



Pyrolysis reaction models of waste tires: Application of Master-Plots method for energy conversion via devolatilization



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ABSTRACT

Land applied disposal of waste tires has far-reaching environmental, economic, and human health consequences. Pyrolysis represents a potential waste management solution, whereby the solid carbonaceous residue is heated in the absence of oxygen to produce liquid and gaseous fuels, and a solid char. The design of an efficient conversion unit requires information on the reaction kinetics of pyrolysis. This work is the first to probe the appropriate reaction model of waste tire pyrolysis. The average activation energy of pyrolysis was determined via iso-conversional methods over a mass fraction conversion range between 0.20 and 0.80 to be $162.8 \pm 23.2 \text{ kJ mol}^{-1}$. Using the Master Plots method, a reaction order of three was found to be the most suitable model to describe the pyrolytic decomposition. This suggests that the chemical reactions themselves (cracking, depolymerization, etc.), not diffusion or boundary layer interactions common with carbonaceous biomasses, are the rate-limiting steps in the pyrolytic decomposition of waste tires.

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1. Introduction

Waste tires (WT) are a severe environment hazard. Every year around 1.5 billion tires are dumped into the environment (Su and Zhao, 2009). This figure will continue to increase as more and more automobiles are introduced into the market to meet increasing global demand. Although WT is only 2% of the total wastes of the world, their impact on the environment is massive (López et al., 2010). As tires are non-destructible and non-biodegradable, when disposed of they occupy tremendous amounts of valuable space over decades. These accumulated tires are prone to catch fire, and their smoke is detrimental to ambient air quality and poses risks to nearby populations (Lemieux and Ryan, 1993). Further, landfilled tires pollute groundwater and surface water (Day et al., 1993). Discarded tires serve as breeding sites for mosquitoes, which carry dreadful diseases like Malaria, Dengue, Chikungunya, and Elephantiasis (Miranda et al., 2013). One alternative to reduce their impact is to extract useful energy from WT while simultaneously reducing the solid waste and ensuing consequences of disposal. Energy recovery processes from WT have the potential to deliver useful energy and a number of value added chemicals (Shah et al., 2007). In addition to the fuels that can be

extracted from WT, the solid residue remaining after thermochemical conversions of this carbonaceous waste can be used as a source of activated carbons, with surface areas as high as $1200 \text{ m}^2 \text{ g}^{-1}$ (Mui et al., 2004).

Turkey is a fast-growing country that relies heavily upon automobile industries for its development. In 2012, the country manufactured around one million motor vehicles. The country generates close to 0.284 MT of WT annually. Of the total WT, around 0.130 MT is utilized as an alternative fuel in cement plants and 0.061 MT is used as granulated materials for various applications. However, nearly 33% of WT goes unutilized, posing a serious threat to the environment. Further, the generation of WT is going to increase as the Turkish tire industry is expected to grow at 8% between 2014 and 2019. Hence, the country must focus on complete utilization of WT to generate energy and/or value added products.

Tires possess high volatile compounds and low ash content, though also contain steel reinforcements and sulfur as a result of vulcanization. Tires have a heating value higher than coal and biomass. Tires are considered an excellent feedstock for thermochemical processes for energy recovery such as combustion, gasification and pyrolysis (Islam et al., 2008; Ismail et al., 2017). Among these processes, pyrolysis has piqued many researchers' interest as it yields products in solid, liquid and gas forms, including the ability to separate volatile carbonaceous fuels and carbon black (Olazar et al., 2005). Some argue that pyrolysis of the tire causes less harm

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to the environment than during combustion, which is more difficult to capture fugitive sulfur emissions (Kim and Chun, 1995). Pyrolysis of WT is an economically viable process that can be scaled up without substantial adversity (Olazar et al., 2005; Wang et al., 2014). Furthermore, pyrolysis is the initial – and often rate-limiting step – for other thermochemical processes such as combustion, gasification and liquefaction, making kinetic studies essential for the design and fabrication of processing and handling equipment for WT thermochemical conversions (López et al., 2013).

