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Non-isothermal pyrolysis of waste automobile lubricating oil in a stirred batch reactor

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Abstract

Kinetic tests on pyrolysis of waste automobile lubricating were carried out with a thermogravimetric analysis (TGA) technique at heating rates of 0.5, 1.0, and 2.0 °C min^{-1} in a stirred batch reactor. The main region of decomposition of waste automobile lubricating oil was between 400 and 460 °C at each heating rate. The corresponding kinetic parameters including activation energy were determined by the degree of conversions. The ranges of activation energies were from 281.78 to 447.66 kJ mol^{-1} at conversion in the range of 0.11–0.96 and the reaction order was 1.35. The effects of heating rate on the product distribution have been studied. The distribution of the liquid products shifted slightly to smaller carbon numbers as the heating rate decreased.

Keywords: Pyrolysis; Waste automobile lubricating oil; Stirred batch reactor; TGA; Carbon number distribution

1. Introduction

Billions of gallons of waste automobile lubricating oil are generated every year in the world. A number of studies to remove various pollutants existing in the waste lubricating oil and simultaneously to reuse these resources as valuable products have been attempted. Some of the technologies successfully applied the operation of the newly developed regenerating plants and obtained the re-refined lubricating oil. The quality of re-refined lubricating oil is equivalent to that of new lubricating oil [1–3]. The Phillips re-refining process combines chemical demetallization with hydrotreatment to produce high yields of base oils from waste lubes [1]. Kim and co-workers [4,5] investigated a novel technology for obtaining more valuable product oils from the waste lubricating oils. The waste lubricating oils were mixed with atmospheric distillation residuum from a crude oil and then were distilled under a vacuum. These methods of disposal are no longer practicable because it causes an additional sludge disposal. Therefore, a better solution from an environmental and economic standpoint is to thermally reprocess the waste automobile lubricating oil into volatile products.

Pyrolysis studies have been widely attempted to convert solid fossil fuels and organic materials such as coal, tire, waste plastics, waste woods, and oil shales into liquid and gaseous hydrocarbons and a solid char residue [6–18]. Thermogravimetric analysis for the pyrolysis characteristics has been extensively studied by other researchers [19–21]. Liou et al. [9] and Reina et al. [10] studied the behavior of the activation energy with the degree of conversion of rice husk using a thermogravimetric (TGA) technique. The pyrolysis kinetics of waste automobile lubricating oil have received little attention.

The main purpose of this work is to determine the global kinetic parameters during the pyrolysis of waste automobile lubricating oil. A TGA technique was applied to the pyrolysis of waste automobile lubricating oil in a stirred batch reactor. The global pyrolysis kinetic parameters and effect of heating rate on carbon number distribution are investigated.

2. Experiment

A schematic diagram of the autoclave (R-201, Reaction Engineering) for the pyrolysis of waste automobile lubricating oil is shown in Fig. 1. The reaction was carried out in a stirred batch reactor, and the experiment was operated at an atmospheric pressure. The experimental apparatus

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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 $= 8.314\,kJ\,(kmol\,K)^{-1}$
t	pyrolysis time (s)
T	pyrolysis temperature (K)
W	weight of sample at time t (g)
W_0	initial weight of sample (g)
W_∞	final weight of sample (g)
X	conversion of waste automobile lubricating oil

