl. Pyrolysis. 72 (2004) 235-242

Chapter 7: Conclusion and Future Directions

Pyrolysis of polymer wastes is a thermal process involving the heating of the polymers in an inert atmosphere. It is a promising technology to convert polymer waste into valuable hydrocarbons. This process has attracted considerable attentions since it can improve the waste management industry and compensate for the decline in the fossil fuels.

Pyrolysis of waste polymers is a complex phenomenon with production of many intermediates. This means that nature of the products at different extents of the reaction is different. In other words, the kinetic of polymer pyrolysis strongly depends on the extents of reaction.

In Chapter 3, after a critical review on the available kinetic study methods in solid state reactions, a new differential isoconversional method was established to determine kinetic parameters from isothermal TGA tests. Using this approach, kinetic parameters of cracking of HDPE were calculated at different extents of reaction. The obtained kinetic parameters were employed to estimate rate of thermal cracking. Evaluation of the theoretical results against the reaction rates recorded by TGA instrument gave a very good agreement.

In Chapter 4, catalytic cracking of HDPE was studied over ZSM-5 zeolites with Si/Al ratios of 25, 38 and 80. The TGA instrument recorded decomposition curves at different conditions. Catalytic activity of the zeolites were compared in relation to their strength to shift the degradation temperature range towards lower values. ZSM-5 zeolites with Si/Al ratios of 25 and 38 demonstrated very high catalytic activity. The increase of cat/HDPE ratio of ZSM-5 (25) and (38) elevated reaction rate. No significant improvement was observed beyond cat/HDPE ratio of 15%. Therefore, cat/HDPE ratio of 15% was chosen as the proper concentration of these catalysts in the rest of the experiments conducted.

Isothermal catalytic TGA tests were conducted at mild temperatures (330, 340, 350, 360, 370 °C). The kinetic study method developed in the first chapter analyzed the isothermal TGA datasets. Employment of the catalysts decreased activation energy of pyrolysis of high-density polyethylene dramatically.

Using Arrhenius equation and the determined kinetic parameters, the rate coefficients of catalytic cracking were determined at different temperatures, and were compared with those of thermal cracking. It was observed that the difference between thermal and catalytic cracking was more significant at lower temperatures than higher temperatures. It could be due to the higher possibility of coke formation at higher temperature, and losing catalytic activity.

In Chapter 5, Firstly, effect of calcination temperature on activity of the ZSM-5 (Si/Al=25) in the cracking of HDPE was studied. In comparison with the non-calcined catalyst, activity of the 500 °C-calcined catalyst did not show any change. The main cause of deactivation of the 600 and 700 °C-calcined catalyst samples was recognized to be loss of acidic properties due to dealumination reactions.

Furthermore, activity, deactivation behavior, reuse and regenerability of the ZSM-5 catalyst were examined in consecutive HDPE pyrolysis tests at 370 °C. Catalytic activity of the ZSM-5 was referred to its strength to increase the maximum decomposition rate of HDPE. It was observed that activity of the catalyst dropped to 20 % of its initial value due to the presence of only 2 wt % of coke. The regeneration process at 480 °C for 5 h was conducted to burn the coke and regain the initial catalytic activity. However, due to dealumination reactions in the regeneration step, the catalyst encountered further deactivation, and some extent of initial activity could never be recovered.

In Chapter 6, a new methodology was developed to find the heat of solid state reactions using isothermal DSC, TGA and heat loss curves. The developed procedures for net heat of reaction and heat loss measurements were new since all the experiments were conducted isothermally and heat loss was determined as function of both sample weight and temperature. On the contrary, in previous studies, all the experiments were performed non-isothermally, and heat loss was assumed only temperature dependant. Using the developed procedure the average net heat of pyrolysis of HDPE was determined to be 1375±233 kJ/kg.

FUTURE DIRECTION

As a follow-up on my research, it is suggested to conduct pyrolysis of HDPE in a lab-scale batch reactor to analyze the product distribution. The operating conditions such as ratio of catalyst to polymer, reaction time and temperature yielding to high valuable hydrocarbons can be determined. Using the kinetic parameters and the heat of reaction found in this study, and the efficient operating conditions, a pyrolysis reactor can be designed and optimized for larger scales.

In addition, my thesis introduces a new toolbox to solid-state reactions. It is strongly recommended that be used in other fields such as pyrolysis of oil sand bitumen, gasification/pyrolysis of biomass, gasification of oil sand coke, etc.