Pyrolysis Characteristics of Waste Fishing Rope

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Abstract: Pyrolysis characteristics of waste fishing rope were investigated by thermogravimetric analysis (TGA). Pyrolysis started at 320 °C, with the main region of decomposition of the waste fishing rope occurring at temperatures between 370 and 460 °C. The corresponding kinetic parameters, including the activation energy and pre-exponential factor, were determined by using the differential method over the degree of conversions. The values of activation energies were between 166 and 272 kJ/mol when the conversion of the pyrolysis reaction increased from 5 to 95 %. The order of the pre-exponential factor was \(10^0\) to \(10^7\), according to conversion variations. Waste fishing rope was pyrolyzed in a micro-scale tubing reactor at temperatures between 430 and 450 °C for 100 to 200 min. As the reaction temperature increased, the yields of pyrolyzed gas and oil increased. The number of carbon atoms in the produced oil was mostly below C_{15}, and a selectivity for C_{7} hydrocarbon compounds was confirmed.

Keywords: waste fishing rope, pyrolysis, thermogravimetric analysis, waste reutilization, carbon number distribution

Introduction

As environmental contamination emerges as a global problem, we need to develop technologies for disposing of hydrocarbon wastes safely without environmental contamination. For this reason, research on pyrolysis is drawing much attention. When polymer waste is processed through pyrolysis, it produces fuel in the form of inflammable gases or liquids and raw materials for the chemical industry; at the same time, it does not generate secondary waste. Solid hydrocarbon wastes that are highly recyclable as resources include waste plastics, waste agricultural films, waste fishing nets, waste tires, and biomass wastes. Representative liquid hydrocarbon waste is a waste lubricant. Research on pyrolysis is actively pursued with the objective of recovering fuel oil or other useful elements for the chemical industry from waste plastics. In particular, polystyrene is highly recoverable among general waste plastic in the form of styrene monomer, and, thus, it is being researched intensively [1-4]. Polypropylene and polyethylene are also being studied actively with regard to their pyrolytic reaction properties and the recovery of useful elements [1,5-8]. As biomass waste, such as waste wood, is also regarded as a renewable resource there has been much active research on the recovery of, e.g., bio oils [9-11].

Recently, with the rise of marine environmental contamination problems, technologies for processing marine wastes are now required. Representative wastes that are causing marine contamination include waste fishing nets, waste fishing gear, and waste lubricants from ships. The volume of fishing gear and waste fishing nets dumped intentionally or accidently over several decades is scientifically immeasurable, but waste fishing gear accumulating in coastal waters is causing serious environmental problems. Recently, the issue of marine waste has been recognized and waste fishing gear and waste fishing nets are being recollected, but the recovery rate is merely around 20 % [12]. Waste fishing nets are mainly made of polyamide resin, polypropylene (PP), and polyethylene

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(PE). Ropes used to connect fishing nets to fishing gear are usually made of PP. Marine wastes float, deposit, or move along the coast, damaging the marine ecosystem and causing losses in the fishing industry. If marine wastes, such as waste ropes and fishing nets, sink to the bottom of the sea they absorb water and become heavier. Then they become difficult to remove; if they are burned in an ordinary incinerator, the salt they contain may produce environmentally harmful substances, such as dioxin and furan. Taking note of these problems, there have been some research studies using pyrolysis to process marine wastes in Korea [12-16]. Because fishing nets are mostly made of polyamide resin, these studies have examined the pyrolytic reaction properties of polyamide resin and have attempted to recover caprolactam from these materials [17,18]. Prior to this present research, we carried out another study on the pyrolytic reaction properties of fishing nets and waste fishing nets made of nylon-6 [13].

In the present study, we obtained data regarding the change of activation energy, relative to the change in the degree of conversion, by differentiating thermogravimetric curves obtained when changing the heating rate for waste ropes made of polypropylene. In the applied differential equation, the order of the reaction was fixed at the first degree and the pre-exponential factor was obtained. In addition, we examined changes in the properties of the reaction products and the characteristics of the distributions of the number of carbon atoms in the oil produced through pyrolytic reactions performed for 100 and 200 min while changing the reaction temperature in the micro-scale tubing reactor (430~450 °C).

