

Thermal Pyrolysis of Waste Disposable Plastic Syringes and Pyrolysis Thermodynamics

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Abstract

In this study, the convertibility of disposable plastic waste injectors made of HDPE and PP plastics into valuable chemical products by thermal pyrolysis was investigated. While PP plastic wastes were decomposed in the temperature range of 400°C - 445°C, HDPE plastic wastes were decomposed in the higher temperature range (430°C - 475°C). Although the physical appearance of the liquid products obtained in the thermal decomposition of PP plastic wastes are lighter in color and fluid, it has been observed that the liquid decomposition products of HDPE plastic wastes have a more dense and viscous structure. By using the first-order kinetic model, kinetic expressions for both plastic wastes were derived, reaction rate constants, k , and activation energy, E_{act} and thermodynamic quantities such as reaction enthalpy, ΔH^\ddagger , reaction entropy, ΔS^\ddagger ve and Gibbs free energy, ΔG^\ddagger were calculated. In the thermal pyrolysis of PP and HDPE plastic wastes, E_{act} , ΔH^\ddagger , ΔG^\ddagger , ΔS^\ddagger values are 162.30 kJ/mol, 156.52 kJ/mol, 219.50 kJ/mol, -87.71 J/molK, and 201.80 kJ/mol, 195.77 kJ/mol, and 229.14 kJ/mol, -46.48 J/molK, respectively. These thermodynamic quantities calculated for both plastic wastes show that the pyrolytic decomposition studies carried out in an inert gas atmosphere have endothermic reaction behavior.

Keywords

Plastic Waste Injector, Rate Constant, Thermodynamic Quantities

1. Introduction

Today, chemical recycling of plastic waste has become an extremely important process and there are many scientific studies in this field. However, in very few of these scientific studies, "Pyrolysis Thermodynamics" has been evaluated or the pyrolytic approach of thermodynamic principles has not been evaluated. In

this study, the thermodynamic approach, which is one of the less-studied topics in the pyrolysis of plastic waste, has been evaluated. Although reproducibility is very difficult in experimental studies carried out in isothermal conditions, this issue was also studied very carefully in my current study, and experimental data were obtained and interpreted with precision accordingly.

Although the socio-economic structures of today's societies are different, similar basic consumption habits cause the generation of important environmental wastes. A significant part of these wastes is plastic wastes which constitute a considerable proportion of municipal solid waste (MSW). As plastic materials are not biodegradable, they can preserve their structures for a long period of time, which can be expressed in centuries, in nature, and protect their stable structures, hence causing important environmental problems. Especially in recent years, it is attempted to limit the usage of plastic materials in many countries in recent years. However, both the usage habits of people and the ease of processing of plastic materials resulted in becoming waste after the use of these materials. Alternative energy sources such as biomass, hydroelectric and wind energy, which have less negative effects on the environment than fossil fuels, attract a lot of attention today [1] [2]. Low density polyethylene (LDPE) plastic which is a major product within plastics and formed a high amount of waste, was chemically degraded thermally and catalytical in air media. In that study, it was reported that the oxygenated compounds obtained in the oxidative thermal pyrolysis experiments using air were approximately 85% more than the oxygenated products obtained in the catalytic environment [3].

Since plastics are petroleum-derived materials, the increasing demand for plastics is also affecting the current status of petroleum resources as a non-renewable fossil fuel. The recycling of plastic waste to obtain energy shows considerable progress as a result of innovation implementation and extensive research. Since plastics are petroleum products and liquid products obtained by pyrolysis process of them have high calorific value, they can be used as an alternative fuel [4]. Incineration of plastics to obtain energy may result in air pollution problems with pollutants such as chloride compounds, dioxins, and some toxic gases from incineration process. Despite that, since plastics are products obtained from petroleum resources, development of processes for converting these polymers into fuels in order to meet the future fuel demand is of great importance. Thus, the conversion of plastic waste into fuel with clean combustion processes will contribute significantly to the protection of the environment. It has been stated that plastic waste can be effectively reduced by dissolving plastics and applying thermal conversion technology known as thermolysis [5].

Plastic waste recovery can be achieved by four methods, namely primary recovery, secondary recovery, tertiary (chemical) recovery and quaternary (energy production) recovery. The tertiary recovery process is known as pyrolysis, and in this method, plastics are broken down into smaller molecules by thermal decomposition in an oxygen-free environment [6] [7] [8]. In recent years, many scientific and industrial studies have been carried out on the production of new

petrochemical raw materials from these petroleum-derived wastes by pyrolysis which is one of the important processes in recycling methods. With the catalytic pyrolysis processes, these plastic wastes are recycled, reducing their volume in the environment, and at the same time, they are converted into gas, liquid and solid products with economic value [9]. Since plastics are petroleum-derived products, it has gained great importance to convert these wastes into liquid products with high calorific value by pyrolysis process. Reaction conditions such as temperature, residence time, catalyst, pressure, carrier gas, etc. and reactor types such as batch, semi-batch, continuous, etc., play an important role to obtain liquid products with high fuel value through pyrolysis applications [10].

It has been reported that the aromatic hydrocarbon ratio obtained as a result of chemical degradation using PP plastic waste was higher than the aromatic component ratio obtained in the mixed pyrolysis study of polyolefins such as PP, PE, PS. In the same study, it was emphasized that as a result of the chemical decomposition of plastic wastes by pyrolysis, hydrocarbons with similar structure could be obtained in the petroleum industry and this application could be an alternative method [11]. Pyrolysis of polyolefins in the fluidized bed reactor, it was reported that heat transfer in fluidized beds was a crucial advantage. It was stated that cracking process was faster and side reactions were lower. Olefins and oil were obtained in liquid phase and aromatic hydrocarbons were obtained if pyrolysis gas was used as fluidization gas. In the same study, it was also emphasized that fluidized bed pyrolysis of plastics had a significant potential to recycle large amounts of plastic waste [12].

