Simulation of the HDPE Pyrolysis Process

H Eidesen, H Khawaja*, S Jackson
Department of Engineering and Safety, UiT The Arctic University of Norway, Tromsø, Norway

ABSTRACT
Pyrolysis process is the thermochemical decomposition of organic compounds such as High-density polyethylene (HDPE) plastic. The main product of HDPE pyrolysis is usually diesel, but there are some other waste products formed (e.g. carbon black). Pyrolysis reactions are essentially decomposition reactions performed at elevated temperatures in the absence of oxygen. There is a variety of complex reactions taking place during pyrolysis, but in this paper, the focus is on the three main reactions of HDPE pyrolysis, namely: β-scission, hydrogen abstraction and chain fission. Of these, β-scission is known to be the most dominant reaction in HDPE pyrolysis reactions. In this work, the reaction equations and reaction constants were defined and solved in MATLAB® using the in-built ordinary differential equation (ODE) solver. The solution represents the rate of the reaction and the product yield.

1. INTRODUCTION

A good source of the raw materials for pyrolysis is industrial waste. Examples of industrial waste that can be treated in this way include tyres and the HDPE cages used in the fish farm industry. In Norway alone, the total available mass of disposed tyres is around 60000 tons per annum [1]. Unfortunately, there is no established best practice dealing with how waste plastic should be treated. Unfortunately, a great deal of HDPE plastic waste is ground to small pellets and disposed of in landfills. However, efforts are being made to recycle plastic wastes on commercial level [2].

Pyrolysis is one option that is currently being investigated as a replacement for simply storing HDPE plastic wastes or sending to landfill. The HDPE pyrolysis process is basically breaking down the molecules that make up the HDPE and can be split into three simple steps as shown in Figure 1.

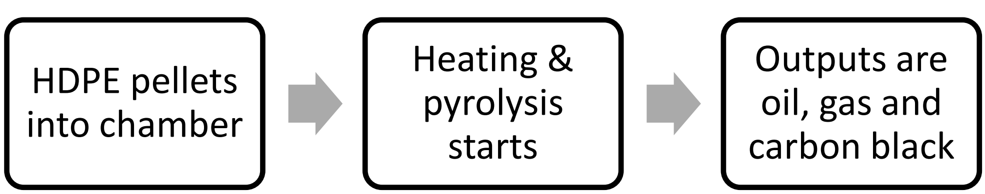


Figure 1: the basics of the pyrolysis process

The pyrolysis process shown in simplified form above contains a number of important steps. As Figure 1 suggests, the plastic must first be processed into small pellets, preferably

*Corresponding Author: hassan.a.khawaja@uit.no

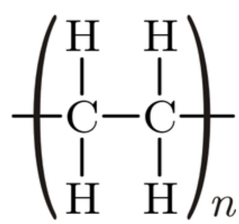
5 mm. This is to ensure as high thermal convection as possible [3]. The pellets are then heated in a chamber to around 400°C – 500°C to begin the pyrolysis process using an external source of fuel. Once this temperature is reached, the gasses that are being produced by the pyrolysis reaction form the primary fuel for the external burners and the process is now more or less self-sustainable. The atmosphere inside the chamber is normally inert to prevent unwanted reactions taking place. During pyrolysis, explosions and fires are an obvious risk because the chamber contains flammable oils and gasses. To limit the risk of explosions and fire, nitrogen (N_2) is pumped into the reaction chamber prior to heating.

As the pyrolysis process progresses, oil will flow from the chamber to storage. The time to ensure complete conversion of the plastic will vary depending on the molecular structure of the plastic, but for 5 mm pellets HDPE, the time is reported to be around 2 hours [4].

In addition to the conventional process of pyrolysis, researchers have considered other ways of treating plastic wastes. Huang et al. [5] investigated the potential of using microwaves to initiate a pyrolysis process. Their results show higher gas and solid yield, but lower oil yield [5]. Although the way a microwave pyrolysis process works is in principle the same as a conventional process: heat is supplied the system and pyrolysis starts, the difference is that the heat is generated by microwave radiation instead of the combustion of a fuel.

2. HIGH DENSITY POLYETHYLENE (HDPE)

High Density Polyethylene (HDPE) is a polymer of ethylene containing many C_2H_4 groups in a chain as shown in Figure 2. In a single HDPE chain, the number of C_2H_4 groups may vary from few hundreds to a few millions.



