

Pyrolysis Kinetics and Characteristics of the Mixtures of Waste Ship Lubricating Oil and Waste Fishing Rope

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Abstract—Kinetic investigations on the pyrolysis of a mixture of waste ship lubricating oil (WSLO) and waste fishing rope (WFR) were carried out using a thermogravimetric analyzer (TGA) at a heating rate of 0.5 °C/min, 1.0 °C/min and 2.0 °C/min. WSLO and WFR were mainly decomposed at the temperature of range of 400 °C to 455 °C and 370 °C to 410 °C, respectively. The WSLO/WFR mixture was mainly decomposed at the temperature range of 300 °C and 450 °C, which is a lower temperature than that for the WSLO or the WFR alone at each heating rate. The ranges of apparent activation energies of the WSLO/WFR mixture were between 137 kJ mol⁻¹ and 197 kJ mol⁻¹ at conversions in the range of 10-95%. The mixture of WSLO and WFR was pyrolyzed in a micro-scale tubing reactor at 440 °C for 60 min and 80 min. The yield of pyrolyzed gases increased from 2.13 wt% to 2.29 wt% with reaction time. The selectivity to C₇ hydrocarbons was shown in the pyrolyzed oil of the mixture.

Key words: Pyrolysis, Polypropylene, Waste Fishing Rope, Waste Ship Lubricating Oil, TGA, DTG, Carbon Number Distribution

INTRODUCTION

Ocean pollution from waste fishing nets (WFN) and waste fishing ropes (WFR) is a serious environmental problem in Korea. For the last three decades WFN and WFR have been dumped without restriction either accidentally or purposely into the oceans near Korea [Choi, 2001]. Nowadays, marine waste is cleared from the bottom of the ocean in the coastal regions of Korea.

The marine wastes recovered from the ocean are now buried; however, a suitable method is needed to recycle troublesome waste. One recycling option is pyrolysis. This technology will not only solve the marine waste disposal but it will convert a potential waste to a valuable product such as pyrolysis oil. Pyrolysis research on WFN and waste fishing tackle has been conducted in Korea [Kim et al., 2001a, b, 2003a]. Many researchers have studied the conversion of waste products into fuel or chemical feedstock, particularly waste products such as polystyrene (PS), polypropylene (PP), polyethylene (PE), nylon-6, and solid waste [Kim et al., 1995, 1999, 2004a; Bockhm et al., 1998; Cardona et al., 2002; Holland et al., 2000; Jha et al., 1998; Lee et al., 2003; Park et al., 2002]. WFN and WFR are made mainly from polyamide and polypropylene resin, respectively. Numerous studies for PP have been conducted to maintain environmentally compatible economic growth and to determine the kinetics of thermal degradation [Ballice, 2002; Bockhorn et al., 1999]. Although waste ship lubrication oil (WSLO) is one of the main ocean pollutants, it is a good source for renewable resources. In 2001 in Korea, 109,000 kL of WSLO was produced, according to the Korea lubricating oil industries association bulletin.

From an engineering viewpoint, low heat transfer rates and high viscosity of the melting polymer can hinder commercial applications for waste plastic recycling by pyrolysis. WSLO can decrease the viscosity of mixtures and, when mixed with waste plastics, it can lead to improved heat transfer. WSLO also can be employed as a solvent to swell waste plastics. Thus, it might serve to decrease the decomposition temperature of a mixture of waste polymeric material.

The main purpose of this work was to determine the global kinetic parameters of the pyrolysis of a WSLO/WFR mixture, and to analyze the products of the pyrolysis. Pyrolyzed oil was characterized by carbon number distribution and FT-IR spectroscopy. Although many papers have been published relating to thermogravimetric analysis for waste plastics and polymeric materials, most of the literature has focused only on a single material or a fresh polymeric mixture. Our study on the pyrolysis of a WSLO/WFR mixture provides a unique comparison of pyrolysis characteristics.