In general, it has been reported that the catalytic cracking of the LDPE-benzene solution in the fixed bed reactor occurred with higher efficiency than the conventional reactors and they had the potential to obtain hydrocarbon energy from recycled plastic waste [13] [14]. In pyrolysis processes, the amount of solid residue remaining in the reactor, which is an important by-product, depends on some factors such as slow heating rate at low temperature and residence time in the reactor. In the pyrolysis of HDPE plastics, it was reported that the main components of the residue were volatile components and fixed carbon, while ash and bound moisture were the least, and it was emphasized that the calorific value and density of the char were also determined and reported as 4500 cal/g and 1.59 g/cm³, respectively [15].

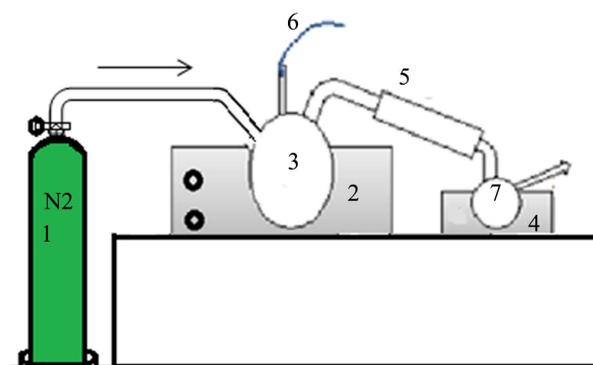
2. Material and Methods

2.1. Experimental Study

In this study, disposable waste plastic injectors produced from HDPE (piston) and PP (transparent body) plastics were thermally decomposed. Thermal degradation experiments of plastic wastes were carried out in an inert environment prepared by using nitrogen gas at a flow rate of 175 mL/min. It has been accepted that the inert nitrogen gas does not react with the decomposition products of the waste plastics in the reactor and has no effect on the chemical struc-

ture of the products. It has been reported that the reaction products and product yield are obtained at different rates in the case of using different carrier gases, [16]. Generally, nitrogen gas is used for two purposes in plastic waste pyrolysis experiments; the first ensures that the environment is in an inert atmosphere, and the second ensures that the gas-steam mixtures formed in the pyrolysis reactions are carried out of the reactor. Since PP and HDPE polymers decompose at different temperatures due to their chain structure (branched, asymmetric spatial arrangement, etc.), different temperature ranges are selected for each plastic. For both plastic wastes, the temperatures were increased at intervals of 15 K, PP plastic wastes were decomposed at 673 - 718 K and HDPE plastic wastes were decomposed in the temperature range of 703 - 748 K. Temperature values of 703 K and 718 K were determined as common decomposition temperatures for both plastics. Waste plastic degradation experiments were carried out in a 500 mL pyrex glass reactor placed in a stirred and temperature-controlled mantle heater. A thermocouple was used to measure the reaction temperature, and a glass tube with a thinned outlet end connected to the nitrogen tube hose was immersed in the hot liquid in the reactor to send nitrogen gas. After passing the vapor-gas mixture products coming out of the reactor through a water-cooled cooler, they were passed through a second cooler containing salt-ice mixture and able to cool down to about 251 K, and the condensable products were collected as liquid (Figure 1). After calculating the yields of collected liquid products for each plastic waste, the liquid products obtained were stored in separate containers.

After weighing the liquid products obtained by the condensation of the vapor from the reactor in the coolers and the heavy residue that decomposed but remained in the reactor, the gas product yield was calculated from the total difference as follows. Gas, liquid and total product conversions (TC) and percent of heavy residue decomposed but remaining in the reactor were calculated as weight percent (% wt) over the plastic waste fed to the reactor using the equations below.



1. N2 gas cylinder, 2. Heater mantle, 3. Reactor, 4. Ece-salt bath, 5. Condenser, 6. Thermocouple, 7. Liquid product container.

Figure 1. The experimental setup of pyrolysis experimental.

$$\text{Liquid yield (wt \%)} = \frac{M_L}{M_{Po}} * 100 \quad (1)$$

$$\text{Gas yield (wt \%)} = \frac{M_G}{M_{Po}} * 100 \quad (2)$$

$$\text{Residue (wt \%)} = \frac{M_R}{M_{Po}} * 100 \quad (3)$$

$$\text{Total Conversion (x, \%)} = \left(\frac{M_L + M_G}{M_{Po}} \right) * 100 \quad (4)$$

The alphabets in Formulas (1)-(4) are as follows: M_{Po} : The plastic weight before experiment (g), M_G : The gas weight after experiment (g), M_L : The liquid weight after experiment (g), M_R : The residue weight after experiment (g).

