

PYROLYSIS OF SCRAP TIRE RUBBERS: RELATIONSHIPS OF PROCESS VARIABLES WITH PYROLYSIS TIME

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Abstract – The functional relationships of industrially interesting variables such as pyrolysis temperature, heating rate, and sample size with pyrolysis time were explored to provide basic information on designing energy efficient processes. Pyrolysis kinetics of scrap tire rubbers tested in this study were investigated to formulate the functional relationships of pyrolysis temperature and heating rate. The pyrolysis time decreases exponentially with increasing pyrolysis temperature and heating rate, indicating high activation energies of pyrolysis reaction of the scrap tire rubbers tested in this study. The effect of heat transfer on the pyrolysis kinetics was evaluated by seeking the functional relationship between the sample size and pyrolysis time. The pyrolysis time increases linearly with increasing sample diameter. The slope of the straight line is proportional to the specific heat of the sample.

Key words: Heating Rate, Pyrolysis Temperature, Pyrolysis Time, Sample Size, Scrap Tire Rubbers

INTRODUCTION

Fast industrialization in Korea leads to high generation and accumulation rate of scrap tires; but few methods have been proposed to tackle the problematic wastes in a systematic and efficient way. The scrap tires will soon emerge as one of the most burdensome wastes. It is, hence, time to review existing techniques and suggest appropriate ones to fully reflect specific management conditions of scrap tires in Korea.

Since natural resources in Korea are scarce, it is desirable to adopt a method which can close a recycling loop of solid wastes. In the case of scrap tires, there is no feasible techniques to convert them completely into new tires. Among various treatment options, pyrolysis of scrap tires is considered to be one which may be a closet option to close their recycling loop because of recovery of authentic carbon black and generation of valuable by-products [Kim, 1995a; Kim et al., 1995b]. Economic marginality of tire pyrolysis, however, has been pointed out frequently [Clark et al., 1991; US. Environmental Protection Agency, 1991; Eastman, 1993]. Despite the critics, any systematic research has been rarely achieved on seeking optimum process conditions to increase the process economics because of complex decomposition reactions of scrap tires.

Recent studies opened a new avenue to estimate the kinetic parameters of complex decomposition reactions [Kim, 1995a; Kim et al., 1995b; Kim and Park, 1995c; Kim and Chun, 1995d]. The present author developed the subtraction method to estimate kinetic parameters of complex decomposition reactions of a heterogeneous substance like scrap tire rubbers [Kim, 1995a; Kim et al., 1995b]. The kinetic parameters derived by the subtraction method were verified experimentally under isothermal conditions [Kim et al., 1995e]. It was concluded that the subtraction method may be a reliable tool to estimate the kinetic parameters of complex independent decomposition reactions

[Kim and Chun, 1995d].

The effect of heat transfer on the pyrolysis kinetics of scrap tire rubbers was also investigated [Kim and Chun, 1995d]. Owing to the recent developments, it was possible to clarify the roles of operating variables in designing energy efficient processes.

The objective of this research was to investigate the role of process variables in designing pyrolysis processes by means of developing functional relationships of the process variables with design criteria. The process variables tested here were pyrolysis temperature, sample size, and heating rate. As a design criterion, pyrolysis time, operationally defined as the time it takes for degradable tire rubbers a conversion of 99.99%, was used in this study [Kim, 1995a; Kim et al., 1995b; Kim and Park, 1995c].

THEORETICAL

The functional relationships of the process variables with the pyrolysis time were implemented mathematically in this section. It was proposed that the pyrolysis reaction of scrap tires would be accounted for by first-order irreversible independent reactions of compositional components.

1. Pyrolysis Temperature

The kinetic equation for pyrolysis reaction is expressed by:

$$\frac{dx}{dt} = \sum_{i=1}^n \frac{dx_i}{dt} = - \sum_{i=1}^n A_i \exp \left(- \frac{E_i}{RT} \right) (1 - x_i) \quad (1)$$

where x =weight conversion fraction of degradable tire rubber; n =total number of compositional components; A =frequency factor (min^{-1}); E =activation energy (J/mol); R =gas constant ($\text{J/mol} \cdot \text{K}$); T =absolute temperature (K); and subscript i =degradable compositional component i .