(a)

(b)

(c)

Figure 2: (a) the chemical formula of polyethylene, (b) illustrates a space fill model of the HPDE. (c) illustrates a potential branching structure of polyethylene.

Figure 2(a) shows the chemical formula for HDPE, where n represent the total number of molecules in the chain; Figure 2(b) shows a space fill model of the polyethylene and Figure 2(c) illustrates the branching nature of HDPE. This seemingly random structure results from the formation of free radicals during the production of the plastic. During the production of polyethylene, ethylene is subjected to high pressures and high temperatures. Because of these two conditions, free radicals are formed. The result of these radials is a positive charge at the extremities of the branch [6].

2.1. Chemical breakdown of HDPE during pyrolysis

The first thing that happens during pyrolysis is that the covalent bonds holding the ethylene together start to break. This only takes place when HDPE is heated or energized beyond the reaction activation energy. The result of this breaking is that the molecules have an unpaired electron, henceforth turning into free radicals. These radicals are the key to pyrolysis. They are attracted towards the larger chains and split them into smaller chains. The chain splitting is complex and may happen in different ways, however, we can simplify to three main free radical splitting processes: chain fission, β −scission and hydrogen abstraction. Out of these three, the β −scission reaction is the most dominant in the pyrolysis process [7].

2.1.1. β −scission

With the initial break in the bonds, the free radicals generated can undergo the β −scisson splitting process. The β −scisson splitting process occurs at the β −carbon in the molecule. The process of β −scission results in the formation of an olefin, ethylene, and a free radical that has two fewer carbon atoms. This radical undergoes further β −scission producing more ethylene [8]. The process can be described using Equation (1) and Figure 3. Additionally, we can have mid-chain scission and end chain scission, all of which have their own set of reaction equations.

$$R - CH_2 - CH_2 - \dot{C} - H_2 \rightarrow R - \dot{C} - H_2 + H_2C = CH_2 \tag{1}$$

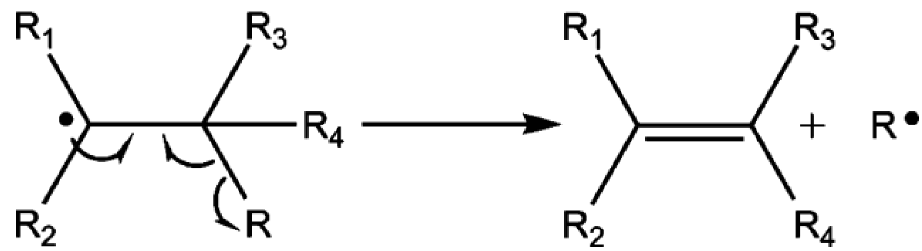
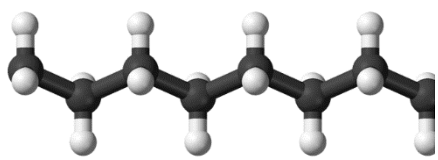


Figure 3: β –scission [9]

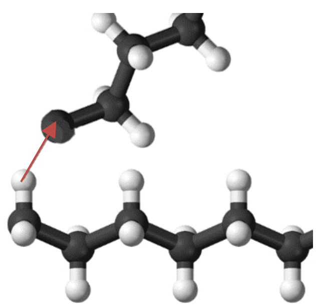
2.1.2. Hydrogen abstraction

Hydrogen abstraction is a chemical reaction where a hydrogen free radical is abstracted from the polymer [10] as shown in Equation (2) and visualized in Figure 4.

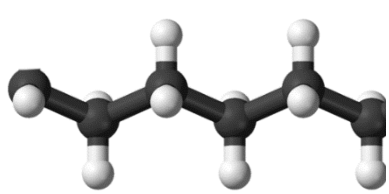
$$\dot{X} + H - Y \rightarrow X - H + \dot{Y} \tag{2}$$



(a)



(b)



(c)

Figure 4: Hydrogen abstraction

In Figure 4, (a) represents the undisturbed HDPE chain, (b) illustrates an interaction of the undisturbed HDPE chain with a chain that has undergone β −scission (hydrogen atom is missing hence carbon is acting like a free radical), and (c) shows the product after hydrogen abstraction has taken place.