Theoretically, kinetic experiments performed under non-isothermal conditions provide kinetic parameters such as reaction models, activation energies and pre-exponential factors. However, with heterogeneous solids such as WT, these kinetic studies are sometimes inaccurate and misleading as they are based on single step kinetic models whose predictions are made based on fitting data (Wanjun et al., 2006; Çepeliogullar et al., 2016). On the other hand, model-free approaches characterized by iso-conversional methods yield reasonably consistent, reproducible activation energies (Vyazovkin et al., 2014; 2011; Fernandez-Lopez et al., 2016). The obtained activation energy can, in turn, be used to determine reaction mechanism(s). The present study of WT pyrolysis is a kinetic analysis of solid-state devolatilization and decomposition using both differential and integral methods to determine kinetic parameters via a graphical analyses method called ‘master plots’ (MP) (Kim et al., 1992; Fernandez-Lopez et al., 2016) These theoretical MP depend on kinetic models, not on the kinetic parameters of the process, such that comparing experimental MP with theoretical ones provides insight into the mechanism(s) of the pyrolysis process (Gotor et al., 2000). While there are several studies that apply thermogravimetric analysis (TGA) to WT pyrolysis to determine activation energies, there is scant literature that tries to elucidate the decomposition mechanisms of nonisothermal degradation of such complex media (Alonso et al., 2010).

2. Materials and methods

Although there are many techniques to determine the kinetics of WT pyrolysis, thermogravimetric analysis (TGA) is considered the best available technique as it is straightforward, reliable and cost effective (López et al., 2010).

2.1. Characterization of WT sample

WT used in the present study was procured from a local recycling company. The steel wires (reinforcing agent) usually of diameter 1–5 mm were removed from the tires and discarded. The steel-free sample was mechanically ground using a kitchen blender. The sample was reduced to a size below 250 μm as to avoid heat and mass transfer limitations. A proximate analysis was carried out according to standard methods in an ash oven. Ash and volatile matter contents were determined according to the ASTM standard method of D5142-09. Fixed carbon ratio was calculated by subtracting percent ratios of volatile matter and ash from a sum of 100. A Leco CHNS-932 analyzer working on ASTM D5373-16 was used for the elemental analysis. The higher heating value of the sample was determined using CAL-2 K oxygen bomb calorimeter with a ASTM D5865-13 standard procedure. The sulfur content was determined employing a LECO SC-432 analyzer according to ASTM D4239-14.

2.2. Thermogravimetric analysis

The thermal behavior of WT sample under pyrolysis conditions was investigated using a Thermogravimetric analyzer (Shimadzu,

Japan). The instrument continuously records mass loss as a function of time and temperature. About 10 mg of WT was loaded into the analyzer. Thermogravimetric analysis was performed under an inert nitrogen atmosphere with a flow rate of 80 ml min^{-1} . TGA was conducted at various heating rates (5, 10, 20 and 40 $^{\circ}\text{C min}^{-1}$) from room temperature to 800 $^{\circ}\text{C}$. Each sample was held at 110 $^{\circ}\text{C}$ for 20 min to remove moisture and at 800 $^{\circ}\text{C}$ for 20 min to provide full pyrolytic decomposition of sample. Kinetic analyses were based off of the dry mass as the initial mass.

2.3. Determination of activation energy

The solid state decomposition reaction can be written broadly as:



where k is the temperature dependent reaction rate constant, which is often expressed by the Arrhenius equation, Eq. (1);

$$k(T) = A \exp(-E/RT) \quad (1)$$

In Eq. (1), E is the activation energy (kJ mol^{-1}), T is the absolute temperature (K), R is the Universal gas constant ($8.314 \times 10^{-3} \text{ kJ (mol.K)}^{-1}$) and A is the pre-exponential factor (sec^{-1}).

The conversion rate of solid fuel into products during decomposition can be expressed as

$$\frac{dx}{dt} = k(T)f(x) \quad (2)$$

In Eq. (2) x , t , $k(T)$, $f(x)$ are the mass fraction conversion degree, time, the temperature dependent rate constant, and unknown reaction mechanism, respectively.

The degree of conversion is expressed as:

$$x = \frac{m_0 - m}{m_0 - m_\infty} \quad (3)$$

where m_0 , m and m_∞ describe mass at start of decomposition, instantaneous mass (at any time t) and final mass of the sample, respectively.