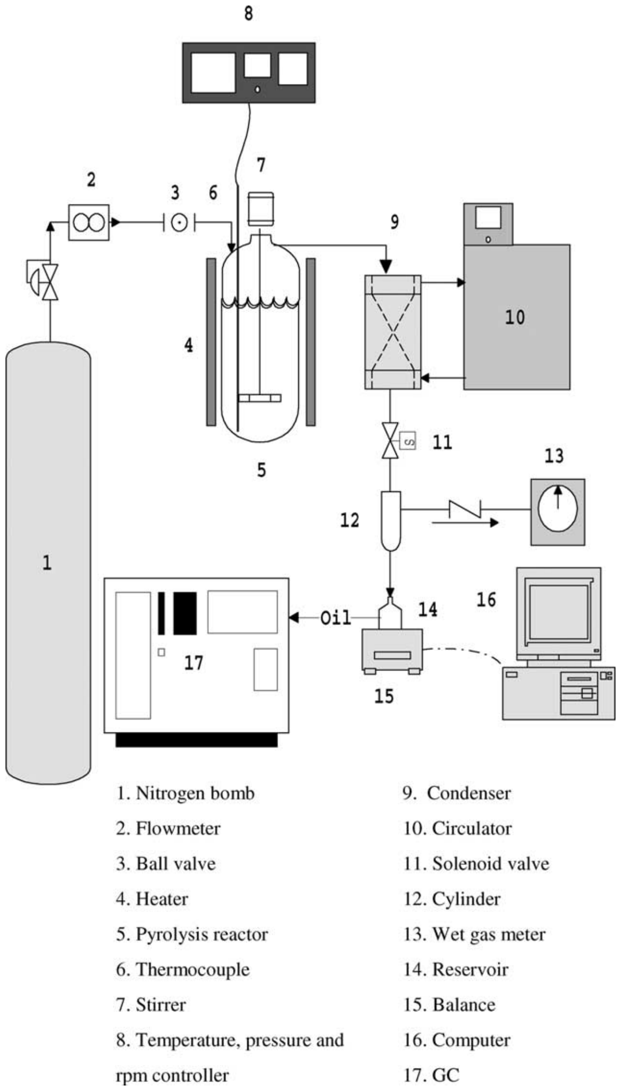

Fig. 1. Schematic diagram of pyrolysis reactor. (1) Nitrogen bomb; (2) Flowmeter; (3) Ball valve; (4) Heater; (5) Pyrolysis reactor; (6) Thermocouple; (7) Stirrer; (8) Temperature, pressure and rpm controller; (9) Condenser; (10) Circulator; (11) Solenoid valve; (12) Cylinder; (13) Wet gas meter; (14) Reservoir; (15) Balance; (16) Computer; (17) GC.

Table 1
Properties of waste automobile lubricating oil

Dynamic viscosity ($m^2\,s^{-1}$)	0.50
Density (at 20 °C, $g\,cm^{-3}$)	0.8797
Gravity (15.4/4)	0.8833
Paraffin (wt.%)	58
Naphthane (wt.%)	42
C_{12}–C_{25} (wt.%)	16.58
$>C_{25}$ (wt.%)	83.42

is characterized as a semi-batch operation, because pyrolyzed vapors are removed continuously during the course of the reaction. The cylindrical pyrolysis reactor of stainless steel has a volume of $1000\,cm^3$. The reactor is equipped with a mechanical agitator to minimize the temperature profile in the reactor. The temperature of the pyrolysis reactor was adjusted by means of a PID temperature controller equipped with a programmable device. A standard thermocouple (chromel–nickel) was installed into the sample material to provide an accurate temperature of the sample during the analysis. This procedure allowed the temperature of the sample to be registered at every moment and the inaccuracy of the measurements caused by the temperature gradient was minimized.

The experimental sample was waste automobile lubricating oil from an automobile maintenance shop. Table 1 shows the characteristics of the sample used in this study. The properties of the sample were characterized according to ASTM D 2140.

A sample mass of 300 g was employed for all experimental runs. To make an oxygen-free atmosphere, nitrogen was introduced into the reactor at a large rate of flow; then the nitrogen was cut off and the mixing rate was set at 100 rpm throughout the experiment. The heating rate was controlled at 0.5, 1.0, or 2.0 $°C\,min^{-1}$ in order to heat up the pyrolysis temperature from 300 to 500 °C. At temperatures below 300 °C, the heating rate was controlled 10 $°C\,min^{-1}$ because waste automobile lubricating oil did not decompose under 300 °C. The deviation of temperature in the reactor was ±1 °C for the pyrolysis temperature of 300–500 °C. The decomposed gas was condensed with cooling fluid at a temperature of 0 °C in the condenser. The cooling fluid was made up of the mixture of ethanol and deionized water. The yields of liquid pyrolysis products were determined gravimetrically by weighing condensed liquid product, while the volume of uncondensed gases were determined by using a wet gas meter. The experimental data were recorded on a personal computer during the entire period every 10 s. The raw hexadecimal data were then converted to ASCII format using a user-written BASIC program. The liquid products were analyzed by gas chromatography with a flame ionization detector (Young Lin-M600D). A capillary column HP-1 of 0.53 mm i.d., and 5 m length was employed. The peaks were identified by matching retention times with reference compounds [22]. The conditions for the gas chromatogra-