2.2. Kinetic Analysis and Pyrolysis Thermodynamics

While examining the reaction kinetics and thermodynamics, besides determining the reaction rate constants, it is of great importance to interpret the parameters related to reaction thermodynamics such as reaction enthalpy, reaction entropy, Gibbs Free energy. The mathematical equation between the reaction rate constant, k , and the activation energy, E_a , which is the relative indicator of the reaction rate, can be interpreted using Arrhenius's Law (Equation), and reaction thermodynamics can be interpreted by using Eyring Equations [17] and classical thermodynamic equations. The Eyring equations can facilitate the thermodynamic interpretation of the absolute reaction rate constants associated with the formation of the activated complex. Since the Arrhenius equation (Equation 5(a)) is an exponential expression, it is of great importance to linearize (Equation 5(b)) the equation by taking its natural logarithm so that it can be interpreted meaningfully.

$$k = A \exp\left(-\frac{E_{act}}{RT}\right) \quad (a) \quad (5)$$

$$\Rightarrow \ln k = \ln A - \frac{E_{act}}{R} \frac{1}{T} \quad (b)$$

The equations proposed in the kinetic studies are given below depending on the conversion.

$$\frac{dx}{dt} = k(1-x)^n; \quad (nth \text{ order kinetics}) \quad (6)$$

If the k value from (5-a) is written in Equation (6) and the logarithm of the equation is taken, a linear line equation is obtained.

$$\frac{dx}{dt} = A \exp\left(-\frac{E_{act}}{RT}\right)(1-x)^n$$

$$\ln\left(\frac{dx}{dt}\right) = \ln A + n \ln(1-x) - \frac{E_{act}}{R} \frac{1}{T} \quad (7)$$

where, x is the conversion of plastic (by weight), A is the frequency factor (s^{-1}),

E_{act} is the activation energy (J/mol), R is the universal gas constant (8.314 J·mol⁻¹·K⁻¹), T is the absolute temperature (K), and n is the overall reaction order. In the 1st order reaction kinetics, $n = 1$ and then the following equation (Equation (8)) is written.

$$\ln\left(\frac{dx}{dt}\right) = \ln A + \ln(1-x) - \frac{E_{act}}{R} \frac{1}{T}, \quad (n=1) \quad (8)$$

From the first-order kinetic assumption and the definition of the reaction rate law, the conversion-time, (x ; t) relationship was written and the reaction rate constants, k , (1/s) were determined using the equations below.

$$(-r_A) = -\frac{dC_A}{dt} = kC_A; \text{ or by conversion, } \frac{dx}{dt} = k(1-x) \quad (9)$$

Equation (9) was arranged and integrated, and Equation (10) below, which gives the relationship between conversion and time, was obtained.

$$\int \frac{dx}{1-x} = k \int dt \Rightarrow -\ln(1-x) = kt; \quad (x = 1 - e^{-kt}) \quad (10)$$

From Equation (10), [t ; $-\ln(1-x)$] is plotted and the reaction rate constant is calculated. After calculation the rate constants, ($\ln k - 1/T$) graph was drawn from Equation (5) and activation energy (E_{act}) and frequency factor (Arrhenius constant, A) were calculated.

Eyring equations (Equation (11) and Equation (13)) which interpret the thermodynamic quantities together with the reaction rate constant and are very important in chemical kinetics can be written in different ways as follows.

$$k = \left(\frac{k_B T}{h}\right) \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (11)$$

In this equation, k_B is Boltzman's constant and h is Planck's constant and their values are respectively (1.380649×10^{-23} J·K⁻¹) (6.626×10^{-34} J·s). The Equation (12) between Gibbs free energy and reaction enthalpy and reaction entropy can be written from classical thermodynamics.

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (12)$$

If Equation (12) is written and arranged in Equation (11), the reaction rate constant and thermodynamic quantities are interpreted together as follows.

$$k = \left(\frac{k_B T}{h}\right) \left(e^{\frac{\Delta H^\ddagger}{RT}} \right) \left(e^{\frac{\Delta S^\ddagger}{R}} \right)$$

$$\ln k = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \ln\left(\frac{k_B T}{h}\right) + \frac{\Delta S^\ddagger}{R} \quad (13)$$

where k is reaction rate coefficient (first order kinetics, min⁻¹), T is absolute temperature (K), ΔH^\ddagger is reaction enthalpy (J·mol⁻¹), R is ideal gas constant (J·mol⁻¹·K⁻¹) and ΔS^\ddagger is the reaction entropy (J·mol⁻¹·K⁻¹). If Equation (5) and Equation (8) are derived according to temperature ($d\ln k/dT$) and evaluated together, the Equation (13) between activation energy, (E_{act}) and reaction enthalpy, is obtained as follows.

$$E_{act} = RT + \Delta H^\ddagger \quad (14)$$

Similarly, using Equations (12) and (14), taking into account Equations (5) and (13), the difference between reaction entropy (ΔS^\ddagger), Arrhenius constant (frequency factor, A) and reaction temperature, (T), the following equation can be written [10] [18].

$$\Delta S^\ddagger = R \left(\ln A - \ln \left(\frac{k_B}{h} T \right) - 1 \right) \quad (15)$$

In many scientific studies [19] [20] [21] on plastic degradation (pyrolysis), the degradation (thermal or catalytic) of polyolefins (PEs, PP, PET, PS and PVC) has been explained by **1st** order reaction kinetics and determination of kinetic constants are discussed. In these studies, when the kinetic parameters obtained under thermal or catalytic decomposition conditions were evaluated, it was stated that the activation energy values were mostly lower in catalytic decomposition studies. In this study, first-order reaction kinetics were chosen as the model and using experimental values, kinetic parameters such as reaction rate constants, activation energy values and Arrhenius constants calculated. With the help of these kinetic parameters, thermodynamic properties such as reaction enthalpy, reaction entropy, Gibbs free energy were calculated and interpreted using the equations given above. Equation (13) is rearranged depending on the temperature and a straight line (16) was obtained as follows.

$$\ln \left(\frac{k}{T} \right) = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \ln \left(\frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} \quad (16)$$