EXPERIMENT

A thermogravimetric analyzer (TGA; Cahn, TG-2171) was used for the pyrolysis of the mixture of WSLO and WFR. We obtained the experimental sample of the WSLO from a ship, and the WFR from a place that stores WFRs recovered from the ocean on the east coast of Korea. Table 1 shows the results of an elemental analysis of our sample, and Table 2 shows the properties of WSLO. The specific chemicals such as antioxidants and pigment are added during the processing of fishing ropes to enhance the physical characteristics. Those kinds of inorganic materials, however, could produce ash when the fishing rope is burning. The WFR had been repeatedly immersed in seawater for fishing and then abandoned for a long time at the storage location. We expected the WFR to contain

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Table 1. Elemental analysis of waste ship lubricating oil (WSLO) and waste fishing rope (WFR)

| Sample | Element (%) | | | | | H/C ratio |
|--------|-------------|-------|------|------|---|-----------|
| | C | H | N | O | S | |
| WSLO | 82.67 | 14.63 | 1.37 | 1.75 | - | 2.12 |
| WFR | 83.22 | 13.74 | - | 0.24 | - | 1.98 |

Table 2. Properties of waste ship lubricating oil (WSLO)

| Test Items | Test results | Test method |
|--|--------------|----------------|
| Dynamic viscosity (mm ² /sec) | 40 °C | 99.86 |
| | 100 °C | 13.49 |
| Viscosity index | 135 | KS M 2014-1999 |
| Sulfur content (wt%) | 0.27 | |
| Ash content (wt%) | 1.13 | KS M 2044-2000 |
| Density (15 °C, g/cm ³) | 0.8819 | KS M 2002-2001 |

salt and ash from the fishing and from being abandoned at the storage location. Kim and Park [2001a] analyzed the metal content of a WFN for ICP/MS by using distilled water for 3 days. The net had higher levels of sodium and chlorine than other materials. The shortfall of 2.80% for the WFR from the elemental analysis may have been due to the specific chemicals such as antioxidants, pigments and salts. The WFR showed a lower H/C ratio than the WSLO, and that the oxygen content was 1.75% for the WSLO and 0.24% for the WFR.

A sample mass of 400 mg was employed for thermogravimetric analysis in TGA, and the mixing ratio of WSLO and WFR was 1 : 1. To make an oxygen-free atmosphere, nitrogen was introduced into the reactor with a flow rate of 20 ml/min. To minimize the temperature gradients, the heating rate was controlled at 0.5 °C/min, 1.0 °C/min and 2.0 °C/min from 20 °C to 500 °C.

A tubing reactor was employed to elucidate the pyrolyzed liquid products of the WSLO/WFR mixture. The volume of the tubing reactor was 40 ml. The details of the experimental apparatus have been reported elsewhere [Kim et al., 2000]. A sample mass of 5 g was charged into the tubing reactor, and the mixing ratio of WSLO and WFR was 1 : 1. The pyrolysis temperature of the tubing bomb reactor was 440 °C, which we determined on the basis of the thermogravimetric analysis. The pyrolysis reactions were performed over two different reaction times: 60 min and 80 min. With samples taken from each of these reaction times, we then analyzed the reaction products for the amount of gas and oil formed. Tubing reactor was opened after cooling at room temperature to allow the gases to evolve gently. Gas yield was obtained by weighing the tubing reactor before and after the gases were vented. The gas yield is defined as (gas weight)×100/(sample weight), while the oil yield is defined as (100-gas yield). Pyrolyzed liquid products include small amounts of solids such as coke, char and ash. In this work, the products we obtained from the WSLO/WFR mixture were limited to the gas yield and the liquid yield.

Liquid products from the tubing bomb reactor were analyzed by gas chromatography (GC; Young Lin-M600D) with a flame ionization detector. A capillary column HP-1 of 0.53 mm i.d. and 5 m length was employed with the oven temperature programmed of

between 70 °C and 370 °C. The peaks were identified when retention times were matched with the reference compounds from a normal paraffin mixture (C₅-C₄₄). The carbon number was analyzed by ASTM D 2887. One of the liquid samples was analyzed by FT-IR (Thermo Nattson-60AR) to identify specific stretching bands.

RESULTS AND DISCUSSION

1. Thermogravimetric Analysis Results

The degree of conversion (X) is defined as Eq. (1) for pyrolysis reaction of the WSLO/WFR mixture in TGA.

$$X = \frac{W_0 - W}{W_0 - W_\infty} \quad (1)$$

where W_0 is the initial mass of the sample, W is the mass of the pyrolyzed sample, and W_∞ is the final residual mass that corresponds to the final residual mass of the solid by-products.