Table 2
Condition of gas chromatography

Detector	FID	
Column	i.d. 0.53 mm × 5 m, HP-1 capillary column	
Carrier gas	Helium, 17 ml min^{-1}	
Injector temperature programming	Initial temperature	100 °C
	Final temperature	400 °C
	Heating rate	10 °C min^{-1}
Oven temperature programming	Initial temperature	50 °C
	Final temperature	350 °C
	Heating rate	10 °C min^{-1}
Detector temperature	350 °C	

phy used in the analysis of hydrocarbons are represented in Table 2.

3. Results and discussion

3.1. Thermogravimetric analysis results

For all thermogravimetric experiments, the results are expressed as a function of the degree of conversion X, which is defined as

$$X = \frac{W}{W_0 - W_\infty} \tag{1}$$

where W_0 is the initial mass of sample; W the mass of product oil; and W_∞ is the mass of unpyrolyzed oil sample. As mentioned in Section 2, the condenser temperature was maintained at 0 °C to condense the products. The volume of gas was in the range of 0.87–2.81 l for 0.5–2.0 °C min^{-1} and that of produced oil was 91.64–93.28 wt.%. Variation of heating rate did not have a significant effect on the formation of oil in a stirred batch reactor. The weight of uncondensed gas is much smaller than that of waste automobile lubricating oil and produced oil. In this study, the calculation of conversion was limited to produced oil.

Fig. 2 shows the degree of conversion versus temperature for dynamic experiments at different heating rates of 0.5, 1.0, and 2.0 °C min^{-1}. For a low heating rate of 0.5 °C min^{-1}, it can be observed that the degree of conversion increases sharply until $T = 440$ °C and $X = 0.92$. At temperatures above 440 °C, the curve has a smooth slope and tends asymptotically to the maximum degree of conversion. All three heating rates exhibited the same patterns of thermal decomposition. These results indicate that waste automobile lubricating oil is pyrolyzed in one stage in the temperature range of 300–500 °C.

3.2. Rate of reaction

An instantaneous rate of conversion, dX/dt is obtained from the curve in Fig. 3 at the given reaction temperature. One maximum rate of conversion occurs at a specific reaction temperature for each heating rate. As shown in Fig. 3, the increase of heating rate shifted the rate curve rightwards and made the maximum rate. As the heating rates increased, the rate curves showing maximum rate of dX/dt also increased. As the heating rate increases, higher instantaneous thermal energy is released into the reaction system and results in higher rate of conversion. The results of Fig. 3 also indicate that a larger fraction of waste lubricating oil is pyrolyzed in the reaction temperature range of 430–460 °C

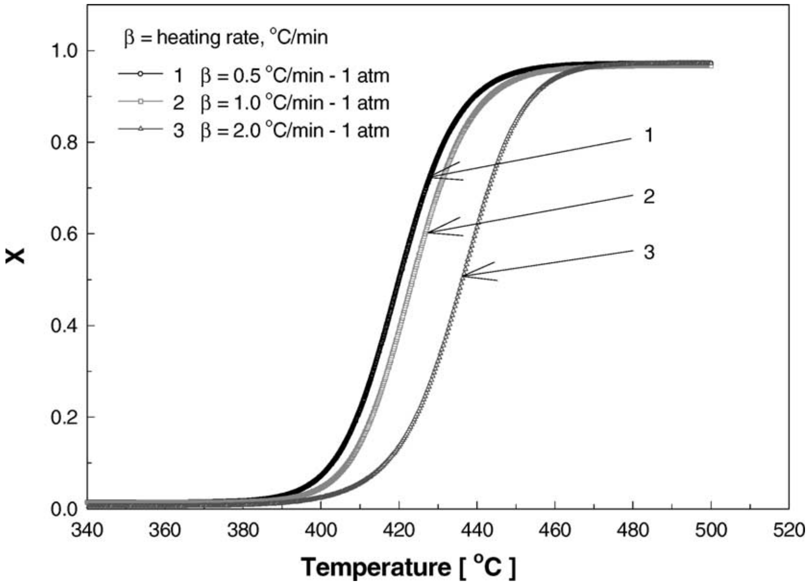

Fig. 2. The effect of pyrolysis rate waste automobile lubricating oil on heating rate.