Integration of the above kinetic equation yields a functional

relationship of the pyrolysis time of a compound i with isothermal pyrolysis temperature [Kim, 1995a; Kim et al., 1995b].

$$\tau_i = \frac{9.2103}{A_i \exp(-E_i/RT)} \quad (2)$$

The pyrolysis time of a tire rubber (τ) is determined by that of the most thermally stable degradable component in a tire rubber.

2. Heating Rate

At a linear heating rate, a first-order kinetics of component i is described by:

$$\frac{dx_i}{dT} = \frac{A_i}{\beta} \exp\left(-\frac{E_i}{RT}\right) (1 - x_i) \quad (3)$$

Integrating Eq. (3) gives:

$$-\ln(1 - x_i) = \left(\frac{A_i E_i}{\beta R}\right) P(u_i) \quad (4)$$

where $u = \frac{E}{RT}$ and

$$P(u_i) = -\int_{\infty}^{u_i} \frac{\exp(-u)}{u^2} du. \quad (5)$$

Taking a natural logarithm of Eq. (4) yields:

$$\ln\{-\ln(1 - x_i)\} = \ln\left(\frac{A_i E_i}{R}\right) - \ln \beta + \ln P(u_i). \quad (6)$$

If Doyle's approximation [Doyle, 1962; Ozawa, 1970; Kim and Chun, 1995d] where $\ln P(u) \approx -5.3305 - 1.0516 \left(\frac{E}{RT}\right)$ is adopted, the above equation is approximated as:

$$\begin{aligned} \ln\{-\ln(1 - x_i)\} &\approx \ln\left(\frac{A_i E_i}{R}\right) - \ln \beta \\ &- 5.3305 - 1.0516 \left(\frac{E_i}{R}\right) \frac{1}{T}. \end{aligned} \quad (7)$$

A final temperature (T_f) where a conversion of 99.99% is accomplished is described as a function of the heating rate:

$$T_f = \frac{E_i}{k_1 \ln \beta + k_2} \quad (8)$$

where $k_1 = -0.9509 R$ and $k_2 = 0.9509 R \left\{ \ln\left(\frac{A_i E_i}{R}\right) - 7.5508 \right\}$;

and subscript i =compositional component which determines the pyrolysis time of the tire sample. Thus, the pyrolysis time is expressed as a function of heating rate:

$$\tau = \frac{T_f - T_0}{\beta} \quad (9)$$

where T_0 =room temperature (K).

3. Sample Size

As sample size increases, heat transfer effects become significant. Hence, it is necessary to formulate heat balance acting on a tire sample. The heat balance is expressed mathematically by:

$$\frac{\partial E}{\partial t} = -\nabla \cdot \mathbf{q} + \dot{m} \Delta H_{rxn} \quad (10)$$

where $\nabla \cdot \mathbf{q}$ =rate of heat transfer by conduction per unit volume ($J/m^3/sec$); \dot{m} =decomposition rate of tire rubbers per unit volume [Eq. (1); $kg/m^3/sec$]; and ΔH_{rxn} =heat of reaction per unit mass (J/kg). If temperature gradients within a sample become negligible, the heat balance equation becomes [Kim, 1995a; Kim and Chun, 1995d]:

$$m C_p \frac{dT}{dt} = -(\dot{m} C_p + h_{all} A_s) T + h_{all} A_s T_r + \sum_{i=1}^n \dot{m}_i \Delta H_{rxn,i} \quad (11)$$

where m =tire weight at a time t ; C_p =specific heat of tire ($J/kg \cdot K$); h_{all} =overall heat transfer coefficient ($W/m^2 \cdot K$); A_s =surface area of sample (m^2); T_r =isothermal reaction temperature (K); and ΔH_{rxn} =heat of reaction per unit mass (J/kg).