From Equation (16), the enthalpy (ΔH^\ddagger) and entropy (ΔS^\ddagger) values were calculated by plotting [$1/T: \ln(k/T)$]. In addition, the following expression (17) can be written from the last two terms of Equation (16);

$$\ln \left(\frac{k_B}{h} \right) + \frac{\Delta S^\ddagger}{R} = \ln \left(\frac{1.380649 \times 10^{-23} \text{ J/K}}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}} \right) + \frac{\Delta S^\ddagger}{R} = 23.76 + \frac{\Delta S^\ddagger}{R} \quad (17)$$

We can extract the value of ΔH^\ddagger and ΔS^\ddagger from kinetic data and Equation (16), then the Gibbs free energy, ΔG^\ddagger , can be calculated by Equation (12) for the suitable reaction temperature. ΔG^\ddagger represents the determining driving power for a reaction [20]. The sign of ΔG^\ddagger determines if a reaction spontaneous or not; also we know that if,

- $\Delta G^\ddagger < 0$, reaction is spontaneous;
- $\Delta G^\ddagger = 0$, system at equilibrium;
- $\Delta G^\ddagger > 0$, reaction is not spontaneous. (18a)

$$\text{and also if } \frac{-\Delta G^\ddagger}{RT} \gg 1 \text{ The pyrolysis process is called completed.} \quad (18b)$$

3. Results and Discussion

3.1. Pyrolysis Product Yields

The variation of the recycling of waste HDPE plastics (plunger, HDPE100) with

the chemical decomposition method (pyrolysis) with temperature at different pyrolysis durations is given in **Figure 2**. As seen in **Figure 2**, the lowest total conversion took place in 1200 seconds and the highest total conversion took place in 4500 seconds.

At the end of the lowest pyrolysis time of 1200 s, the total pyrolysis conversion increases rapidly with temperature, while this increase occurs more slowly at the highest reaction time of 4500 s. At the end of the shortest pyrolysis time of 1200 s, the total product conversion was 8.5% and 96.5% (by weight) at temperatures of 703 K and 748 K, respectively. However, for the longest reaction time of 4500 s, the increase in total conversion was from 47% to 99.5% at the same temperatures. At 748 K, the highest temperature studied, the total conversion was between 96.5% and 99.6% for all reaction times. At all reaction temperatures, when the pyrolysis time was increased by 600 s, different rates of increase in the total conversion occurred despite each 15 K increase in the reaction temperature. The reason for this difference can be explained by the fact that endothermic plastic decomposition reactions occur more voluntarily at higher reaction temperatures. Because, at high reaction temperatures, due to the greater free mobility of the decomposition products, the increase in their entropy is greater and molecular interactions lead to the emergence of new compounds.

The variation of the total product conversion obtained from the thermal decomposition reaction of HDPE plastic wastes during the reaction at different temperatures is given in **Figure 3**. As seen in **Figure 3**, the total conversion increases significantly with time in the temperature range of 703 - 733 K. However, the change obtained at 703 K temperature is higher than other temperatures. Contrary to the other three temperature values, although there was not much change in the product efficiency during the reaction at 748 K, the total conversion was approximately 98% at the highest value.

This change did not come as a surprise; Because the thermal pyrolysis reactions of plastics carried out in an inert atmosphere are endothermic and the total conversion increases rapidly as the reaction temperature increases. It has been reported that oxidative pyrolysis reactions of LDPE plastic wastes are exothermic

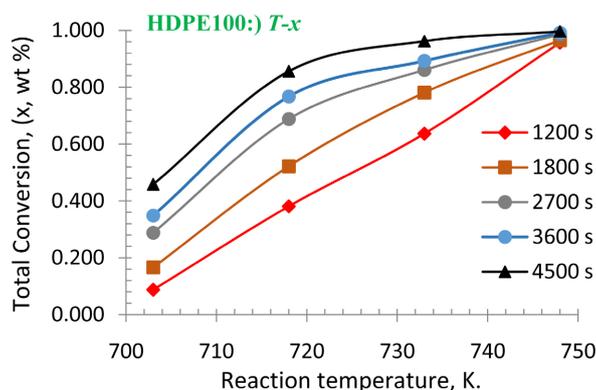


Figure 2. In thermal pyrolysis of HDPE plastic wastes, variation between reaction temperature and total conversion at different pyrolysis times.

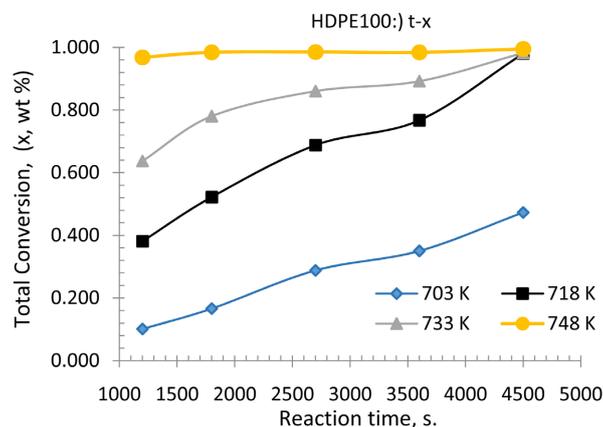


Figure 3. Variation between reaction time and total conversion in thermal pyrolysis of HDPE plastic wastes at different reaction temperatures.

and occur much faster than endothermic thermal pyrolysis reactions [20]. As a result, in the thermal degradation study of HDPE waste plastics, it was observed that the total product conversion increased significantly both with increasing the temperature and longer reaction times.