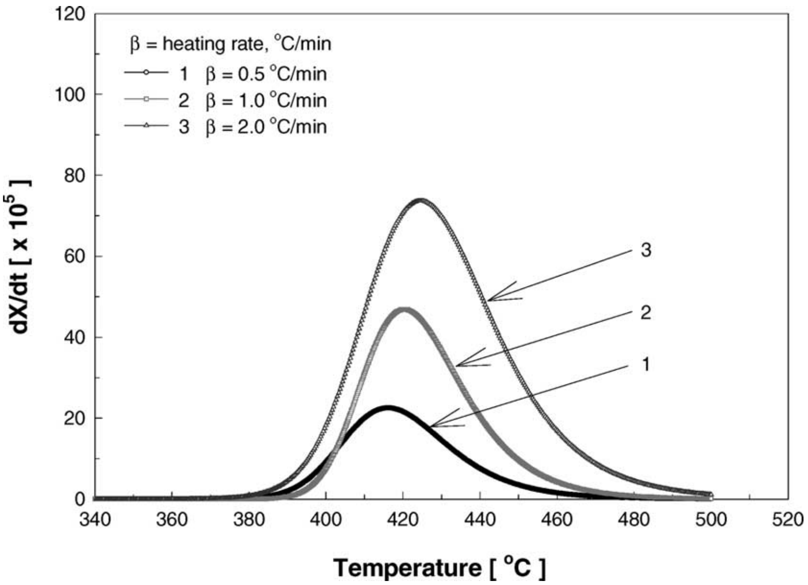

Fig. 3. Variation of the instantaneous reaction rate with temperature at different heating rates for pyrolysis of waste automobile lubricating oil.

and the maximum rate of conversion occurred at 416, 420 and 425 °C for heating rate of 0.5, 1.0 and 2.0 °C min^{-1}, respectively. The rate of weight variation reflects the lateral shift with an increase in the rate, as the heating rate was increased from 0.5 to 2.0 °C min^{-1}. The lateral shift to higher temperatures for the maximum region of weight variation was observed by other workers. For example, Liou et al. [9] showed a lateral increase in the maximum rate of weight change of 20 °C, as heating range was increased from 2 to 5 °C min^{-1} for acid-leached rice husk.

3.3. Activation energy

Thermogravimetric analysis for the differential method and for the integral method has been extensively studied by other researchers [19–21]. The derivation of pyrolysis kinetic data in this work follows that of previous investigators [9,10]. The rate of conversion, $\mathrm{d}X/\mathrm{d}t$, in thermal decomposition is expressed by

$$\frac{\mathrm{d}X}{\mathrm{d}t} = kf(X) \tag{2}$$

The reaction rate constant k is expressed by the Arrhenius equation

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

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

$$f(X) = X^n \tag{4}$$

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

$$\ln\left(\frac{\mathrm{d}X}{\mathrm{d}t}\right) = \ln(AX^n) - \frac{E}{R}\frac{1}{T} \tag{5}$$

Activation energy E, based on Eq. (5), is determined from a relationship between $\ln(\mathrm{d}X/\mathrm{d}t)$ and $1/T$. Thus, a family of parallel straight lines of slope $-E/R$ was obtained. The activation energy (E) corresponding to the selected conversion was obtained. For example, when the conversion was 11%, temperatures were 403.42, 407.50, and 417.33 °C with the heating rates of 0.5, 1.0, and 2.0 °C min^{-1}, respectively. The values of $\ln(\mathrm{d}X/\mathrm{d}t)$ were 2.33, 3.06, and 3.48, with corresponding values of $1/T[K^{-1}]$ at 1.478×10^{-3}, 1.469×10^{-3}, and 1.448×10^{-3}. The activation energy was 287.32 kJ mol^{-1} at 11%. Fig. 4 was shown like this: $\ln(\mathrm{d}X/\mathrm{d}t)$ as a y-axis and $1/T[K^{-1}]$ as an x-axis at conversions of 11, 30, 50, 70, and 90%.