It is difficult to analytically derive a functional relationship of the pyrolysis time with sample size (A_s) from two coupled ordinary differential Eqs. (1) and (11) (ODEs). Instead, the Runge-Kutta 4th order method was introduced to solve the ODEs numerically, thus seeking empirical relationship between the pyrolysis time and sample size.

EXPERIMENTAL

1. Tire Sample

A scrap tire (195/60 R15 86H) produced by the Bridgestone Company in Japan was used throughout this study. Elemental and proximate analysis of the tread and sidewall rubbers tested in this study were reported elsewhere [Kim and Chun, 1995d]. The rubber samples were obtained from sidewall and tread section of the tire. Fibers and steel wires were removed and the tire rubbers were shredded into granules with a cutting knife. The tire samples were sieved into four classes with mean diameters of 0.45, 0.73, 0.93 and 1.2 mm. Then, the samples were washed and dried at 50°C for two hours and put in a desiccator before analysis.

2. Thermobalance

The thermobalance consisted of a laboratory scale pyrolysis reactor and a weight detection unit (Fig. 1). The device was designed to constitute a reliable isothermal environment in the reactor, to minimize the thermal decomposition during the course of sample insertion, and to continuously monitor the weight loss with respect to time.

A high stainless steel tube (5.5 cm i.d. \times 1.0 m) was used as a pyrolysis reactor. The reactor was heated to a reaction temperature under a stream of nitrogen with a linear velocity of 8.3 cm/sec, yielding a laminar flow ($Re < 100$ at most reaction temperatures). Tire rubber samples were suspended in a 100 mesh stainless steel wire basket. The sample basket was connected to an electric balance (Presisa Model 205-A) by a 0.3 mm diameter nichrome wire. The balance was lowered down quickly by a winch to insert samples to a reaction zone after a reaction temperature was stabilized. Weight loss of a sample with re-

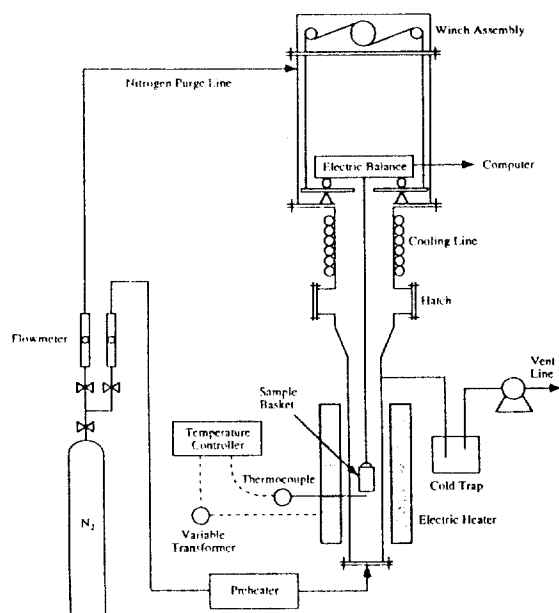


Fig. 1. Schematic diagram of the thermobalance unit.

Table 1. Activation energies, frequency factors and weight fraction of the compositional components of the sidewall and tread rubber [Kim et al., 1995b]

Compound	Tread rubber			Sidewall rubber		
	E ¹	ln A ²	wt%	E ¹	ln A ²	wt%
1	127.3	20.59	63.6	203.9	32.95	69.5
2	209.0	38.17	21.3	195.1	35.27	22.5
3	38.7	6.84	15.0	42.1	7.27	7.7

1: Activation energy (kJ/mol)

2: Frequency factor (min⁻¹)

spect to time was recorded continuously over time by an on-line personal computer.

RESULTS AND DISCUSSION

Previous studies demonstrated that there were three thermally degradable compounds in both the tread and sidewall rubbers [Kim, 1995a; Kim et al., 1995b] and their kinetic parameters for pyrolytic decomposition reactions are listed as Table 1. Among the three degradable compounds, the pyrolysis times of the scrap tire rubbers may be determined by the decomposition rate of the most thermally stable compound, named here as compound 1. In the previous research, natural rubber (NR) and butadiene rubber (BR) were tentatively assigned as compound 1 of the tread and sidewall rubber, respectively [Kim et al., 1995b].