The variation of the total conversion with temperature in the pyrolysis of PP plastic wastes (transparent body of the injector) at different pyrolysis times is given in Figure 4. It can be seen from Figure 4 that the total conversion in low pyrolysis time was lower than in other pyrolysis times, but it increased rapidly with the increase in temperature. At the lowest pyrolysis time of 1200 s, the total conversion took place at the rate of approximately 40% at the lowest temperature, while it increased to approximately 87% at the highest temperature with the increase in temperature.

The highest pyrolysis time of 3600 seconds; While the total product conversion was approximately 50% at the lowest pyrolysis temperature, approximately 98.6% was obtained at the highest temperature in parallel with the increase in temperature. With the exception of the 3600 s reaction time, the total conversion in other reaction times was 98%, starting from about 40%, with an increase of approximately 2.5 times at the end of the 45 K temperature increase with a 15 K temperature increase.

The variation of the total product conversion obtained from the thermal decomposition reaction of PP plastic wastes during the pyrolysis at different temperatures is given in Figure 5. According to Figure 5, there was no significant increase in total product conversions at temperatures of 673 K and 718 K. However, especially at 688 K pyrolysis temperature, the total conversion increased from about 42% to 85% with increasing pyrolysis time. The total product conversion at the highest pyrolysis temperature ranged from about 92% to 98%. In this way, it is an expected result that the total product conversion will differ at different pyrolysis temperatures. Because the pyrolysis reactions carried out in an inert environment are sensitive to temperature and it is an expected result that the total yield will be obtained at high temperatures.

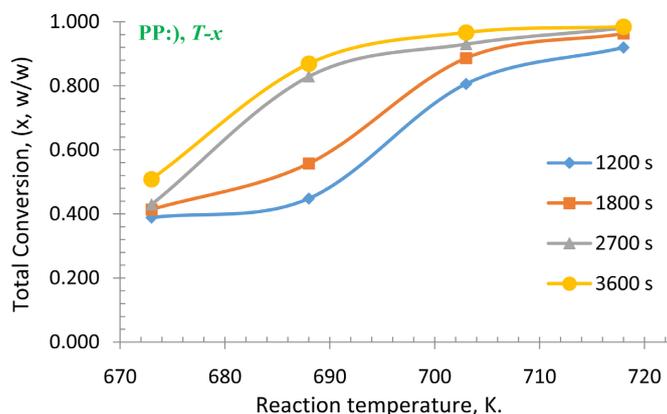


Figure 4. Variation between reaction temperature and total conversion in thermal pyrolysis of PP plastic wastes at different reaction times.

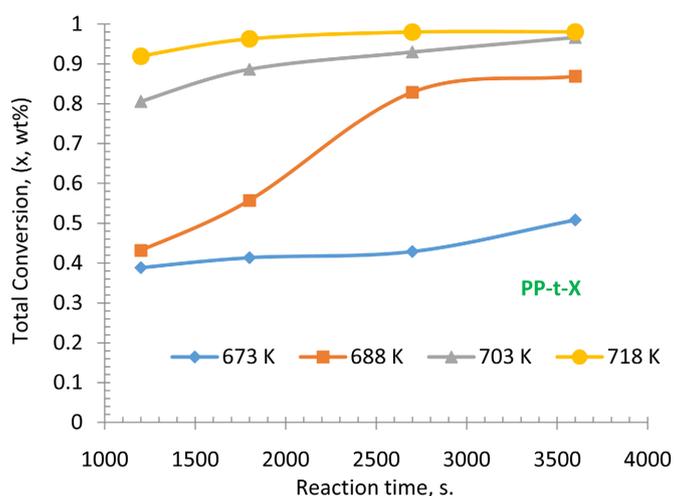


Figure 5. Variation between reaction time and total conversion in thermal pyrolysis of waste PP at different reaction temperatures.

3.2. Kinetic Analysis and Pyrolysis Thermodynamics

In order to elucidate the pyrolysis reaction mechanisms, kinetic analyzes are of great importance. For this purpose, the kinetic data of the pyrolysis of HDPE and PP plastic wastes, whose pyrolysis conversion results were interpreted in the paragraphs above, were obtained. Calculation of these kinetic constants can be done by using some model equations as well as a first-order reaction kinetic model can be applied [22]. In this study, first-order reaction kinetics was chosen as the model and according to this assumption; kinetic constants were calculated by drawing appropriate graphs from Equation (10). In **Figure 6**, the variation of experimental data obtained at different temperatures according to the 1st order reaction kinetics in HDPE plastic waste pyrolysis with time is shown.

The graph of $[t: -\ln(1 - x)]$ drawn according to Equation (10), changes linearly as in **Figure 6** and therefore it is seen that the 1st order kinetic model assumption made for the experimental data is appropriate. According to the graph, especially at the temperature of 718 K the linearity coefficient was

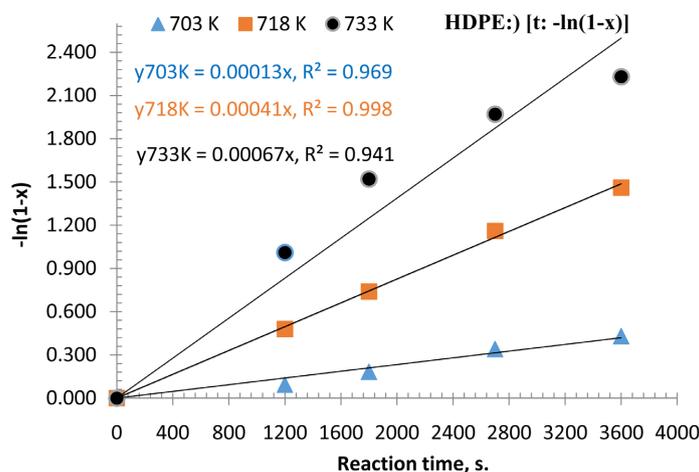


Figure 6. The variation of the data obtained as a result of the pyrolysis of HDPE wastes at different temperatures with the pyrolysis time according to the first-order kinetic model.