Fig. 1 shows the degree of conversion versus temperature for the dynamic experiments at the different heating rates of 0.5 °C/min, 1.0 °C/min and 2.0 °C/min in a TGA. The pyrolysis of the WSLO was slowly carried out above 250 °C, and then rapidly carried out at a temperature range of 300 °C to 360 °C. The slope was almost linear at a temperature range of 325 °C and 400 °C, and 70 percent of WSLO was decomposed at this range. The pyrolysis of the WFR was initiated at 320 °C, and then rapidly carried out at a temperature range of 370 °C to 460 °C. The pyrolysis of the WSLO/WFR mixture, on the other hand, was initiated at 240 °C. The mixture decomposed at a lower temperature than either the WSLO or the WFR alone at heating rates of 0.5 °C/min, 1.0 °C/min and 2.0 °C/min. It is considered that the WSLO had a role as a swelling agent for the WFR. Accordingly, heat transfer in the mixture could be improved in comparison with the WFR. The WFR could be easily

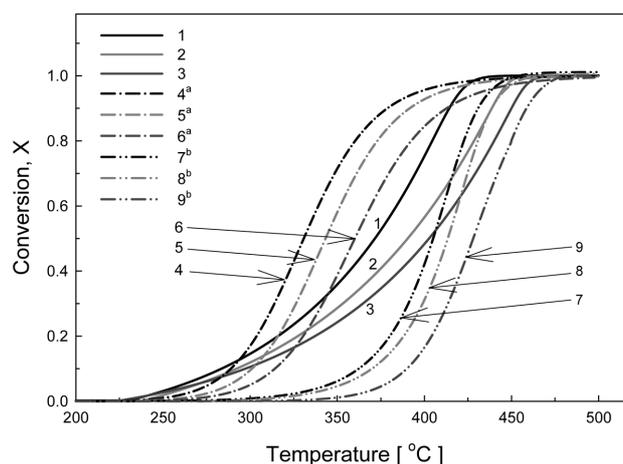


Fig. 1. The effect of pyrolysis rate of the mixture of waste ship lubricating oil (WSLO) and waste fishing rope (WFR) on heating rates: 1, SLO : WFR=1 : 1 wt ratio; β =0.5 °C/min; 2, WSLO : WFR=1 : 1 wt ratio; β =1.0 °C/min; 3, WSLO : WFR=1 : 1 wt ratio; β =2.0 °C/min; 4, WSLO; β =0.5 °C/min; 5, WSLO; β =1.0 °C/min; 6, WSLO; β =2.0 °C/min; 7, WFR; β =0.5 °C/min; 8, WFR; β =1.0 °C/min; 9, WFR; β =2.0 °C/min.

a: Kim et al., 2004b, b: Kim et al., 2004c

decomposed in a lower temperature after being swelled with the WSLO. As such, the WSLO/WFR mixture could be pyrolyzed in a lower temperature compared to pyrolysis conducted separately for each component. The decomposition patterns of the WSLO and the WFR were more rapid than those of the WSLO/WFR mixture at the thermogravimetric curves (Fig. 1). The curves for the WSLO and the WFR have a smooth slope and tends asymptotically to the maximum degree of conversion. The curves for the WSLO/WFR mixture increased more slowly to the maximum degree of conversion than those for the WSLO and the WFR. As can be seen in Fig. 1, the decomposition temperature of the WSLO was lower than that of the WFR. For the WSLO/WFR mixture, the decomposition at lower temperature seems to be attributed to the dominant of the WSLO, and decomposition at higher temperature to the dominant decomposition of the WFR. All three heating rates yielded the same patterns of thermal decomposition.

An instantaneous rate of conversion (dX/dt) is shown in Fig. 2, which is obtained from differential thermogravimetric analysis (DTG) at the given reaction temperature. As shown here, the height of the peaks gradually increases with increasing heating rates. Also, the position of the maximum peak is shifted to higher temperature, and the peak height is directly proportional to the reactivity. Thus it appears that as the heating rates increase, higher instantaneous thermal energy is released into the reaction system, and results in a higher rate of conversion. The results of Fig. 2 also indicate that a larger fraction of WSLO/WFR mixture is decomposed at a temperature range of 300 °C to 460 °C. Pyrolysis of a single component (WALO and WFR, respectively) displays bilateral symmetry in Fig. 2, and one maximum peak occurs at a specific reaction temperature for each heating rate. The WSLO/WFR mixture, however, does not display bilateral symmetry, but shows an asymmetrical curve with tail section