First, it was necessary to verify the theoretical relationships of the process variables, pyrolysis temperature and heating rate, with pyrolysis time [Eqs. (2) and (9)]. As shown in Eqs. (2) and (9), the reliability of the theoretical relationships was solely dependent of whether or not the kinetic parameters were estimated correctly. Hence, the theoretical relationships would be applicable only if the kinetic parameters were estimated correctly. The present author developed the subtraction method to estimate kinetic parameters of pyrolytic reactions of the scrap

Table 2. Comparison of pyrolysis time between theoretical and experimental results at various heating rates

Heating rate (°C)	Theoretical results (min)	Experimental results (min)	Relative error (%)
5	93.25	104.95	12.6
7.5	64.17	63.77	0.6
10	49.23	53.80	9.3
12.5	40.08	40.18	0.3
15	33.89	32.78	3.3

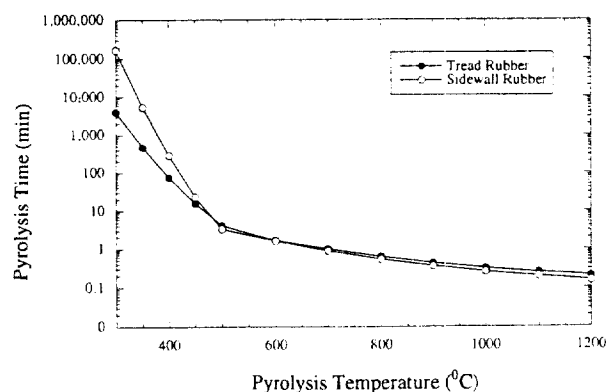


Fig. 2. Pyrolysis times of tire tread and sidewall rubber with respect to pyrolysis time.

tire rubbers and verified the subtraction method experimentally [Kim et al., 1995b; Kim, 1995e]. Also, it was already demonstrated that the theoretical pyrolysis times under isothermal operating conditions were in good agreement with the experimental results [Kim, 1995a; Kim, 1995e].

In the case of variable temperature operations, the theoretical pyrolysis times duplicate experimental ones relatively well (Table 2). Most theoretical results were a little lower than the experimental ones. The deviation is mainly due to the Doyle's approximation [Eq. (7)] which overestimates the $P(u)$. If possible experimental errors would be considered, the theoretical method estimating pyrolysis time for variable temperature operations seems to be reliable.

The pyrolysis times of both rubbers were estimated as a function of isothermal pyrolysis temperature (Fig. 2). The pyrolysis time decreases exponentially with increasing the isothermal pyrolysis temperature. Above an isothermal temperature of 500°C, the pyrolytic decompositions of both rubbers seem to be accomplished rapidly (<5 minutes), while pyrolysis process of the scrap tire rubbers may be energy inefficient below 500°C because of extremely high pyrolysis times. Since marketable oil by-products are produced mainly at low temperatures [Kim, 1995a; Kaminsky and Sinn, 1980; Mirmiran et al., 1992; Pakdel et al., 1991; Roy, 1988; Roy et al., 1990], their market values have to justify high operational costs; otherwise, the pyrolysis process at low temperatures becomes economically in-viable.

In the case of variable temperature operation, the pyrolysis time decreases exponentially as linear heating rate increases (Fig. 3), but the final temperature where the reaction is completed increases exponentially until reaching asymptotic region (Fig. 4). Thus, it is difficult to conclude that high heating rates are pre-

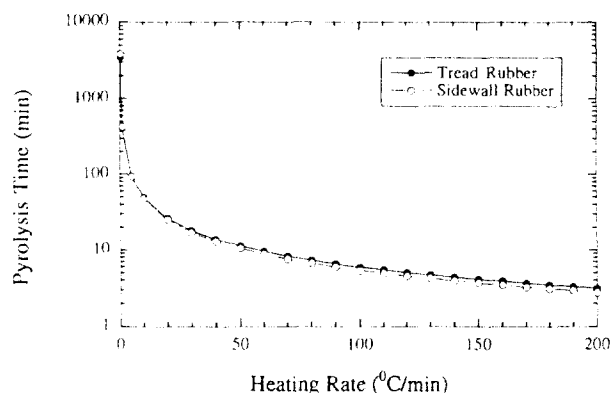


Fig. 3. Pyrolysis times of tire tread and sidewall rubber with respect to linear heating rate.