realized at a high value ($R^2 = 0.998$) and the rate constant was calculated as $4.1 \cdot 10^{-4} \text{ s}^{-1}$ at this temperature. The rate constants were calculated from the slope of the lines in the graph, and they were found to be $1.3 \cdot 10^{-4} \text{ s}^{-1}$ at the lowest pyrolysis temperature of 703 K, and $6.7 \cdot 10^{-4} \text{ s}^{-1}$ at the highest pyrolysis temperature of 748 K. These numerical values of the rate constants obtained for different temperatures show that as the reaction temperature increases, the reaction rate constant and therefore the reaction rate increases. In the change given in **Figure 3**, it was stated that the total product conversion was much higher at high pyrolysis temperatures. When these reaction rate constants and the results obtained from **Figure 3** are evaluated together, it is seen that there are results that support each other.

There are some important differences between the calculated reaction rate constants in the thermal pyrolysis of PP and HDPE plastic wastes decomposed at different temperatures. The variation of the data obtained as a result of the pyrolysis of PP plastic wastes at different temperatures with the pyrolysis time according to the first-order kinetic model is given in **Figure 7**. In **Figure 7**, it is seen that the pyrolysis rate constants of PP plastic wastes increase with increasing pyrolysis temperature. The pyrolysis rate constants of PP waste plastics at 703 K and 718 K temperatures were calculated as $10.2 \cdot 10^{-4} \text{ s}^{-1}$ and $13.9 \cdot 10^{-4} \text{ s}^{-1}$, respectively.

These numerical values show that the rate constants are also higher at higher temperatures. However, it was stated that the rate constants of HDPE plastic wastes were found to be lower at the same pyrolysis temperatures (in **Figure 6**). When the thermal pyrolysis rate constants of HDPE plastic wastes and PP plastic wastes are compared for 703 K and 718 K temperatures, it is seen that the PP rate constants are 8.5 and 3.4 times higher, respectively.

The higher reaction rate of thermal pyrolysis of PP plastic waste under the same temperature conditions indicates that PP plastic waste pyrolysis can be completed earlier than HDPE plastic waste pyrolysis. The differences in the rate

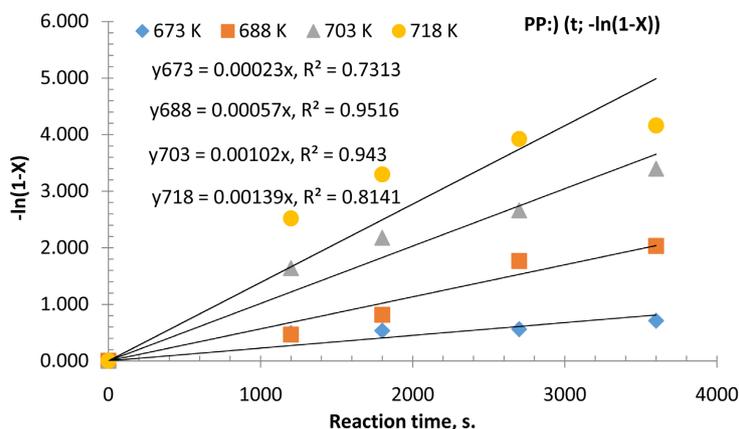


Figure 7. The variation of the data obtained as a result of the pyrolysis of PP plastic wastes at different temperatures with the pyrolysis time according to the first-order kinetic model.

constants of the two plastic waste pyrolysis at the same temperature conditions also showed differences in the total conversion in the pyrolysis reactions. For example, was emphasized in the paragraphs above that the total conversion rates of HDPE and PP plastic waste pyrolysis were approximately 34.9% (in **Figure 2**) and 96.7% (in **Figure 4**), respectively, at 703 K temperature and 3600 s pyrolysis time. Similarly, from the same graphs, the total conversion values of HDPE and PP waste plastics for 3600 s pyrolysis time and 718 K temperature were approximately 76.7% and 98.4%, respectively.

The reaction rate constants, linearity coefficients (R^2) and rate equations in terms of transformation obtained from **Figure 6** and **Figure 7** at different pyrolysis temperatures are given in **Table 1**. The rate constants in this table, together with the pyrolysis temperatures, were evaluated in the Arrhenius equation (Equation 5(b)) (**Figure 8**).

Activation energies (E_{act} , kJ/mol) of HDPE and PP plastic waste pyrolysis were calculated from the slope of the lines in the graph drawn according to Equation 5(b) and Arrhenius constants (frequency factor, A , s^{-1}) were calculated from the axis intercept value and summarized in **Table 2**.

As seen in **Table 2**, the activation energies obtained in the pyrolysis of PP and HDPE plastic wastes were calculated as 162.3 kJ/mol and 201.8 kJ/mol, respectively. Arrhenius constants in the pyrolysis of PP and HDPE plastic wastes were calculated as $1.02 \cdot 10^9$ and $1.53 \cdot 10^{11}$, respectively. When these activation energy values and rate constants are evaluated together, it is seen that there are results that support each other. The higher the activation energy of a chemical reaction, the more strongly the rate constant of the reaction depends on temperature. Namely, we have discussed above that the rate constants calculated in the pyrolysis of both PP and HDPE plastic wastes increase with the increase in temperature. However, at the same temperature (e.g. 718 K), the calculated rate constant for PP plastic waste was found to be approximately 3.4 times higher than the calculated rate constant for HDPE. The fact that the activation energy calculated

for HDPE plastic wastes is higher than the calculated value for PP indicates that the pyrolysis of HDPE took place at higher temperatures and therefore requires more energy. Because we discussed above that the product conversion of HDPE plastic waste pyrolysis is much lower than PP pyrolysis at the mentioned temperature (718 K).