**Calculation of Activation Energy**

TGA (Thermogravimetric Analyzer) is used to measure the change of activation energy continuously as a function of temperature. It has been used frequently to measure the overall reaction rate based on the change of mass when the component analysis of the reaction products is difficult to monitor for the pyrolytic reactions of polymers. We obtained activation energies, the orders of reactions, and reaction rate constants, by differentiating and integrating curves obtained from the TGA. Equation (1) is the degree of conversion (X) of a pyrolytic reaction for waste fishing ropes, according to the increase of temperature, in TGA.

\[ X = \frac{W - W_\infty}{W_0 - W_\infty} \]  

Here, \( W_0 \), \( W \), and \( W_\infty \) are, respectively, the weight of the sample used in the experiment, the weight of the sample pyrolyzed at certain temperature, and the weight of the remaining sample in the pan after pyrolytic reaction in the TGA.

The conversion rate, \( \frac{dX}{dt} \), in a pyrolytic reaction is expressed as Equation (2).

\[ \frac{dX}{dt} = k f(X) \]  

The reaction rate constant, \( k \), is expressed as Equation (3); the Arrhenius equation shows a temperature dependency.

\[ k = A \exp \left( \frac{-E}{RT} \right) \]  

The degree of conversion function \( f(X) \), independent of the temperature, can be expressed as Equation (4).

\[ f(X) = (1 - X)^n \]  

If Equations (3) and (4) are substituted into Equation (2), Equation (5) is obtained.

\[ \frac{dX}{dt} = A \exp \left( \frac{-E}{RT} \right) (1 - X)^n \]  

The logarithm of Equation (5) provides Equation (6).

\[ \ln(\frac{dX}{dt}) = \ln[A(1-X)^n] - \frac{E}{R} \frac{1}{T} \]  

Here, \( A \): pre-exponential factor (min\(^{-1}\))
\( n \): the order of reaction
\( E \): activation energy (kJ/mol)
\( R \): gas constant (8.314 J/mol \cdot K)
\( T \): temperature (K)
\( t \): time (min)
\( X \): degree of conversion

In Equation (6) above, the activation energy (E) of waste fishing rope was obtained at a fixed degree of conversion using the relationship between \( \ln(\frac{dX}{dt}) \) and \( \frac{1}{T} \).

The intercept in Equation (6) is expressed as Equation (7). Using this equation, the pre-exponential factor was obtained at a fixed degree of conversion, assuming that the order of the reaction is first degree.

\[ \ln[A(1-X)^n] = \ln(A) + n \ln(1 - X) \]  

**Experimental**

The thermogravimetric experiments on waste fishing
Table 1. Elemental Analysis of Waste Fishing Rope

<table>
<thead>
<tr>
<th>Element (wt%)</th>
<th>Element (wt%)</th>
<th>H/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>Waste fishing rope</td>
<td>83.22</td>
<td>13.74</td>
</tr>
</tbody>
</table>

Table 2. Conditions for Gas Chromatography

<table>
<thead>
<tr>
<th>Detector</th>
<th>FID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>HP-1 capillary column (5 m × 0.53 mm × 2.65 μm thickness, Methyl Silicon Gum)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Nitrogen, 17 mL/min</td>
</tr>
<tr>
<td>Injector temperature programming</td>
<td>Heating rate</td>
</tr>
<tr>
<td>Final temperature</td>
<td>370°C</td>
</tr>
<tr>
<td>Oven temperature programming</td>
<td>Heating rate</td>
</tr>
<tr>
<td>Final temperature</td>
<td>350°C</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>350°C</td>
</tr>
</tbody>
</table>

Table 3. Application of Eq. (7) to Calculate Pre-exponential Factor (Reaction Order : 1st)

<table>
<thead>
<tr>
<th>Conversion [%]</th>
<th>5 %</th>
<th>10 %</th>
<th>20 %</th>
<th>30 %</th>
<th>40 %</th>
<th>50 %</th>
<th>60 %</th>
<th>70 %</th>
<th>80 %</th>
<th>90 %</th>
<th>95 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste rope</td>
<td>2.34×10^2</td>
<td>1.60×10^2</td>
<td>5.11×10^4</td>
<td>7.77×10^4</td>
<td>1.91×10^5</td>
<td>8.07×10^3</td>
<td>2.09×10^3</td>
<td>2.87×10^3</td>
<td>1.88×10^3</td>
<td>2.77×10^1</td>
<td>1.74×10^2</td>
</tr>
</tbody>
</table>