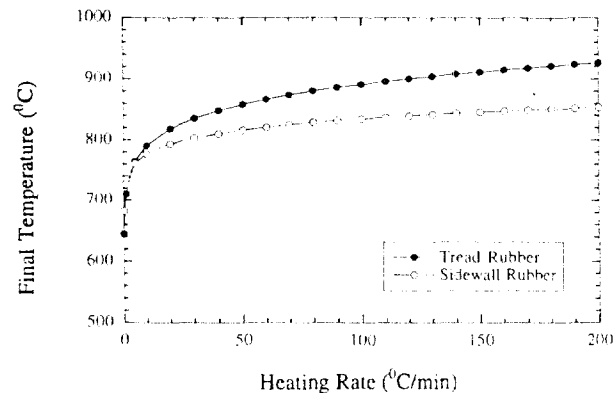


Fig. 4. Final temperatures with respect to linear heating rate.

ferred in light of energy efficiency. The energy efficiency of a system is judged by total input energy during the course of pyrolysis process. The total input energy is denoted by [Kim, 1995a; Kim et al., 1995e]:

$$E_{in} = \sum_{i=1}^n m_{i,0} \Delta H_{rxn,i} + U A_r (T_r - T_{\infty}) \tau \quad (12)$$

$$= \sum_{i=1}^n m_{i,0} \Delta H_{rxn,i} + \frac{U A_r (T_r - T_{\infty})^2}{2\beta} \quad (13)$$

$$= \sum_{i=1}^n m_{i,0} \Delta H_{rxn,i} + \frac{U A_r \beta \tau^2}{2} \quad (14)$$

where E_{in} =total input energy (J); $m_{i,0}$ =initial mass of component i ; ΔH_{rxn} =heat of reaction per unit mass (J/kg); U =overall heat transfer coefficient from reactor to ambient environment ($W/m^2 \cdot K$); A_r =surface area of reactor (m^2); and T_{∞} =ambient temperature (K).

As shown by Eq. (14), the total input energy is proportional to heating rate and pyrolysis time. Pyrolysis time, however, decreases exponentially with increasing the heating rate (Fig. 3). Thus, it is necessary to seek an optimum combination of heating rate and pyrolysis time where the total input energy is minimum. The total input energy may be minimum at a heating rate where the partial derivative of total input energy [Eq. (12)] with respect to heating rate is equal to zero. The heating rate permitting the minimum total energy was estimated to be 8.8×10^6 and $3.4 \times 10^{10} \text{ } ^\circ\text{C/min}$ for the tread and sidewall rubber, respectively [Kim, 1995a; Kim et al., 1995e]. The extremely high heating rates were expected because of the high activation energies of decomposition reactions of the rubbers, reported to be 203.9 and 127.3 kJ/mol for the sidewall and tread rubbers, respectively [Kim, 1995a; Kim et al., 1995b]. Hence, it is desirable to select a heating rate as high as possible in light of energy efficiency.

Sample sizes of scrap tires are closely related to operational costs because of high shredding costs. Application of whole tires may be economically desirable, but the effect of heat transfer may be so dominant that the pyrolysis time may be extended significantly, thus nullifying the advantage of treating whole tires.