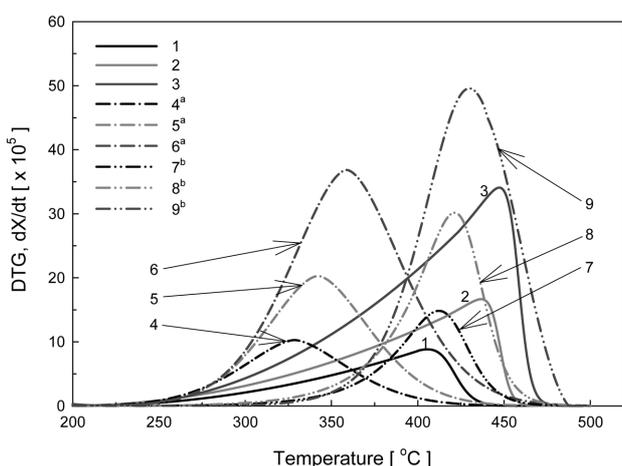


Fig. 2. Variation of the instantaneous reaction rate with temperature at different heating rates for pyrolysis of the mixture of waste ship lubricating oil (WSLO) and waste fishing rope (WFR): 1, WSLO : WFR=1 : 1 wt ratio; $\beta=0.5^\circ\text{C}/\text{min}$; 2, WSLO : WFR=1 : 1 wt ratio; $\beta=1.0^\circ\text{C}/\text{min}$; 3, WSLO : WFR=1 : 1 wt ratio; $\beta=2.0^\circ\text{C}/\text{min}$; 4, WSLO; $\beta=0.5^\circ\text{C}/\text{min}$; 5, WSLO; $\beta=1.0^\circ\text{C}/\text{min}$; 6, WSLO; $\beta=2.0^\circ\text{C}/\text{min}$; 7, WFR; $\beta=0.5^\circ\text{C}/\text{min}$; 8, WFR; $\beta=1.0^\circ\text{C}/\text{min}$; 9, WFR; $\beta=2.0^\circ\text{C}/\text{min}$.

a: Kim et al., 2004b, b: Kim et al., 2004c

in the main decomposition range. It is considered that the slope of the flat-tail section is mainly attributed to the thermal decomposition of the WSLO in the mixture because the WSLO decomposes at a lower temperature compared to the WFR. The maximum rate of the WSLO/WFR mixtures occurred at 405 °C, 436 °C, and 448 °C for heating rates of 0.5 °C/min, 1.0 °C/min, and 2.0 °C/min, respectively. The maximum rate of WSLO occurred at 328 °C, 342 °C, and 359 °C, and that of WFR occurred at 412 °C, 421 °C, and 430 °C for each heating rate [Kim et al., 2004]. The temperature of maximum peaks for the WSLO/WFR mixture was higher than the WSLO and the WFR. The conversions of maximum peak for the WSLO and the WFR were 48% and 59%; however, those of WSLO/WFR mixtures were approximately 85% for each heating rate. It is considered that the swelling effect of WSLO on WFR might be attributed to higher conversions at maximum peak for the mixture.

2. Activation Energy

We followed the differential method to derive the pyrolysis kinetic data from thermogravimetric analysis. Friedman [1963] suggested this approach to analyze thermogravimetric data. The rate of conversion (dX/dt) in the thermal decomposition is expressed by

$$\frac{dX}{dt} = kf(X) \quad (2)$$

The reaction rate constant k is expressed by the Arrhenius equation

$$k = A \exp\left(\frac{-E}{RT}\right) \quad (3)$$

A function of the conversion that is independent of temperature, $f(X)$, is expressed as

$$f(X) = (1-X)^n \quad (4)$$

Substituting Eqs. (3) and (4) into Eq. (2) and taking a natural logarithm, the above equation yields

$$\ln\left(\frac{dX}{dt}\right) = \ln[Z(1-X)^n] - \frac{E}{RT} \quad (5)$$

The activation energy E , which is based on Eq. (5), is determined from a relationship between $\ln(dX/dt)$ and $1/T$. Consequently, the activation energy (E) corresponding to the specific conversion could be obtained from a family of parallel straight lines of slope $-E/R$. For example, when the conversion of the WSLO/WFR mixture was 10%, temperatures were 283.49 °C, 292.17 °C and 297.17 °C with the heating rates of 0.5 °C/min, 1.0 °C/min and 2.0 °C/min, respectively. The values of $\ln(dX/dt)$ were -11.1488 , -10.5271 and -10.1225 , where the corresponding values of $1/T[\text{K}^{-1}]$ were 1.7965×10^{-3} , 1.7689×10^{-3} and 1.7534×10^{-3} . $\ln(dX/dt)$ vs. $1/T[\text{K}^{-1}]$ at conversions between 10% and 95% for the mixture of WSLO and WFR is shown in Fig. 3.