2.1.3. Chain fission

The chain fission reaction takes place predominantly in the initial stages of pyrolysis, but may occur throughout the process. The fission occurs because the energy of the system is larger than the activating energy. When the chain breaks, a free radical is formed at the two extremities of the chain as illustrated below in Figure 5.

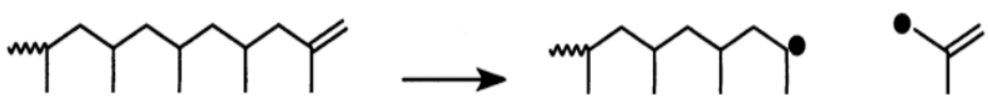


Figure 5: Chain fission [7].

2.2. Conceptual visualisation

Pyrolysis of HDPE can be conceptually visualised using a shrinking core model. An initial unreacted particle of HDPE is shown in Figure 6(a). During the pyrolysis reaction, layer by layer of HDPE tears off as shown in Figure 6(b). It is important to note that this stage would only activate when required reaction activation energy is achieved. With time the particles reach a stage as shown in Figure 6(c) and eventually disappear as indicated in Figure 6(d).

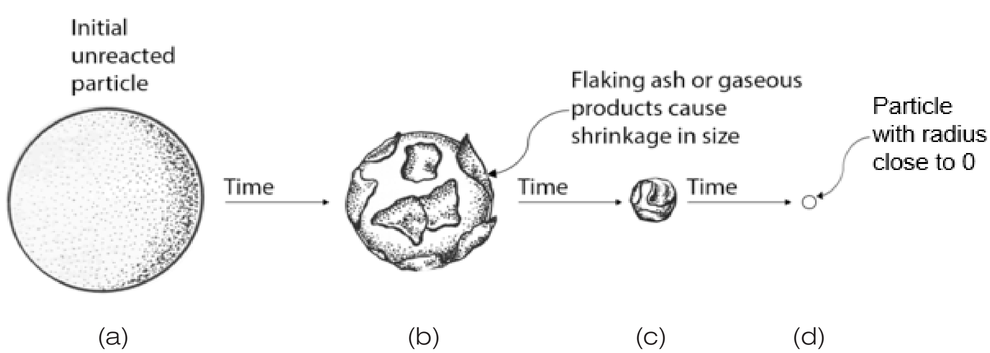


Figure 6: Conceptual visualisation of HDPE pyrolysis via shrinking core model [11].

2.3. Properties of HDPE pyrolysis products (pyrolysis oil)

The oil product produced is called pyrolysis oil and can be used as fuel for turbines and/or furnaces for refineries. It is, however, normal that diesel is mixed with the pyrolysis oil to provide more conventional fuel properties.

The typical aromatics content of pyrolysis oil has been measured to be approximately 40% [12]. For diesel, the aromatic content is typically under 35% [13]. Pyrolysis oil typically also has a higher heating value than diesel [14]. Some typical properties for pyrolysis oil in comparison to diesel oil are presented in Table 1.

Table 1: Properties of pyrolysis oil and diesel oil [14].

Property	Unit	HDPE pyrolysis oil	Diesel
Heating value	MJ/kg	46.2	45.8
Carbon	mass %	83.8	87
Hydrogen	mass %	11.4	13
Oxygen	mass %	2.0	N/A
Chloride	mass %	0.03	N/A
Density	g/cm^3 at 30°C	0.8147	0.7994
Viscosity	cP at 40°C	2.49	1.00 - 4.11
Flashpoint	°C	100	70

3. METHODS

As described above, the pyrolysis reaction consists of multiple steps before all HDPE is converted to the end products of oil, gas, and carbon black. In addition, before the pyrolysis process reaches a steady state, HDPE is also converted into several other organic substances called 'waxes'. In this paper, these substances are referred to as 'light' and 'heavy' waxes. There are many other substances present in the mixture of reaction products, but these are generally in low concentrations [7].

The waxes (light, heavy) mainly consist of aromatics, kerosene, and paraffin. Due to the high temperature, a small portion of these waxes may begin to break down further in to smaller molecules resulting in 'carbon black'. This carbon black is mostly carbon, and contains very fine particles. The carbon black is highly stable and it will not react further.