The pyrolysis time is composed of heating-up time and a

period of isothermal decomposition where chemical reaction controls overall reaction rate. The pyrolysis time may increase with increasing sample size because of an increase in the heating-up time. The increasing pattern may exhibit a specific functional relationship between them. However, the relationship was rarely derived analytically, as already mentioned. Instead of developing analytical relationships, empirical relationships were obtained. As shown in Fig. 5a and 5b, the pyrolysis times at isothermal temperatures of 673 (Fig. 5a) and 770 K (Fig. 5b) exhibit linear relationships with sample sizes. Also the same pattern was observed at an isothermal temperature of 573 K. The heating-up time is inversely proportional to heat transfer conditions (heat transfer coefficient and surface area), but is proportional to the thermal capacitance of a sample, which in turn is expressed as:

$$C_t = \frac{\int_0^{\tau_h} m C_p dt}{\tau_h} = \bar{m} \bar{C}_p \quad (15)$$

where C_t =thermal capacitance (J/K); τ_h =heating-up time (sec); and \bar{m} =average sample weight during the period of heating-up time (kg).

Thus, the proportionality of heating-up time (τ_h) is described as:

$$\tau_h \propto \left(\frac{\bar{\rho} \bar{C}_p}{h} \right) D \quad (16)$$

where $\bar{\rho}$ =average sample density during the period of heating-up time (kg/m^3).

The slope of the straight line in Fig. 5a and 5b is closely related to the sensitivity of heating-up time to sample size and may increase with increasing the specific heat of tire sample, as shown by the above relationship [Eq. (16)]. The sidewall rubber is more sensitive to the variation of sample size (Fig. 5a and 5b), due to its higher specific heat. Hence, it is appropriate to come to a conclusion that the pyrolysis time increases linearly with the sample diameter of the scrap tire rubbers at low and medium pyrolysis temperatures.

The characteristics of pyrolysis products as to operating variables would be considered together with the energy-efficient operation to evaluate the economics of tire pyrolysis. As isothermal pyrolysis temperature increases, gas by-products increase considerably, whereas solid products decreases (Table 3). If one

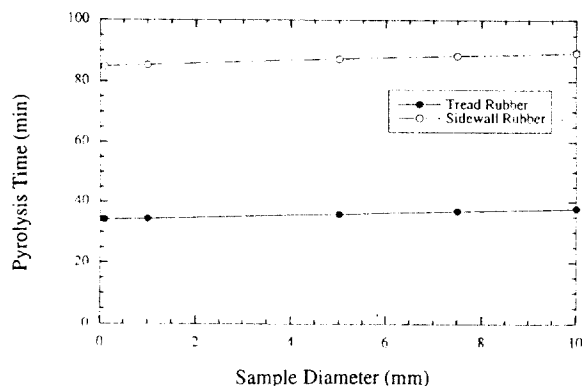


Fig. 5a. Pyrolysis times of tread and sidewall rubber as a function of sample diameter at an external temperature of 673 K.

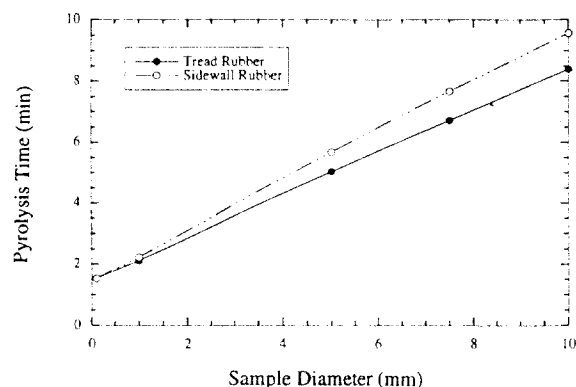


Fig. 5b. Pyrolysis times of tread and sidewall rubber as a function of sample diameter at an external temperature of 770 K.

would like to recover or generate a specific marketable substance in an energy-efficient manner, it seems to choose a pyrolysis temperature as high as possible within the temperature range where the specific compound is recovered or generated considerably. On the other hand, there was a little effect of heating rate on the product yield [Williams, 1990], implying that, in case of variable temperature operations, the economics of tire pyrolysis would be mainly affected by energy-efficient operations. The sample size may influence the product yields because of non-isothermal decomposition during the heating-up time. Thus, the product yields at the beginning of the pyrolysis process may be deviated from what are expected at an operating temperature. If one would design a pyrolysis plant of scrap tires, the sample size would be determined carefully because of heat transfer effects. A systematic research on heat transfer effect may be carried out to determine the sample size prior to designing a pyrolysis plant. Although engineering data directly applicable for process design were rarely demonstrated in this study, this research may provide an insight into designing the pyrolysis process.