Table 4. Yield of Gas, Oil, and Coke According to the Solubility of the Pyrolysis Products (wt%) from Waste Rope

<table>
<thead>
<tr>
<th>Residence time (min)</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>430°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas (wt%)</td>
<td>2.14</td>
<td>2.50</td>
</tr>
<tr>
<td>oil (wt%)</td>
<td>88.74</td>
<td>94.05</td>
</tr>
<tr>
<td>coke (wt%)</td>
<td>9.12</td>
<td>3.45</td>
</tr>
<tr>
<td>440°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas (wt%)</td>
<td>3.89</td>
<td>3.17</td>
</tr>
<tr>
<td>oil (wt%)</td>
<td>90.69</td>
<td>94.33</td>
</tr>
<tr>
<td>coke (wt%)</td>
<td>5.42</td>
<td>2.50</td>
</tr>
<tr>
<td>450°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>gas (wt%)</td>
<td>4.32</td>
<td>5.13</td>
</tr>
<tr>
<td>oil (wt%)</td>
<td>95.30</td>
<td>93.85</td>
</tr>
<tr>
<td>coke (wt%)</td>
<td>0.38</td>
<td>1.02</td>
</tr>
</tbody>
</table>

ropes used TGA (Cahn, TG-2171); 400 mg of sample was used in each experiment. The temperature was raised at rates of 0.5, 1.0, and 2.0 °C/min within the range of reaction temperatures (20 ~ 500 °C); nitrogen was supplied at a constant rate (20 mL/ min).

The equipment for the pyrolytic reaction experiment was a micro-scale tubing bomb reactor comprising a micro-scale tubing reactor, salt bath, agitator, and thermostat. The experimental equipment and methods that we reported previously were applied [13,14,19]. In this experiment, 5 g of sample was placed in the micro-scale tubing reactor and, after the reaction was complete, the yields of hydrocarbon gas, liquid, and solid were calculated. In addition, the number of carbon atoms in the produced oil was analyzed.

Table 1 shows the results of the elemental analysis of the waste fishing rope used in the experiment and the H/C ratio. The sample we used contained 83.22 wt% of carbon, 13.74 wt% of hydrogen, and a very small amount of oxygen; its H/C ratio was 1.98.

The distribution of the number of carbon atoms in the oil produced after pyrolytic reaction was determined using the distribution of the boiling points. This analysis used gas chromatography (GC; Younglin, M600D) and the distribution of the number of carbon atoms in the oil was determined by measuring the distribution of the boiling points through a distillation simulated using the ASTM D 2887 method, and then using the data on the relationship between the number of carbon atoms and the boiling point. Table 2 shows the conditions used for the GC analysis of the number of carbon atoms in the products.

Results and Discussion

Pyrolysis Rate of Waste Fishing Ropes

Figure 1 shows the curves of thermal gravity when the
temperature was raised at rates of 0.5, 1.0, and 2.0 °C/min, within a range below 500 °C, during the thermo-gravimetric experiment on waste fishing ropes. At each heating rate, the pyrolytic reaction started at over 320 °C and became rapid at 370–460 °C. A previous study into the pyrolytic reaction of waste fishing nets made of nylon-6 under the same conditions, found that the reaction started slowly at over 320 °C and became rapid at 350–440 °C [13]. In an experiment on waste lubricant from ships performed under the same conditions, a rapid pyrolytic reaction occurred at 280–430 °C [14]. In the curve for the thermal gravity obtained at a heating rate of 0.5 °C/min, the range of temperature where the inclination was almost straight was between 375 and 475 °C; within this range ca. 80% of the waste ropes made of polypropylene were decomposed. The range of temperatures for rapid pyrolytic reactions decreased upon decreasing the heating rate because, under the same reaction conditions, if the heating rate is low it takes longer to reach a certain temperature and, as a result, the staying time for waste ropes to be decomposed in the TGA sample pan is lengthened. This situation means that, if the heating rate is fixed at 0.5 °C/min, the staying time of the reactants to reach a certain temperature is 4 times longer than that when the heating rate is 2.0 °C/min. Thus, at the same temperature, the change in the degree of conversion comes from the change in the staying time.

In a thermogravimetric curve, its inclination indicates the degree of pyrolysis of reactants according to the change of temperature. This situation means that, under the conditions of the pyrolytic reaction in the present experiment, the pyrolytic reaction of waste fishing ropes was a prevalent reaction.