The pyrolysis reaction is a combination of multiple reactions with varying reaction constants [15]. The reaction constants determine the rate of each reaction and may depend on the concentration of reactants and products. Temperature and presence of catalyst may also affect its value. An overview of HDPE pyrolysis reactions is given in Figure 7.

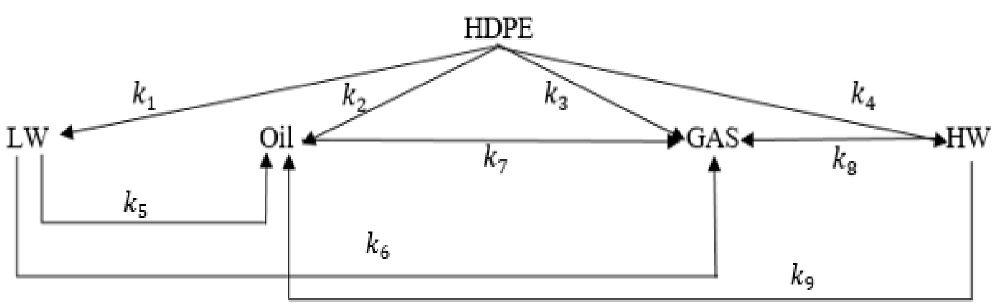


Figure 7: The complete conversion process of HDPE

As shown in Figure 7, when the conditions are met for the pyrolysis reaction to progress, the dominant product is the light wax (LW) (with reaction constant = k_1), oil (with reaction constant = k_2), gas (with reaction constant = k_3) and heavy wax (HW) (with reaction constant = k_4). In addition, the free radicals break down LW to oil (with reaction constant = k_5), LW to gas (with reaction constant = k_6), HW to gas (with reaction constant = k_8) and oil (with reaction constant = k_9). It can also be seen that some of the oil goes directly to gas (with reaction constant = k_7). The values of reaction constants 'k' at 420°C are shown in the Table 2 [13].

Table 2: The values of the reaction constants 'k' at 420°C [15]

reaction constants	min^{-1}	s^{-1}
k_1	0.170	0.00284
k_2	2.43x10^{-8}	4.05x10^{-10}
k_3	0.0301	0.000502
k_4	0.206	0.00344
k_5	0.0146	0.000243
k_6	0.0104	0.000173
k_7	2.25x10^{-14}	3.75x10^{-16}
k_8	0.0205	0.000342
k_9	3.48x10^{-10}	5.80x10^{-12}

The model that was chosen to describe the pyrolysis reactions is based upon work by [7] and [15]. The reaction equations are ordinary first order differential equations as shown in Equations (3) to (7). These equations are solved in MATLAB®. The method used to solve these equations is provided in reference [16].

$$\frac{dP}{dt} = -k_1P - k_2P - k_3P - k_4P \tag{3}$$

$$\frac{dHw}{dt} = k_4P - k_8Hw - k_9Hw \tag{4}$$

$$\frac{dLw}{dt} = k_1P - k_6Lw - k_5Lw \tag{5}$$

$$\frac{dOil}{dt} = k_2P + k_5Lw + k_9Hw - k_7Oil \tag{6}$$

$$\frac{dGas}{dt} = k_3P + k_6Lw + k_7Oil + k_8Hw \tag{7}$$

In Equations (3) to (7), $\frac{dP}{dt}$ represents the mass rate at which HDPE is being consumed; P is the mass of HDPE (reactant); Hw is the mass of heavy wax; Lw is the mass of light wax; and the values of reaction constants (k_1, k_2, k_3, k_4, k_5, k_6, and k_7) are given in Table 2.

4. RESULTS AND DISCUSSIONS

The equations presented in Section 3.1 were solved in MATLAB© using the ordinary differential equations (ODE) 23s solver (the method of solution can be downloaded from reference [16]). The results are shown in Figure 8.

The results show that HDPE is broken down relatively quickly and after about 20 minutes very little of the HDPE is left. The conversion of both heavy wax and light wax begins when the majority of the HDPE has been broken down. The production of oil and gas is rapid in the initial phases of the process and begins to level-off as the light and heavy wax produced in the early phase of the process is used-up. At approximately 2 hours, there is roughly 75% gas and 24% oil. The remaining 1% is carbon black. It is suggested in [1], [3] and [4] that the percent yield of gas should be around 70-80%. The presented results are consistent with the literature.