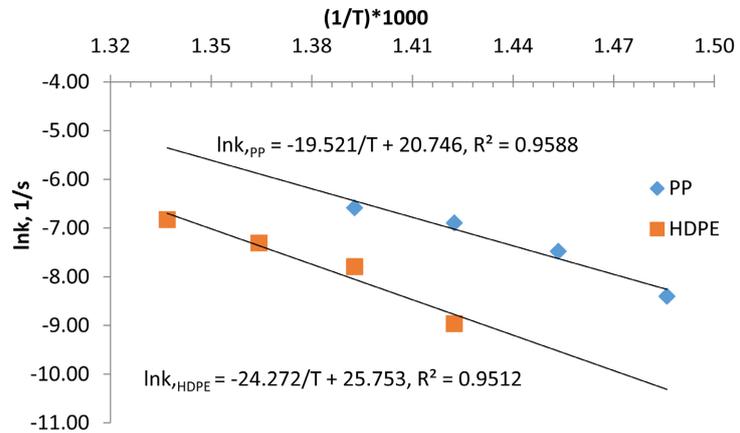


Figure 8. $1/T$ - $\ln k$ change in the pyrolysis of PP and HDPE plastic wastes (From Equation 5(b)).

Table 1. Variation of reaction rate constants with temperature and rate equations obtained from $[t; -\ln(1-x)]$ graph for thermal pyrolysis of PP and HDPE plastic wastes.

Waste Plastic	Pyrolysis Temperature, K	Rate coefficients, (k , 1/s)	R^2	Rate equations
PP	673	2.3×10^{-4}	0.734	$x_{673} = 1 - e^{-2.3 \times 10^{-4} t}$
	688	5.7×10^{-4}	0.952	$x_{688} = 1 - e^{-5.7 \times 10^{-4} t}$
	703	10.2×10^{-4}	0.943	$x_{703} = 1 - e^{-10.2 \times 10^{-4} t}$
	718	13.9×10^{-4}	0.814	$x_{718} = 1 - e^{-13.9 \times 10^{-4} t}$
HDPE	703	1.3×10^{-4}	0.958	$x_{703} = 1 - e^{-1.3 \times 10^{-4} t}$
	718	4.1×10^{-4}	0.999	$x_{718} = 1 - e^{-4.1 \times 10^{-4} t}$
	733	6.7×10^{-4}	0.959	$x_{733} = 1 - e^{-6.7 \times 10^{-4} t}$
	748	10.9×10^{-4}	0.968	$x_{748} = 1 - e^{-10.9 \times 10^{-4} t}$

Table 2. Activation energy and frequency factor values obtained in the pyrolysis of HDPE and PP plastic wastes (from Figure 8).

Plastic waste	$\ln k; \frac{1}{T}$ equation	R^2	Slope = $-\frac{E_{act}}{R}$	E_{act} kJ/mol	Intercept = $\ln A$	$A, 1/s$
PP	$\ln k_{PP} = -\frac{19.521}{T} + 20.746$	0.9588	-19.521	162.30	20.746	1.02×10^9
HDPE	$\ln k_{HDPE} = -\frac{24.272}{T} + 25.753$	0.9512	-24.272	201.80	25.753	1.53×10^{11}

The ΔS^\ddagger values calculated using experimental values provide important information about the nature of the transition state and the structure of the activated complex. Loosely bound complexes have higher entropy than tightly bound complexes. Positive activation entropy means that the entropy of the complex is greater than that of the reactants. For a chemical reaction to occur spontaneously, the Gibbs free energy change must be negative. During a chemical reaction, some chemical bonds are broken; some new chemical bonds are formed or rearranged. In this case, the change in enthalpy of the system and the change in Gibbs free energy play a big role.

According to the first law of thermodynamics, the enthalpy change gives the basic information necessary for an engineering significant analysis of the system. Similarly, Gibbs free energy changes in a chemical reaction give information about whether there is a chemical equilibrium state in the system in question [23] [24].

Some thermodynamic magnitudes of pyrolysis reactions of HDPE and PP plastic wastes were calculated by using the reaction rate constants determined as described above. In an experimental study [25] it has been reported that thermodynamic parameters such as activation energy, enthalpy, entropy, and Gibbs free energy may be advantageous to reduce the degree of disorder in the thermal pyrolysis of the plastic waste mixture. $1/T - \ln(k/T)$ graph was drawn according to Equation (16) and lines with negative slope were obtained for both plastic wastes pyrolysis (Figure 9). The enthalpy (ΔH^\ddagger , kJ/mol) of pyrolysis was calculated from the slope of these lines ($\Delta H^\ddagger/R$), and the pyrolysis entropy (ΔS^\ddagger , J/molK) was calculated from the intercept value ($23.76 + \Delta S^\ddagger/R$). Using these calculated enthalpy and entropy values, the Gibbs free energy of the pyrolysis reaction (ΔG^\ddagger , kJ/mol) at certain temperatures was calculated. These calculated thermodynamic magnitudes are summarized in Table 3.