The intercept ($\ln(AX^n)$) can be calculated from Fig. 4 at each conversion. The apparent order of reaction (n) and the pre-exponential factor (A) are obtained by curve fitting based on Eq. (6).

$$\ln(AX^n) = \ln A + n\ln(X) \tag{6}$$

The variation of activation energy as a function of conversion is presented in Fig. 5. The activation energies increased with the conversions increasing. As mentioned in Table 1, the composition above C_{25} was 83.42% and that of between C_{12} and C_{25} was 16.58% at the waste automobile lubricating oil. Also, the waste automobile lubricating oil was the mixture of paraffin (58%) and naphthane (42%), respectively. Thus, the decomposition of waste automobile lubricating oil involves the breaking of relatively weak chemical bonds at low conversion. The greater activation energy is observed in the later period of the conversions. That is, as the conversions increased, E also increased and seemed to be approaching relatively stronger chemical bond dissociation energy. Waste automobile lubricating oil chains are not branched at all and polystyrene and polypropylene are highly branched.

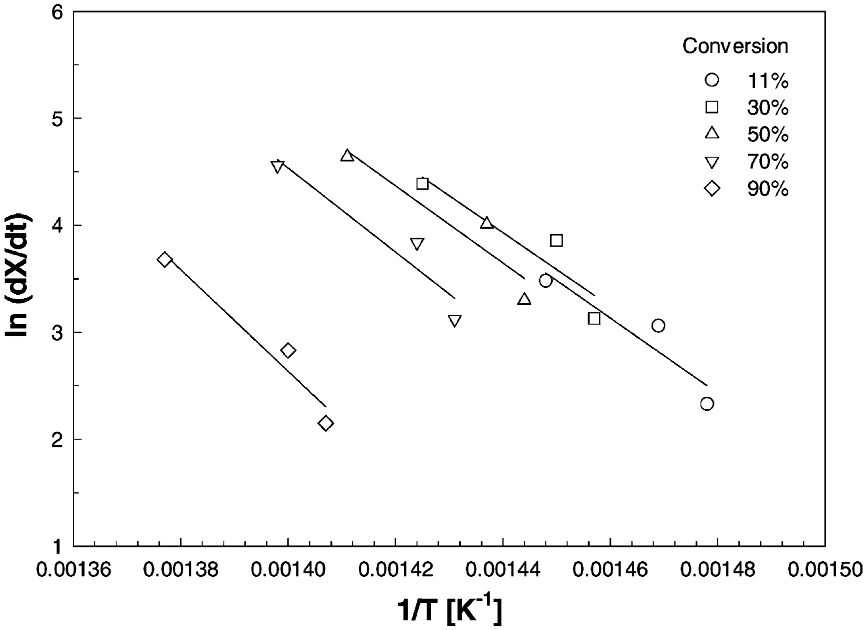

Fig. 4. Application of Eq. (5) with heating rate of 0.5, 1.0, and 2.0 °C min^{-1}. The conversion values are: 11, 30, 50, 70, and 90%.