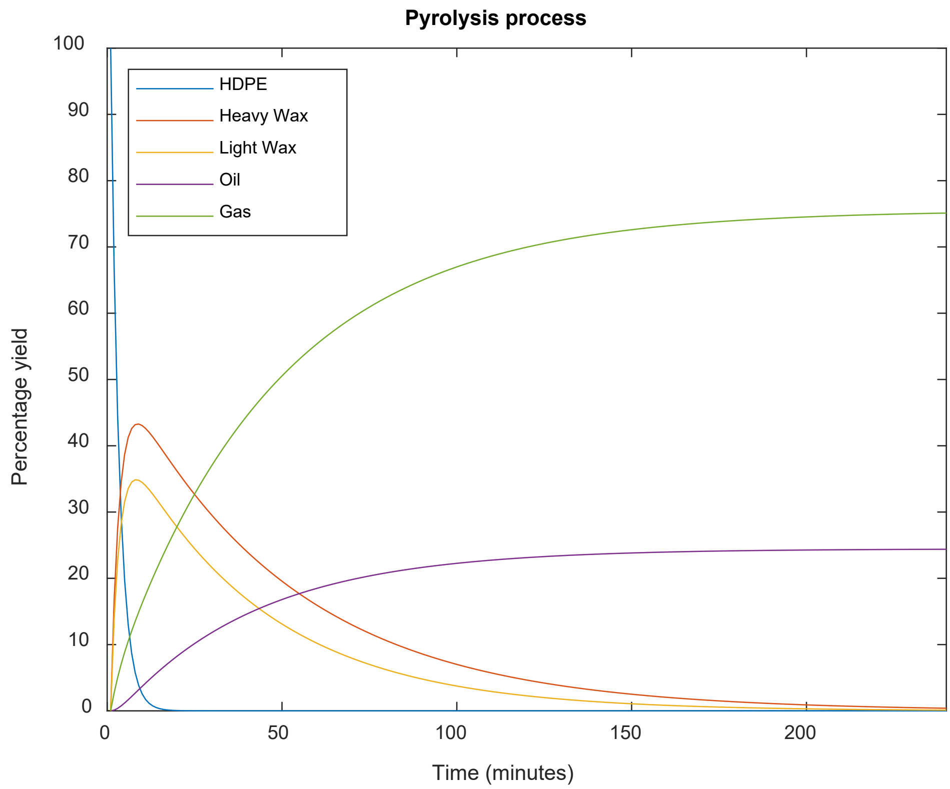


Figure 8: Simulation of pyrolysis of HDPE

The given study is only valid at 420°C and uses the assumption that no pyrolysis takes place prior to temperature reaching at 420°C. The temperature is also assumed constant throughout the duration of the pyrolysis process.

This study uses fixed values of reaction constants, however, in reality, the reaction constants are temperature dependent variables. Similarly, addition of catalysts will also affect the values of reaction constants, e.g. aluminum titanate (AlTi) powder can increase the thermal convection, hence increase the pyrolysis reaction rate [17].

5. CONCLUSIONS

This paper presents a simplistic reaction model for the HDPE pyrolysis reaction. The reaction equations are first order differential equations, which are solved in MATLAB® using ode23s solver. Results are in agreement with the literature. In order to improve the accuracy of the model, more detailed description of reaction constants is needed.

REFERENCES

[1] T. Syversen, “Pyrolyse av plast og gummi,” 26 04 2017. [Online]. Available: https://www.sintef.no/prosjekter/pyrolyse-av-plast-og-gummi/. [Accessed 26 01 2018].

[2] “Swerec AB,” [Online]. Available: http://www.swerec.se. [Accessed 25 01 2017].

[3] K. J. Mohammed, A. A. Chowdhury and M. G. Rasul, “Pyrolysis of Municipal Green Waste: A Modelling,” Energies, 2015.

[4] A. S. Abbas and S. D. Shubar, “Pyrolysis of High-density Polyethylene for the Production of Fuel-like Liquid Hydrocarbon,” 2008.