CONCLUSIONS

Since the chemical compositions of tire vary widely with manu-

Table 3. Approximate product of distribution as a function of pyrolysis temperature [Dodd et al., 1983]

Pyrolysis temperature (°C)	Product weight percent		
	Gas	Oil	Char
773	6	42	52
873	10	50	40
973	15	47	38
1,073	31	40	29

facturing recipes, conclusions derived here may be limited to the specific scrap tire rubbers tested in this study. The following conclusions can be drawn:

1. The functional relationship of pyrolysis time with isothermal pyrolysis temperature is expressed as:

$$\tau_i = \frac{9.2103}{A_i \exp(-E_i/RT)}$$

As shown by the above, the pyrolysis time at an isothermal temperature is linearly proportional to frequency factor, whereas is inversely proportional to activation energy. Since the pyrolysis time decreases exponentially as the activation energy increases, it is expected that the pyrolysis time varies more sensitively with activation energy. Thus, a compositional compound exhibiting high activation energy may determine the pyrolysis time of a heterogeneous substance like scrap tire rubbers. On the other hand, the pyrolysis time of a specific scrap tire rubber decreases exponentially with increasing pyrolysis temperature. Pyrolysis products generated at low pyrolysis temperatures (573-673 K), hence, should be marketable enough to compensate high operating costs due to slow decomposition rates.

2. The functional relationship of pyrolysis time with linear heating rate is expressed as:

$$\tau = \frac{T_f - T_0}{\beta}$$

The pyrolysis time at a heating rate is proportional to the activation energy and frequency factor of pyrolytic decomposition reaction [Eq. (8) and (9)], whereas decreases exponentially with increasing heating rate. The higher heating rate may be desirable because of the shorter pyrolysis time, provided that the quality and quantity of by-products would be rarely varied with heating rate.

3. It was impossible to analytically derive the functional relationship between pyrolysis time and sample size. Instead, a numerical method was used to determine the relationship between them and was verified experimentally. It was founded that the pyrolysis time increases linearly with increasing sample diameter. The slope of the straight line may be proportional to the specific heat of sample, as shown by Eq. (16).

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advice.

NOMENCLATURE

A	: pre-exponential factor [min^{-1}]
A_r	: surface area of reactor [m^2]
A_s	: surface area of sample [m^2]
C_p	: specific heat of tire [J/K]
C_r	: thermal capacitance [$\text{J/kg} \cdot \text{K}$]
E	: activation energy [J/mol]
E_{in}	: total input energy [J]
n	: total number of compositional components
h_{ait}	: overall heat transfer coefficient [$\text{W/m}^2 \cdot \text{K}$]
l	: total number of sample
m	: tire weight at a time t
$m_{i,0}$: initial weight of component i
\dot{m}	: decomposition rate of component
\bar{m}	: average weight during the period of heating-up time [kg]
n	: number of compositional components
$P(u_i)$: defined as Eq. (5)
R	: gas constant [$\text{J/mol} \cdot \text{K}$]
Re	: Reynold number
T	: absolute temperature [K]
T_0	: room temperature [K]
T_f	: final temperature where a conversion of 99.99% is accomplished [K]
T_r	: isothermal reaction temperature [K]
T_∞	: room temperature [K]
x	: conversion fraction of degradable tire rubber
U	: overall heat transfer coefficient from reactor to ambient environment [$\text{W/m}^2 \cdot \text{K}$]

Greek Letters

β	: linear heating rate [$^{\circ}\text{C/min}$]
$\nabla \cdot \mathbf{q}$: rate of heat transfer by conduction per unit volume [$\text{J/m}^3/\text{sec}$]
$\Delta H_{r,m}$: heat of reaction per unit mass [J/kg]
$\bar{\rho}$: average sample density during the period of heating-up time [kg/m^3]
τ	: pyrolysis time [min]
τ_r	: heating-up time [min]