Figure 2 shows the changing rate of the degree of conversion according to the rise in temperature when the heating rates were 0.5, 1.0, and 2.0 °C/min. The temperatures at which the rates of change of the degree of conversion were highest were 412, 421, and 430 °C, respectively, for the three heating rates. The average degree of conversion of waste fishing rope was 59%. With a rise in the heating rate, the temperature at which the changing rate of the degree of conversion was highest increased slightly. In the pyrolytic reaction using 300 g of polypropylene resin in a semi-batch reactor, within the range 300–500 °C and with fixed heat rates of 0.5, 1.0, and 2.0 °C/min, the temperatures at which the rates of change the degree of conversion were highest were 407, 423, and 431 °C, respectively [1]. For polypropylene, the temperatures at which the rates of change of the degree of conversion were highest were similar when the waste fishing ropes were pyrolyzed in TGA and when the resin was pyrolyzed in a semi-batch reactor.

In this study, we used a method proposed by Friedman, in the form of Expression (6), to determine the activation energy (E) and the pre-exponential factor (A). Using Expression (6), we obtained the activation energy according as a function of the degree of conversion in the pyrolytic reaction of waste fishing ropes.

Figure 3 shows the process of calculating the activation energy from the rate of change of the degree of conversion, \[\ln\left(\frac{dX}{dt}\right)\] in Expression (6) when the heating rate was changed at a fixed degree of conversion. The following is a specific example of how we obtained the activation energies using TGA. If the degree of conversion was 10% when pyrolyzing waste fishing ropes, \[\frac{1}{T}\] was \[1.5736 \times 10^3\], \[1.5553 \times 10^3\], and \[1.5080 \times 10^3\] respectively, when the heating rates were 0.5, 1.0, and 2.0 °C/min. Here, the values of \[\ln\left(\frac{dX}{dt}\right)\] the logarithm of the changing rate of the degree of conversion at the same degree of conversion, were -10.3354, -9.6625, and -8.6808, respectively. Figure 3 shows the plot of \[\frac{1}{T}\] in on the x axis and \[\ln\left(\frac{dX}{dt}\right)\] on the y axis according to the degree of conversion. When the degree of conversion
was 10% in the pyrolytic reaction of waste fishing ropes made of polypropylene, the activation energy calculated from the slope in Figure 3 was 202.29 kJ. Here, the intercept is equivalent to ln[A · (1 - X)ⁿ] in Expression (6); it was 28.0476 when the degree of conversion was 10%.

When assuming a first-order reaction for the conversion using Expression (7), we obtained the pre-exponential factor. The pre-exponential factor (A) obtained on the assumption of a first order reaction was $1.60 \times 10^{12}$. Table 3 shows the pre-exponential factors (A) obtained when changing the degree of conversion up to 95%.

Figure 4 shows the distribution of activation energies when the degrees of conversion were in the range 5 ~ 95% for the pyrolytic reactions of waste fishing ropes. The activation energies are distributed within the range 166 ~ 272 kJ/mol; they show a tendency to increase until the degree of conversion in the pyrolytic reaction of waste fishing ropes reached 30%, then decrease until the degree of conversion reached 70%, and then increased again. The average activation energy we obtained, according to the degree of conversion in the pyrolysis of waste fishing ropes, was 211 kJ/mol. When polypropylene resin was pyrolyzed in a semi-batch reactor, the activation energies ranged between 208 and 288 kJ/mol [1]. The physical strength of waste fishing ropes may be weakened by their repeated use in seawater and exposure to sunlight, which may result in partial decomposition. Partial decomposition resulting from the repeated exposure of nylon-6,6 to UV light was described by Krejia and coworkers [19]. In case of waste fishing ropes made of polypropylene, their activation energy may have been lowered below that of the resin because of long-term exposure to sunlight during fishing.

![Figure 3](image-url) **Figure 3.** Application of equation (6) with heating rates of 0.5, 1.0, and 2.0 °C/min. The conversion values are 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 0.95.

![Figure 4](image-url) **Figure 4.** Calculated activation energies at different conversions for the pyrolysis of waste rope.