[5] Y.-F. Huang, P.-T. Chiueh and S.-L. Lo, “A review on microwave pyrolysis of lignocellulosic biomass,” Sustainable Environment Research, no. 26, pp. 103 - 109, 2016.

[6] Norsk kjemisk selskap, “Polymerisasjonskjemi,” 2007. [Online]. Available: http://www.naturfag.no/artikkel/vis.html?tid=689055. [Accessed 18. 10. 2016].

[7] T. M. Kruse, O. S. Woo, H.-W. Wong, S. S. Khan and L. J. Broadbelt, “Mechanistic Modeling of Polymer Degradation: A Comprehensive Study of Polystyrene,” Macromolecules, vol. 35, no. 20, pp. 7830-7844, 2002.

[8] S. Matar and L. F. Hatch, Chemistry of Petrochemical Processes, 2nd ed., Oxford: Gulf Professional Publishing, 2001.

[9] A. Ratkiewicz and T. N. Truong, “Kinetics of the C−C Bond Beta Scission Reactions in Alkyl Radical,” 2012.

[10] W. Lai, C. Li, H. Chen and S. Shaik, “Hydrogen-Abstraction Reactivity Patterns from A to Y: The Valence Bond Way,” Angewandte Chemie International Edition, vol. 51, no. 23, pp. 5556-5578, 2012.

[11] O. Levenspiel, Chemical Reaction Engineering, 2nd ed., Wiley , 1972.

[12] P. T. Williams, “Pyrolysis of Waste Tyres: A Review,” White Rose Research Online, Leeds, 2013.

[13] “Advanced Motor Fuels,” 2010. [Online]. Available: http://www.iea-amf.org/content/fuel_information/diesel_gasoline. [Accessed 04 11 2016].

[14] C. Wongkhorsub and N. Chindaprasert, “A Comparison of the Use of Pyrolysis Oils in Diesel Engine,” Energy and Power Engineering, vol. 5, pp. 350-355, 2013.

[15] Y. Safadi, J. Zeaiter and M. Ahmad, “Advanced Modeling of High Density Polyethylene Pyrolysis,” Int. J. of Thermal & Environmental Engineering, vol. 5, no. 2, pp. 123-128, 2013.

[16] H. Khawaja, “mathworks,” mathworks, 5 2 2018. [Online]. Available: https://se.mathworks.com/matlabcentral/fileexchange/65954-hdpe-pyrolysis-reaction. [Accessed 5 2 2018].

[17] D. Fabbri, C. Torri and I. Mancini, “Pyrolysis of cellulose catalysed by nanopowder metal oxides: production and characterisation of a chiral hydroxylactone and its role as building block,” Green Chemistry, vol. 9, no. 12, pp. 1374 - 1379, 2007.

[18] N. C. Norman, Periodicity and the S- and P-block Elements, Oxford University Press, 1997.

[19] S. H. Ng and Y. Sugimoto, “Conversion of Polyethylene to Transportation Fuels,” 1995.

[20] J. M. Kuchta , “Investigtion of Fire and Explosion Accidents in the Chemical, Mining, and fuel-Related Industries - A manual,” 1985.

[21] E. Khaghanikavkani and M. M. Farid, “Thermal Pyrolysis of Polyethylene: Kinetic Study,” Energy Science and Technology, vol. 2, no. 1, pp. 1-10, 2011.

[22] H. James and T. L. Cottrell, The Strengths of Chemical Bonds, 2nd ed., 1958.

[23] D. Cremer, A. Wu, A. Larsson and E. Kraka, “Some Thoughts about Bond Energies, Bond Lengths, and Force Constants,” 2000.

[24] C.-E. Boström, P. Gerde, A. Hanberg, B. Jernström, C. Johansson, T. Kyrklund, A. Rannug, M. Törnqvist, K. Victorin and R. Westerholm, “Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air,” Environmental Health Perspectives, vol. 110, no. 3, pp. 451-488, 2002.

[25] J. C. Earl, Carbon-Carbon Bond Energies, 1959.

[26] R. Sadeghbeigi, Fluid Catalytic Cracking Handbook, 3rd ed., Oxford: Elsevier, 2012.

[27] Balboa Pacific, “Balbia Pacific,” 2004. [Online]. Available: http://www.balboa-pacific.com/Papers/HistoryOfPyrolysis.pdf. [Accessed 03. 11. 2016].