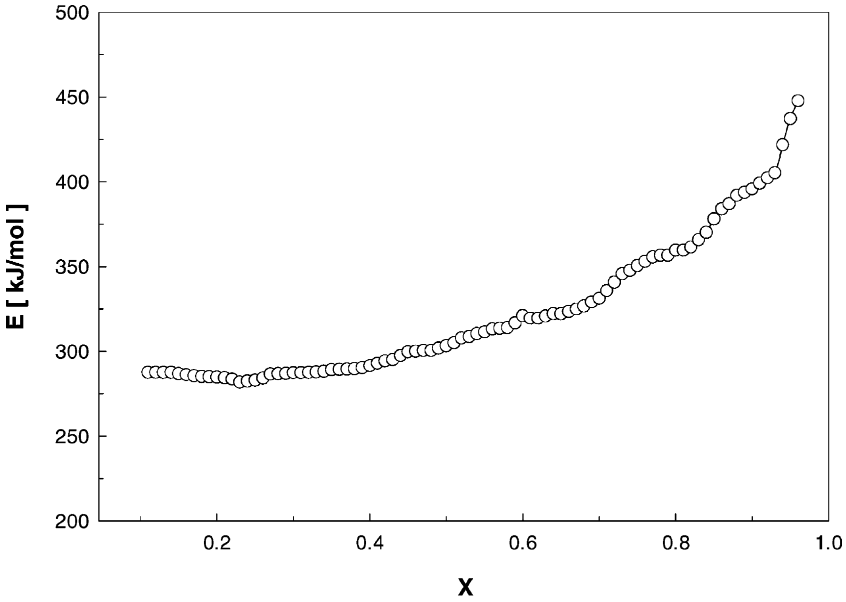

Fig. 5. Calculated activation energies at different conversions for pyrolysis of waste automobile lubricating oil.

Westerhout et al. [24] studied the pyrolysis of HDPE, LDPE, PP and PS using a TGA in the temperature range of 365–450 °C. They reported that the pyrolysis rate increased in the following order: HDPE < LDPE < PP < PS, which implies that the pyrolysis rate increases to the extent of branching. This means that the polymer having a side chain decomposes at low temperature and the activation energy is relatively low.

In order to obtain the order of reaction, plotting of data was as shown in Fig. 6. Fig. 6 showed such linear relations that reaction order (n) of 1.35 was determined. The average activation energy (E), overall order of reaction (n), and pre-exponential factor (A) are listed in Table 3.

Table 3
Kinetic parameters of waste automobile lubricating oil

Avg. E (kJ mol^{-1})	322.69
n	1.35
A (s^{-1})	334.22

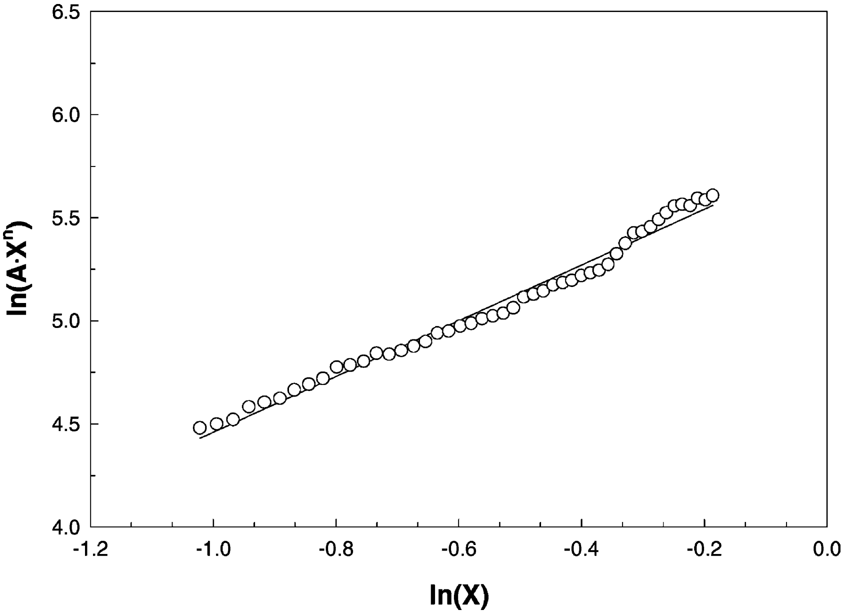

Fig. 6. The overall reaction order for pyrolysis of waste automobile lubricating oil.