Substituting Eq. (1) in Eq. (2) gives:

$$\frac{dx}{dt} = A e^{(-\frac{E}{RT})} f(x) \quad (4)$$

The heating rate, β ($^{\circ}\text{C min}^{-1}$), is given by:

$$\beta = dT/dt \quad (5)$$

When heating rate is introduced into Eq. (4), the Arrhenius equation can be expressed as:

$$\frac{dx}{dT} = \frac{A}{\beta} e^{(-\frac{E}{RT})} f(x) \quad (6)$$

Model free methods do not require prior knowledge of the reaction mechanism for estimating the activation energy of decomposition. Therefore, with such heterogeneous samples as WT, these methods are more reliable than model fitting methods in calculating activation energy. In this study, the activation energy was determined via widely used model free non-isothermal methods such as Ozawa-Flynn-Wall (OFW) and Kissinger-Akahira-Sunose (KAS) (Ceylan, 2015).

The OFW method uses Eq. (7) for the calculation of activation energy, which is given by:

$$\log(\beta) = \log \left[\frac{AE}{Rg(x)} \right] - 2.315 - 0.457 \frac{E}{RT} \quad (7)$$

While plotting $\log(\beta)$ vs. $1/T$, the slope gives $-E/R$. The KAS method can be represented as:

Table 1
Most common reaction mechanisms for solid-state degradation processes in differential and integral form.

Symbol	Reaction mechanism	$f(x) = (1/k)(dx/dt)$	$G(x) = kt$
Reaction order			
F0	Zero-order	1	α
F1	First-order	$(1 - \alpha)$	$-\ln(1 - \alpha)$
F2	Second-order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
F3	Third-order	$(1 - \alpha)^3$	$(1/2)[(1 - \alpha)^{-2} - 1]$
Autocatalytic			
B1	Autocatalytic reaction	$\alpha(1 - \alpha)$	$\ln(\alpha(1 - \alpha)^{-1})$
Mampel			
P(2/3)	Power law	$(2/3)\alpha^{1/2}$	$\alpha^{3/2}$
P2	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P3	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P4	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
Nucleation			
A1.5	Avrami-Erofeev	$(1.5)(1 - \alpha)[- \ln(1 - \alpha)]^{1/3}$	$[- \ln(1 - \alpha)]^{3/2}$
A2	Avrami-Erofeev	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
A3	Avrami-Erofeev	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
A4	Avrami-Erofeev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
Contracting geometry			
R2	Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
R3	Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
Diffusional			
D1	One dimensional diffusion	$1/(2\alpha)$	α^2
D2	Two dimensional diffusion (Valensi)	$[- \ln(1 - \alpha)]^{-1}$	$(1 - \alpha) \ln(1 - \alpha) + \alpha$
D3	Three dimensional diffusion (Jander)	$(3/2)(1 - \alpha)^{2/3} [1 - (1 - \alpha)^{1/3}]^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
D4	Three dimensional diffusion (Ginstling-Brounshtein)	$(3/2)[(1 - \alpha)^{-1/3} - 1]^{-1}$	$1 - (2/3)\alpha - (1 - \alpha)^{2/3}$

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE}{Rf(x)}\right] - \frac{E}{RT} \tag{8}$$

Similarly, while plotting $\ln(\frac{\beta}{T^2})$ vs. $1/T$ (using Eq. (8)) the slope gives $-E/R$ from which the activation energy can be calculated.

2.4. Determination of reaction model

The MP method can be used to determine the reaction model that describes the decomposition of WT. In this method, the integrated form of Eq. (6) can be obtained as:

$$g(x) = \frac{AE}{\beta R} P(u) \tag{9}$$

where $P(u)$ is the temperature integral which can be defined as:

$$P(u) = \int_{\infty}^u -\left(\frac{e^{-u}}{u^2}\right) du \tag{10}$$

where $u = E/RT$. $P(u)$ has no exact solution. However, Doyle's approximation (Doyle, 1965; Flynn, 1983) gives sufficiently reliable results, expressed as:

$$P(u) = 0.00484 \exp(-1.0516u) \tag{11}$$

For a single step decomposition process with invariant $g(x)$, MP method confirms an appropriate kinetic decomposition model with a high degree of certainty. In this single step process, A and E values are treated as constants; using $x = 0.5$ as a reference point, Eq. (9) can be expressed as:

$$g(0.5) = \frac{AE}{\beta R} P(u_{0.5}) \tag{12}$$

where $u_{0.5} = E/RT_{0.5}$ (Pkrež-Maqueda et al., 1996).