Subscripts

1	: compound 1
2	: compound 2
i	: compound i
t	: compositional component which determines the pyrolysis time of the tire sample

REFERENCES

Clark, C., Meardon, K. and Russell, D., "Burning Tires for

- Fuel and Tire Pyrolysis: Air Implications", EPA-450/3-91-024, U. S. Environmental Protection Agency, 1991.
- Dodds, J., Domenico, W. F., Evans, W. F., Fish, D. R., Lasahn, P. L. and Toth, W. J., "Scrap Tires: A Resource and Technology Evaluation of Tire Pyrolysis and Other Selected Alternative Technologies", EGG-2241, U. S. Department of Energy, 1983.
- Doyle, C. D., "Estimating Isothermal Life from Thermogravimetric Data", *J. Appl. Polym. Sci.*, **6**(24), 639 (1962).
- Eastman, A. L., "Scrap Tires: Alternatives and Markets in the United States", *Rubber Division, Amer. Chem. Soc.*, Orlando, Florida, 1993.
- Kaminsky, W. and Sinn, H., "Aromatics from Scrap Tires", *Hydroc. Proc.*, **59**(11), 187 (1990).
- Kim, S., "Pyrolysis of Scrap Tire Rubbers", Ph.D. dissertation, Univ. Wisconsin-Madison (1995a).
- Kim, S., Park, J. K. and Chun, H., "Pyrolysis Kinetics of Scrap Tire Rubbers, I: Using DTG and TGA", *J. Envir. Engrg., ASCE*, **121**(7), 507 (1995b).
- Kim, S. and Park, J. K., "Characterization of Thermal Reaction by Peak Temperature and Height in DTG Curve", *Thermochim. Acta*, **264**, 137 (1995c).
- Kim, S. and Chun, H., "Analytical Techniques Estimating Kinetic Parameters for Pyrolysis Reaction of Scrap Tire Rubbers", *Korean J. Chem. Engrg.*, **12**(4), 448 (1995d).
- Kim, S., Park, J. K. and Kim, S. D., "Pyrolysis Kinetics of Scrap Tire Rubbers, II: Heat Transfer Effects", *Submitted for publication in the ASCE J. Environ. Eng.*, (1995e).
- Kim, S. and Park, J. K., "Theoretical Determination of Energy Efficient Pyrolysis Process of Scrap Tire Rubbers", *In preparation to submit to the Environ. Sci. Technol.*, (1995f).
- Mirmiran, S., Pakdel, H. and Roy, C., "Characterization of Used Tire Vacuum Pyrolysis Oil: Nitrogenous Compounds from the Naphtha Fraction", *J. Anal. Appl. Pyrolysis*, **22**, 205 (1992).
- Ozawa, T., "Kinetic Analysis of Derivative Curves in Thermal Analysis", *J. Thermal Anal.*, **2**, 301 (1970).
- Pakdel, H., Roy, C., Aubin, H., Jean, G. and Coulombe, S., "Formation of *dl*-Limonene in Used Tire Vacuum Pyrolysis Oils", *Environ. Sci. Technol.*, **25**, 1646 (1991).
- Roy, C., "Vacuum Pyrolysis of Scrap Tires", U. S. Patent, 4740270, 1988.
- Roy, C., Labrecque, B. and de Caumia, B., "Recycling of Scrap Tires to Oil and Carbon Black by Vacuum Pyrolysis", *Resour. Conserv. Recycling*, **4**, 203 (1990).
- U. S. Environmental Protection Agency, "Markets for Scrap Tires", EPA/530-SW-90-074A, 1991.
- Williams, P. T., Besler, S. and Taylor, D. T., "The Pyrolysis of Scrap Automotive Tyres the Influence of Temperature and Heating Rate on Product Composition", *Fuel*, **69**, 1474 (1990).