The intercept $\ln(A \cdot (1-X)^n)$ can be calculated from Fig. 3 at each conversion. There are many analytical methods to determine kinetic parameters from thermogravimetric data. Most reaction orders are determined such as 0^{th} and 1^{st} when analytical methods such as differential and integral method are applied to thermogravimetric analysis. In this work, reaction order was fixed to 0^{th} and 1^{st} to determine the pre-exponential factor. If the apparent order is fixed at 0 or 1, the pre-exponential factor (A) is obtained by curve fitting based on Eq. (6).

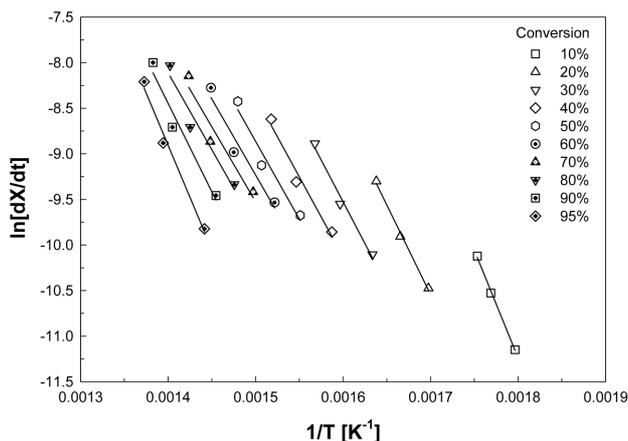


Fig. 3. Application of Eq. (5) with heating rate of 0.5, 1.0 and 2.0 °C/min. The conversion values are: 5, 20, 40, 60, 80 and 95%.

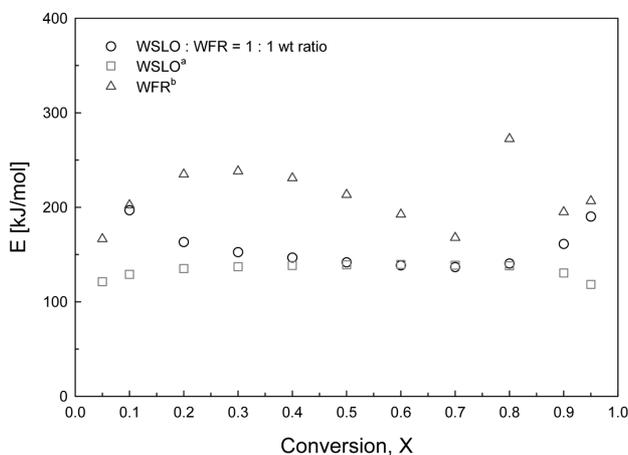


Fig. 4. Calculated activation energies at different conversions for pyrolysis of the mixture of waste ship lubricating oil (WSLO) and waste fishing rope (WFR).

a: Kim et al., 2004b, b: Kim et al., 2004c

$$\ln(A \cdot (1-X)^n) = \ln A + n \ln(1-X) \quad (6)$$

Fig. 4 shows the variations in the activation energies as a function of conversion for the WSLO/WFR mixture. The range of activation energies for the WSLO/WFR mixture was between 137 kJ mol⁻¹ and 197 kJ mol⁻¹. Activation energy of WFR/WSLO mixture showed similar values with WFR at a conversion of 0.1. However, the activation energy of the mixture showed lower values than each component when the conversion was over 0.2. It is considered that higher activation energy of mixtures at a conversion of 0.1 is attributed to the different pyrolysis temperature of each com-

ponent at the same conversion. The average activation energy for the WSLO/WFR mixture was 157 kJ mol⁻¹, while that of the WSLO and the WFR was 133 kJ mol⁻¹ and 211 kJ mol⁻¹, respectively [Kim et al., 2004b, c]. The average activation energy for the mixture was lower than that of the average value for the WSLO and the WFR. Lower values of activation energy resulted from the synergetic effect such as swelling effect of WSLO on WFR and improvement of heat transfer.