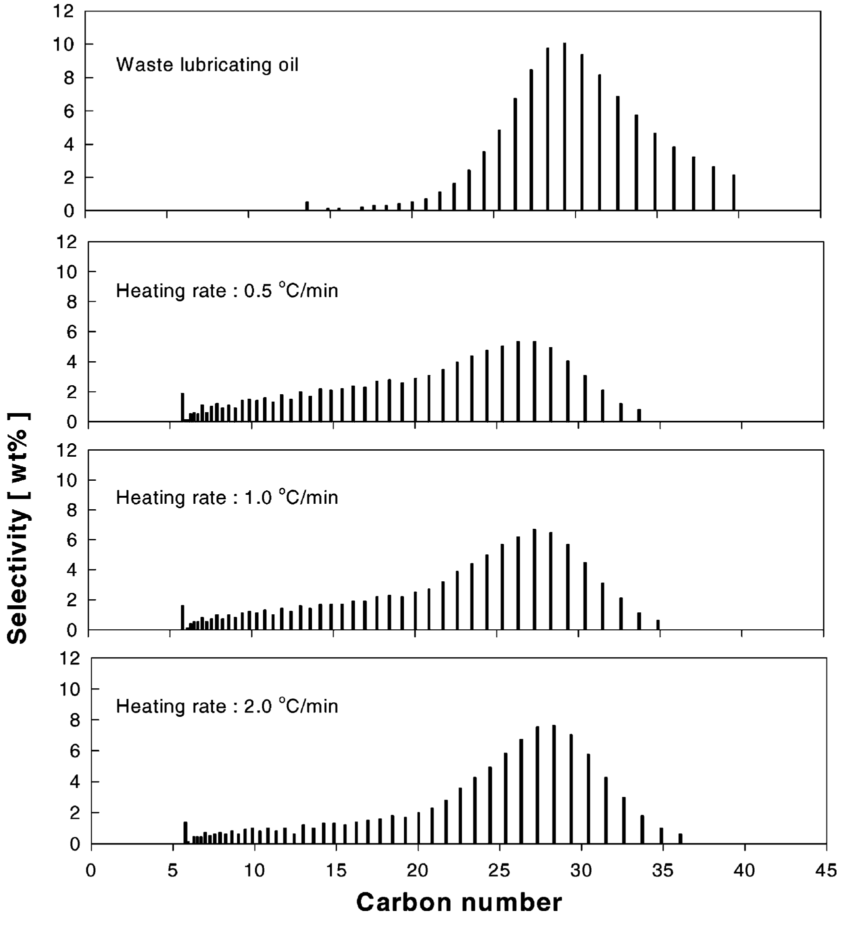

Fig. 7. The effect of heating rate of carbon number distribution on waste automobile lubricating oil.

Table 4
Carbon number distribution of oil according to boiling point distribution of the pyrolysis products (wt.%)

Heating rate (°C min^{-1})	C_5–C_{11} (wt.%)	C_{12}–C_{25} (wt.%)	>C_{25} (wt.%)
Waste automobile lubricating oil	–	16.59	83.41
0.5	16.83	55.85	27.32
1.0	13.39	49.95	36.66
2.0	10.98	42.95	46.07

4. Analysis of product oil

To analyze the reaction products, the samples were dissolved in CS_2. Pyrolyzed oil was quantitatively determined by GC. The most significant results in terms of product distribution according to boiling point of liquid products are represented in Table 4. The carbon numbers of lubricating oil are greater than C_{25} [23]. However, the composition above C_{25} of waste automobile lubricating oil was 83.42% as represented in Table 4. The experimental sample contains 16.58% of light hydrocarbons below C_{25}. It is thought that the light hydrocarbons were produced during the lubrication in automobile engines. Oil products were lumped in two groups of C_5–C_{11} and C_{12}–C_{25} (the carbon number of volatile gasoline is C_5–C_{11}, and the carbon number of fuel oil such as gas oil and heavy gas oil is C_{12}–C_{25}). The selectivity of C_5–C_{11} and C_{12}–C_{25} compounds increased with the heating rates decreasing. Product distribution in terms of carbon number obtained at different heating rate is shown in Fig. 7. The distribution of the product oil shifted slightly to higher carbon numbers with the increase in heating rate. These results suggest that increase in heating rate results in shorter retention. Therefore, the energy required for decomposition of organic matter decreases, which causes carbon numbers to increase.

5. Conclusions

Kinetic tests on pyrolysis of waste automobile lubricating oil were carried out using a thermogravimetric technique (TGA) at heating rate of 0.5, 1.0, and 2.0 °C. The activation energies changed as a function of the conversion during the thermal decomposition. The activation energies increased with the increase of conversions. The average activation energy was 322.69 kJ mol^{-1} at the conversion of 0.11–0.96, and the overall reaction order was 1.35.

The distribution of the product oil shifted slightly to higher carbon numbers with the increase in heating rate. The result shows that the energy for decomposition of organic matter decreased and caused carbon number to increase.

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