The ratio of Eq. (9) and Eq. (12) yields:

$$\frac{g(x)}{g(0.5)} = \frac{P(u)}{P(u_{0.5})} \tag{13}$$

This differential form of the kinetic equation is considered one of the most general applications of the MP method as it is applicable to experimental data across experimental conditions (Gotor et al., 2000).

Table 2
Proximate, ultimate analysis and higher heating value of WT sample.

Proximate analysis ^{db} (wt.%)	
Volatile matter	69.8
Fixed carbon ^a	24.9
Ash	5.3
Ultimate analysis ^{dab} (wt.%)	
C	84.2
H	7.1
N	0.4
S	2.1
O ^a	6.2
Higher heating value (MJ kg ⁻¹)	32.54

^{db}Dry basis.

^{dab}Dry and free basis.

^a Calculated by difference.

Table 1 presents most common reaction models $g(x)$, for solid decompositions. To select the best model, theoretical $g(x)/g(0.5)$ vs. x and experimental $P(u)/P(u_{0.5})$ vs. x were plotted. As seen from Eq. (13), for a given x , the experimental value of $(Pu)/P(u_{0.5})$ and theoretically calculated $g(x)/g(0.5)$ values are equivalent for the most appropriate kinetic model was chosen.

3. Results and discussion

The proximate analysis (Table 2) shows that the sample possessed a volatile matter content of 69.8 wt%, indicating that the sample would yield condensable vapors during pyrolysis. From the ultimate analysis, the sample has a rich carbon content (84.2 wt%), which indicated that the calorific value of the sample would be high. The analysis indicated low nitrogen present in the sample, such that the sample would emit minimal NO_x and had a moderate sulfur content was found to be moderate (2.1 wt%) and correspondingly low SO_x emission, lower than some highly sulfurous coals. The heating value of the sample was determined to be 32.54 MJ kg⁻¹.

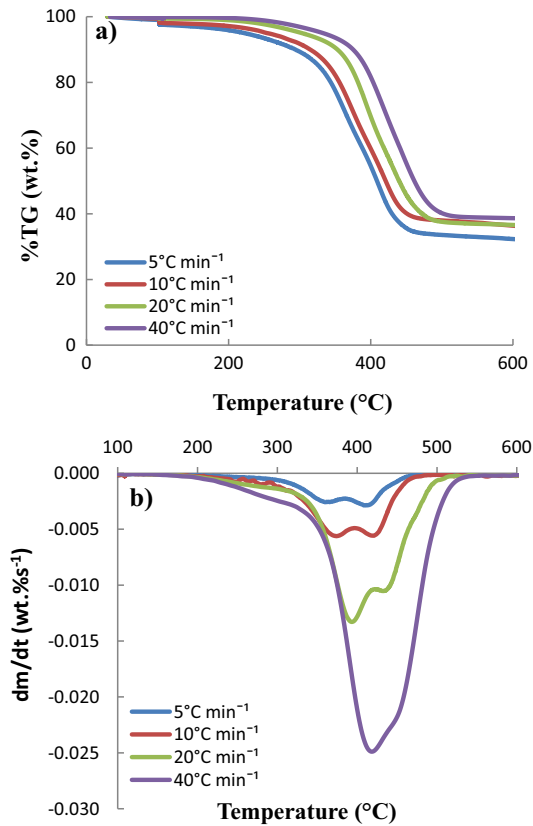


Fig. 1. TG (a) and DTG (b) of WT sample.

3.1. Thermal behavior of WT

Fig. 1b shows the weight loss of sample in the form of thermogravimetric (TG) curves. Fig. 1b illustrates the mass loss rate in the form of derivative (DTG) curves. Both figures represent the thermal behavior of sample carried out under pyrolysis conditions at temperatures between 30 and 600 °C at varying heating rates. As depicted in Fig. 1a, the sample exhibited the same overall weight loss irrespective of the heating rates; the final weight percent decomposition of the samples were between 32 and 38% for all the heating rates. This residual char quantity is slightly lower than that found for waste tire pyrolyzed up to 575 °C, which is not surprising as devolatilization increases as a function of temperature (González et al. 2001). It can be seen from the figure that the pyrolysis process occurred over one main decomposition step between 250 and 550 °C. As shown in Fig. 1b, two peaks are observed in the DTG curves for the lower heating rates. Such peaks are often observed for the pyrolysis of complex structure such as WT, which contains various materials such as plasticizers and other additives (Onay and Koca, 2015). Over this main decomposition step, the principal components of WT sample undergo different degradation reactions such as depolymerization, decarboxylation and cracking. This stage accounts for approximately 62–68% of total weight loss of the sample. The remaining material is attributed to ash and unreacted organic material present in the sample.