The pre-exponential factor can be obtained from Fig. 3 and Eq. (6). The intercept $\ln(A(1-X)^n)$ can be calculated from Figure 3 at each conversion. When the apparent reaction order is fixed at 0 or 1, the pre-exponential factor (A) is obtained from Eq. (6) at the specific conversions, and those of values are listed in Table 3. The pre-exponential factors decreased with the conversion in the range of 0% to 80%, and then increased with the conversion in the range over 80%. The orders of pre-exponential factors were between 10⁶ sec⁻¹ and 10¹³ sec⁻¹.

3. Analysis of Oil Products

A micro tubing reactor was employed to elucidate the pyrolyzed products of the mixture of WSLO and WFR. The pyrolysis temperature of 440 °C in the tubing bomb reactor was selected from the results of thermogravimetric analysis. The reaction products were analyzed for the amount of gas and oil including small amount of coke. The amount of coke produced from reaction, however, was not analyzed. The yield of gas compounds was 2.13 wt% and 2.29 wt%, respectively, for the different times of 60 min and 80 min. The yield of gas compounds increased with the increase of reaction time, whereas the oil products decreased.

Fig. 5 shows the carbon number distribution of the pyrolyzed oil after reaction at 440 °C (60 min and 80 min). In this work, a closed system, namely the tubing reactor was used without a catalyst at 440 °C. Most of the pyrolyzed oil from the WSLO (440 °C, 60 min) was hydrocarbons below C₂₄, and the selectivity of specific hydrocarbons was not detected. For the WFR, most of the pyrolyzed oil was hydrocarbon below C₂₁, and it showed the selectivity to C₇ hydrocarbons. The carbon number distribution for the WSLO/WFR mixture showed the selectivity to C₇ hydrocarbons, and the fraction of light hydrocarbon below C₁₅ was higher than that for the WSLO or WFR alone.

Fig. 6 shows FT-IR spectra for the pyrolyzed oil of the WSLO/WFR mixture (440 °C, 60 min). Table 1 shows that the WSLO and the WFR mainly consisted of carbon and hydrogen atoms. The band of that of C-H stretching was shown at the wavenumber between 2,800 cm⁻¹ and 3,000 cm⁻¹, and C-H scissoring was shown at the wavenumber between 1,350 cm⁻¹ and 1,500 cm⁻¹. No band assigned to a bond including nitrogen atom could be obtained. Because the pyrolyzed oil of the WSLO/WFR mixture does not contain nitrogen atoms that can be a source for NO_x, it can be considered as an alternative fuel for a boiler. Consequently, the recovery of pyrolyzed

Table 3. Pre-exponential factor for pyrolysis of the mixture of waste ship lubricating oil (WSLO) and waste fishing rope (WFR)

| Reaction order | Conversion (%) | | | | | | | | | |
|-----------------|-------------------------|-------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|-------------------------|
| | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 95 |
| 0 th | 4.13 × 10 ¹³ | 8.18 × 10 ⁹ | 3.95 × 10 ⁸ | 6.67 × 10 ⁷ | 1.79 × 10 ⁷ | 6.93 × 10 ⁶ | 3.73 × 10 ⁶ | 5.58 × 10 ⁶ | 1.28 × 10 ⁸ | 1.09 × 10 ¹⁰ |
| 1 st | 4.59 × 10 ¹³ | 1.02 × 10 ¹⁰ | 5.65 × 10 ⁸ | 1.11 × 10 ⁸ | 3.58 × 10 ⁷ | 1.73 × 10 ⁷ | 1.24 × 10 ⁷ | 2.79 × 10 ⁶ | 1.28 × 10 ⁹ | 2.17 × 10 ¹¹ |