**Elemental Analysis of Products from the Pyrolysis of Waste Fishing Ropes**

We placed waste fishing ropes into a micro-scale tubing reactor and, after their reaction at a temperature of 430 ~ 450 °C for 100 to 200 min, we calculated the yields of the gas, liquid, and coke produced from the reaction. For the oil produced, the number of carbon atoms was analyzed using GC. The yield of gas was obtained by calculating the difference between the weight measured before the reaction and that measured after the reaction; when the reactor was cooled down to room temperature, the cap was opened and the gas produced from the pyrolytic reaction was emitted. Table 4 shows the yield of each product according to the reaction time and temperature. The yield of gas from the waste fishing ropes made of polypropylene increased upon increasing the reaction temperature and time. For the same reaction time, the yield of gas doubled when the reaction temperature increased from 430 to 450 °C. This situation arose because the decomposition proceeded further toward primary reaction products upon increasing the pyrolytic reaction temperature and time inside the reactor. The yield of oil produced increased upon increasing the reaction temperature when the reaction time was 100 min, but it stayed at ca. 94 wt% when the reaction time was 200 min.

The degree of conversion of coke contained in the oil phase was obtained after solvent extraction using hexane. The oil produced from the pyrolysis was dissolved in hexane and then oil and solid coke were filtered using a fine filter paper (pore size 0.45 μm). The yield of coke was calculated by measuring the weight of coke remaining on the filter paper. If the pyrolytic reaction time and temperature were not sufficient, the waste ropes made of polypropylene were left in a non-reactive wax-like form. This substance does not pass through the filter paper and is included in the yield of coke. In the case of the 100-min pyrolytic reaction at a temperature of
430 °C, the yield of coke was as high as 9.12 wt% for this very reason. Upon increasing the reaction temperature and time, the yield of coke decreased.

Figures 5 and 6 show the results of analyzing the number of carbon atoms in the oil produced from the pyrolysis of waste fishing ropes at 430, 440, and 450 °C for 100 and 200 min. When the reaction time was 100 min, the quantity of hydrocarbon compounds having a small number of carbon atoms increased at each temperature. Among the oils produced, the selectivity for C7 species was distinct. In the case of polypropylene, the yield of monomer was low because depolymerization occurred gradually through the disintegration of carbon bonds at random positions of the main chain. Radicals formed in pyrolytic reactions generate pyrolytic products by the coupling of small olefins; the selectivity for a specific substance is quite low, and mainly saturated hydrocarbon compounds are produced. Depending on the conditions of the pyrolytic reaction, intermediate cyclo-olefins of C5 and C6 types are formed by Diels-Alder reaction, cycloaddition reactions, and condensation reactions. Again, these species may become stable aromatic hydrocarbon compounds, such as benzene and toluene, through hydrogen atom shifts and dehydrogenation. The mechanism of the formation of aromatic elements in pyrolytic reactions was proposed by Wheeler and Wood [20]. Cyclo-olefins formed as intermediates may be decomposed into radicals by Diels-Alder reaction but it does not occur readily because the activation energy of the reaction is higher than that of dehydrogenation. Aromatic elements, such as benzene, continue coupling under the conditions of the pyrolytic reaction to produce substances such as biphenyl [21]. We believe that, for this reason, the selectivity for hydrocarbon compounds corresponding to C7 appears among the products from pyrolytic reaction of waste ropes made of polypropylene. The results presented in Figure 6 display a tendency similar to that encountered in Figure 5. In particular, the number of carbon atoms was below C15 in most of the oil.

**Conclusions**

In this study we performed experiments on the pyrolytic reactions of waste fishing ropes made of polypropylene at different heating rates and monitored them using TGA. The pyrolytic reactions of waste ropes began at 320 °C and became rapid at 370 ~ 460 °C. The activation energy for the pyrolysis of waste rope fell in the range between 166 ~ 272 kJ/mol, according to the degree of conversion; it averaged 211 kJ/mol. Assuming that the reaction rate was first-order, we obtained the pre-exponential factor according to the degree of conversion using the experimental data. These values ranged between 10^7 and
10^{17} according to the degree of conversion. According to the results of reactions performed for 100 and 200 min at temperatures of 430, 440, and 450 °C (after placing waste fishing ropes into a micro-scale tubing reactor), the yields of the gases and oils produced increased upon increasing the reaction time and temperature. The number of carbon atoms in the oil produced was mostly below C_{15}, and a selectivity for C_{7} hydrocarbon compounds was confirmed.

Acknowledgment

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References