3.2. Effect of heating rate

Though the overall weight loss is not dependent on heating rate, from Fig. 1a it can be observed that there is a delay in the degradation process with the increase in heating rates. That is, the main

degradation process completed at 454 °C for the sample heated at 5 °C/min, but occurred at 510 °C for the sample heated at 40 °C/min. The heating rates influence the temperature range in which the primary stage of pyrolysis occurred. The pyrolytic reaction initially occurs at a lower temperature at slower heating rates, and as the heating rate increases, decomposition shifts to higher temperature. This observation agrees well with the results of TG experiments as reported elsewhere (Goldfarb and Ceylan, 2015; Qian et al., 2016). Some literature suggests that this translocation of thermal profiles is a function of heat and mass transfer limitations (Antal and Varhegyi, 1995). These limitations are significant at higher heating rates, when the reaction time of the sample decreases. The extent of pyrolysis at a given temperature is lower at higher heating rates than at lower heating rates. Considering the sample particle size (<250 μm) and sample size (10 mg) used, it is unlikely that there is a large temperature gradient within each particle of the sample (Biot Number $\ll 1$ and therefore lumped capacitance is a reasonable assumption). Rather, at slower heating rates, the residence time at each temperature is longer and the particles devolatilize more slowly at lower temperatures. Conversely, at higher heating rates the particle “stays” at each temperature for a shorter amount of time, which explains the same total mass fraction conversion (as each sample is brought to and held at the same

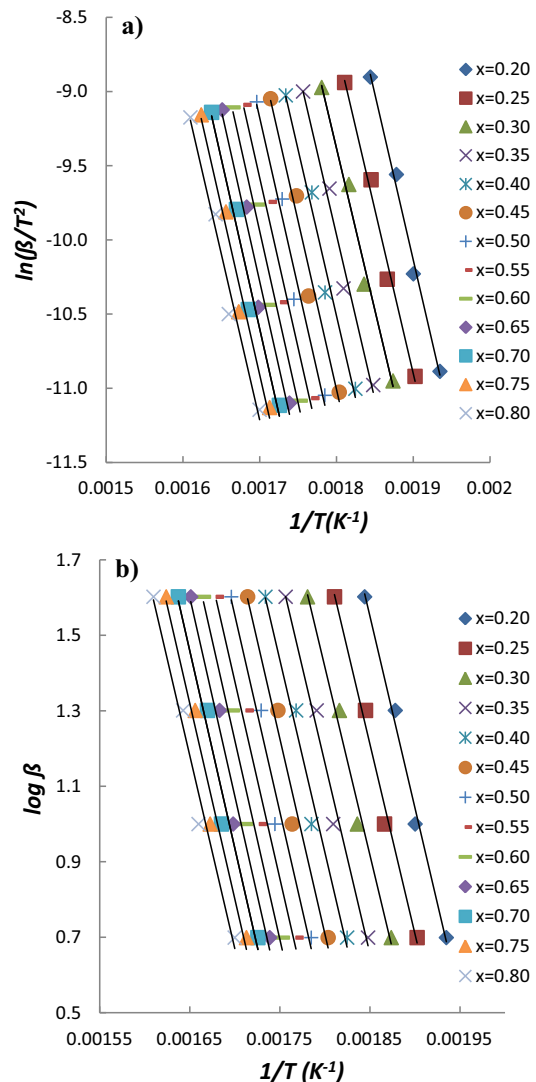


Fig. 2. Kinetic plots of WT using KAS (a) and OFW (b).

final temperature) but variance in temperature and mass loss rates (Ceylan and Goldfarb, 2015; Goldfarb and Ceylan, 2015). This also explains the trends in Fig. 1b, where the thermal degradation rate, (dx/dt), increased with the increase in heating rates, and that the highest heating rate shows a “smoother” DTG curve with only one peak.