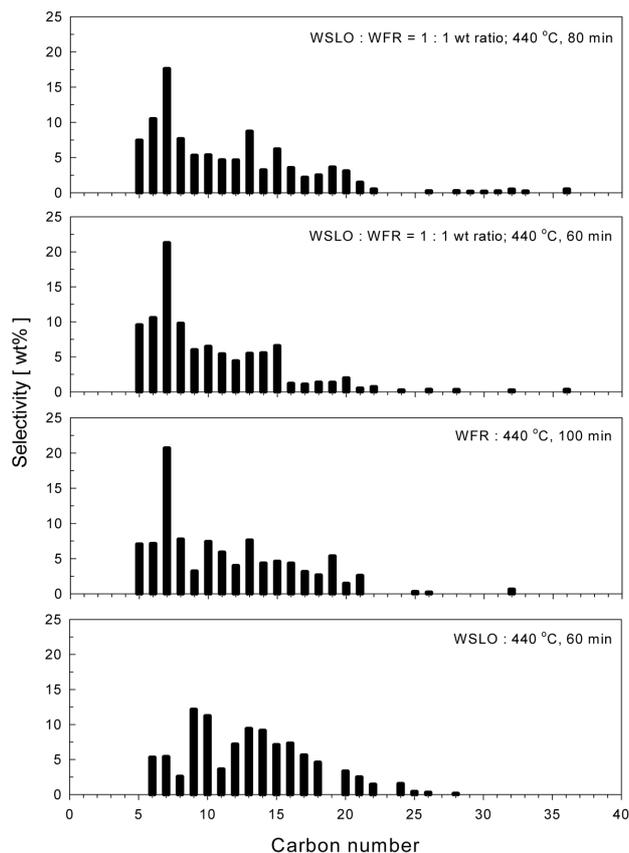


Fig. 5. The effect of residence time on carbon number distribution for the pyrolysis of the mixture of waste ship lubricating oil (WSLO) and waste fishing rope (WFR).

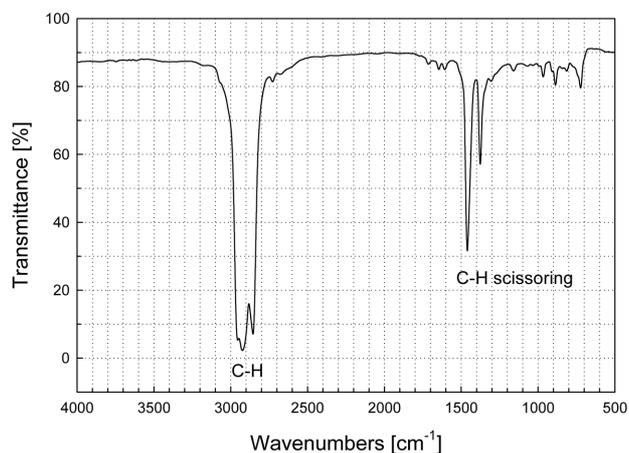


Fig. 6. FT-IR spectra for the pyrolysis of the mixture of waste ship lubricating oil (WSLO) and waste fishing rope (WFR): (440 °C, 60 min).

oil from the WSLO/WFR mixture seems to be promising method from the standpoint of a sustainable environment.

CONCLUSION

A WSLO/WFR mixture was mainly decomposed in the tem-

perature range of 300 °C and 450 °C, which is lower than for the WSLO or the WFR alone at the heating rate of 0.5 °C/min, 1.0 °C/min and 2.0 °C/min. Because the WSLO had a role as a swelling agent for the WFR, the WSLO/WFR mixture could be pyrolyzed at a lower temperature compared to pyrolysis conducted separately for each component.

The apparent activation energies for the WSLO/WFR mixture were between 137 kJ mol⁻¹ and 197 kJ mol⁻¹ at the conversions of 10-95%. The average activation energy for the WSLO/WFR mixture was 157 kJ mol⁻¹, whereas that of the WSLO and the WFR was 133 kJ mol⁻¹ and 211 kJ mol⁻¹, respectively. The orders of pre-exponential factor for the WSLO/WFR mixture were between 10⁶ sec⁻¹ and 10¹³ sec⁻¹.

The fraction of light hydrocarbons below C₁₅ in the pyrolyzed oil of the WSLO/WFR mixture was higher than that of the WSLO or WFR alone. The selectivity of C₇ hydrocarbon was confirmed in the pyrolyzed oil of the WSLO/WFR mixture.

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NOMENCLATURE

- A : pre-exponential factor [s⁻¹]
- E : activation energy [kJ mol⁻¹]
- k : pyrolysis rate constant [s⁻¹]
- n : reaction order
- R : gas constant=8.314 J g·mol⁻¹ K⁻¹
- t : pyrolysis time [s]
- T : pyrolysis temperature [K]
- W : weight of sample at time t [g]
- W₀ : initial weight of sample [g]
- W_t : final weight of sample [g]
- X : conversion of samples

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