As can be seen in Table 3, the calculated reaction enthalpy and Gibbs free energy values for the pyrolysis of both HDPE and PP plastic wastes are positive, while the calculated entropy values are negative for both plastic wastes. Since the

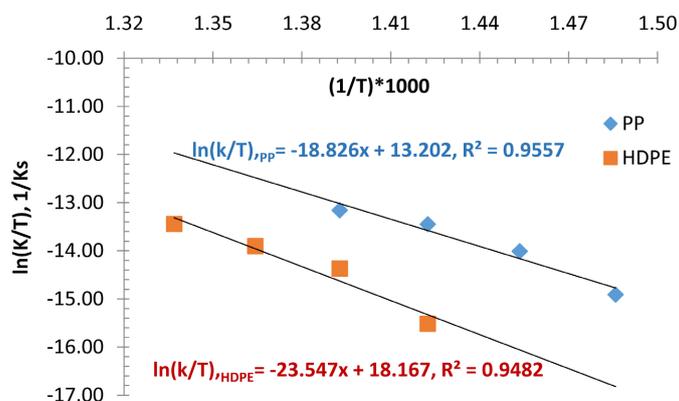


Figure 9. $1/T - \ln(k/T)$ change in the pyrolysis of PP and HDPE plastic wastes (From Equation (16)).

Table 3. Thermodynamic quantities calculated from related graphics (From **Figure 9**).

Plastic	$\ln\left(\frac{k}{T}\right) - \frac{1}{T}$	R^2	Slope = $-\frac{\Delta H^\ddagger}{R}$	ΔH^\ddagger , kJ/mol	Intercept = $23.76 + \frac{\Delta S^\ddagger}{R}$	ΔS^\ddagger J/molK
PP	$\ln\left(\frac{k}{T}\right)_{PP} = -\frac{18.826}{T} + 13.202$	0.9557	-18.826	156.52	13.202	-87.71
HDPE	$\ln\left(\frac{k}{T}\right)_{HDPE} = -\frac{23.547}{T} + 18.167$	0.9482	-23.547	195.77	18.167	-46.48

$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, kJ/mol		
T, K	PP	HDPE
673	215.55	
688	216.86	
703	218.18	228.45
718	219.50	229.14
733		229.84
748		230.54

Table 4. Summarized kinetic and thermodynamic parameters obtained in the pyrolysis of PP and HDPE.

Plastic	E_{act} kJ/mol	A, 1/s	ΔH^\ddagger , kJ/mol	ΔS^\ddagger J/molK	ΔG^\ddagger , kJ/mol, (at 718 K)
PP	162.30	$1.02 \cdot 10^9$	156.52	-87.71	219.50
HDPE	201.80	$1.53 \cdot 10^{11}$	195.77	-46.48	229.14

pyrolysis of plastic waste is an endothermic reaction that requires energy, it was not surprising that the calculated enthalpy values were positive. The positive Gibbs free energy also showed that these pyrolysis reactions could not occur spontaneously (it was involuntary). The fact that both the calculated enthalpy values and the Gibbs free energies are positive supports the basic rules about chemical reactions. Similarly, the calculated reaction entropies were negative for both plastic wastes, resulted in positive Gibbs free energy.

From **Table 4**, we can write that the regularity of quantities as follows;

$$E_{act,HDPE} > E_{act,PP}; \Delta H_{HDPE}^\ddagger > \Delta H_{PP}^\ddagger; \Delta S_{HDPE}^\ddagger > \Delta S_{PP}^\ddagger; \Delta G_{HDPE}^\ddagger > \Delta G_{PP}^\ddagger.$$

This ranking showed that the pyrolysis of HDPE plastic waste was more dependent on temperature than the pyrolysis of PP plastic waste.

4. Conclusion

Thermoplastics such as HDPE and PP are petroleum-derived materials that generate a large amount of waste as a result of their intensive use. By applying chemical recycling methods such as catalytic or thermal pyrolysis, such plastics can be

converted into valuable chemicals. The high-density polyethylene and polypropylene we used in this study turned into liquid products with similar properties, although their decomposition temperatures were different. Although the thermal degradation temperature of polypropylene is lower than that of high-density polyethylene, its transformation was higher at the same temperatures. The liquid products obtained in the thermal pyrolysis of polypropylene plastic wastes are lighter in color than the liquids obtained from the pyrolysis of high-density polyethylene. The pyrolysis kinetics and thermodynamics of both HDPE and PP plastic wastes have been studied. First-order reaction kinetics were found to be suitable for both plastic wastes and rate constants were calculated. For both plastic wastes, it can be said that the reaction rate constants are higher in high-temperature studies and therefore the reactions take place faster. When the kinetic constants, activation energies and thermodynamic quantities calculated using the experimental data are evaluated together, results supporting each other have emerged. The fact that the calculated pyrolysis enthalpies were positive for both plastic wastes showed that the decomposition reactions of these plastic wastes in an inert environment were endothermic. The calculated Gibbs free enthalpy and entropy values also showed that the pyrolysis of these plastic wastes could not be spontaneous and there were involuntary reactions.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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The List of Symbols and Units

ΔG^\ddagger : The free activation enthalpy ($\text{kJ}\cdot\text{mol}^{-1}$)

ΔH^\ddagger : The reaction enthalpy ($\text{kJ}\cdot\text{mol}^{-1}$)

ΔS^\ddagger : The reaction entropy ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

A : The frequency factor (s^{-1})

C_A : Concentration, (mol/L)

E_{act} : The activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)

k : The reaction rate coefficient (s^{-1})

n : The overall reaction order

R : The universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)

$-r_A$: The reaction rate, (mol/Ls)

T : The absolute temperature (K)

x : The conversion of waste plastic