3.3. Determination of activation energy

Iso-conversional methods enable accurate determination of activation energy (E) without assuming a reaction model, and are therefore recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (Vyazovkin et al., 2014). Because the WT's thermal decomposition at the onset and endset of pyrolysis is not stable, the calculated values were determined under the conversion range $\alpha = 0.2$ – 0.8 as per prior literature (Chen et al., 2015).

Applying Eqs. (7) and (8), the E values determined for the main decomposition stage of WT were calculated by OFW and KAS with experimental data at four different heating rates of 5, 10, 20, and $40\text{ }^\circ\text{C min}^{-1}$. Plots of $\log \beta$ (FWO) and $\ln [\beta/T^2]$ (KAS) vs. $1/T$ for the given conversion degrees resulted in straight lines, given in Fig. 2a and b, respectively. E values for each phase of WT at various conversion degrees were estimated from the slope of the regression lines, and are presented in Fig. 3. As seen from Fig. 3., for a given x , the activation energies value using both the method was nearly same. Therefore, the average values of the FWO and KAS models were used as the activation energy in the integral MP method. The average activation energy of the FWO model over all conversion values was $164.1 \pm 22.8\text{ kJ mol}^{-1}$ and for the KAS model was $161.5 \pm 23.7\text{ kJ mol}^{-1}$. There is actually considerable variation of reported activation energies for waste tire in the literature. For example, Singh et al. find an activation energy using a reaction order of 1 with only a single heating rate ($25\text{ }^\circ\text{C min}^{-1}$) for waste tires ranging from 80 to 100 kJ mol^{-1} , but this is only up to temperatures of $500\text{ }^\circ\text{C}$ (Singh et al., 2012). Also with a reaction order of unity, Kim et al. reported activation energies of sidewall tires between 42.1 and 203.9 kJ mol^{-1} and of tread tires between 28.7 and 209.0 kJ mol^{-1} (Kim et al., 1995), whereas Teng et al. report activation energies of general WT from between 125.58 and $244.04\text{ kJ mol}^{-1}$ (Teng et al., 1995). Again with only one heating rate, Leung and Wang found activation energies for powder waste tire ranging from 164.5 to 218.7 kJ mol^{-1} over the temperature range of 300 to $480\text{ }^\circ\text{C}$, and from 450 to $620\text{ }^\circ\text{C}$, ranging from 145.4 to 161.2 kJ mol^{-1} (Leung and Wang, 1998). Using the Friedman method Chen et al. find activation energies for car tire pyrolysis of $147.64\text{ kJ mol}^{-1}$ with a reaction order of 1.98 and for truck tires $148.06\text{ kJ mol}^{-1}$ with a reaction order of 1.63 (Chen et al., 2001). Therefore, the activation energies measured

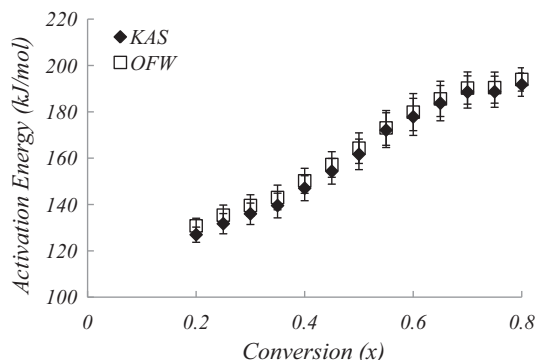


Fig. 3. Activation energy values with the progress in conversion.

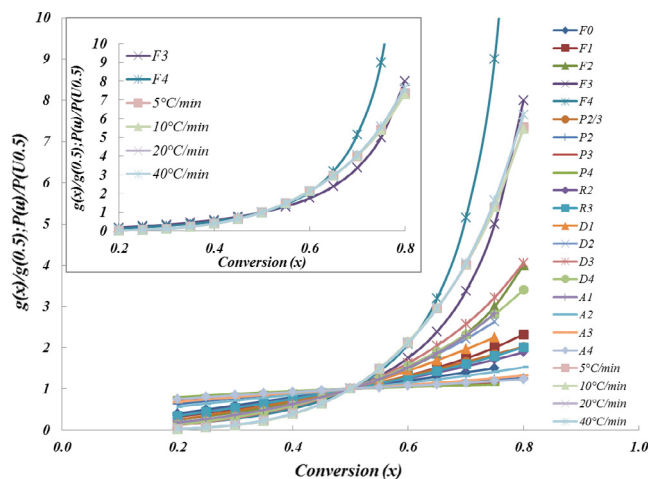


Fig. 4. Comparison of experimental and theoretical mechanism model according to generalized MP method.

in this study agree well with prior literature that uses a myriad of methods to determine the activation energy. To shed light on which of these determination methods is most appropriate to describe the kinetics of waste tire pyrolysis, we turn to the Master Plots method.

3.4. Determination of reaction model by MP method

The study of decomposition kinetics of a given feedstock is essential to the design of any thermal conversion process equipment. The kinetics define the start-up conditions required to initiate decomposition and provide information on the rate of reaction (and therefore residence time) required to complete the decomposition. The reaction model is a theoretical function that describes the nature of the reaction's progress. To obtain a complete picture of the reaction kinetics, the pre-exponential factor, the model and the order of reaction must be calculated. An initial assessment of the reaction mechanism was made with the aid of MP. Fig. 4 shows the MP of WT at different heating rates. By comparing the experimental points with theoretically calculated curves, the model that best fit the experimental curves was obtained. Using the pre-determined activation energies and the temperature measurement as a function of x , the $P(u)$ was calculated directly from Eq. (11). As shown in Fig. 4, the experimental MP of $P(u)/P(u_{0.5})$ versus x at different heating rates are practically identical, indicating that the kinetics of WT pyrolysis could be described by a single kinetic model. The comparison of the experimental MP with the theoretic

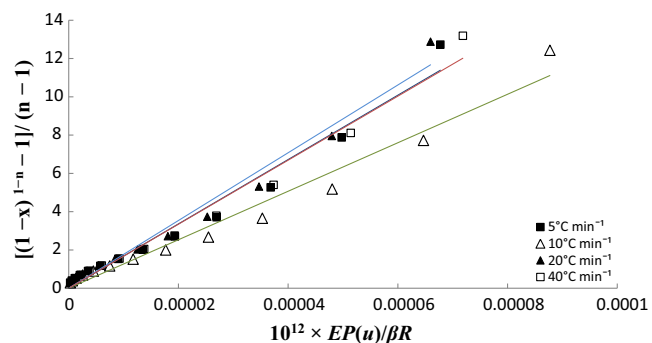


Fig. 5. Plot of $[(1-x)^{1-n} - 1]/(n-1)$ against $10^{12} \times EP(u)/\beta R$ at various heating rates $5\text{ }^\circ\text{C min}^{-1}$ (■), $10\text{ }^\circ\text{C min}^{-1}$ (△), $20\text{ }^\circ\text{C min}^{-1}$ (▲), $40\text{ }^\circ\text{C min}^{-1}$ (□) and their linear regression (solid lines).

cal ones indicates that the kinetic process for the pyrolysis of WT can be described by the F_n model $f(x)=(1-x)^n$, since the experimental MP exist between F_3 and F_4 .

3.5. Determination of pre-exponential factor and reaction order

The pre-exponential factor was determined with the knowledge of the reaction model $f(x)$, which provided a good agreement with the experimental data. The appropriate F_n model function with an exponent of n was used for estimating the pre-exponential factor, A . The expression of the F_n model, $f(x) = (1-x)^n$, is introduced into Eq. (9) and results in the following equation:

$$g(x) = \frac{AE}{\beta R} P(u) = \frac{(1-x)^{1-n} - 1}{n-1} \quad (14)$$

Fig. 5 shows a plot of $[(1-x)(1-n) - 1]/(n-1)$ against $EP(u)/\beta R$. The most suitable n is taken as the value at which the linear intercept is closest to zero with the highest coefficient of determination (Chen et al., 2015; Shuping et al., 2010). The experimental MP was closest to the theoretical MP of the F_n kinetics model, and lies between F_3 and F_4 kinetic models (Fig. 4). To determine the optimal value of n , it was changed from 3 to 4 in increments of 0.01. In the plot of the experimental data in Fig. 5, the coefficient of determination (R^2) was above 0.9700. The slight scattering effect could be due to the presence of two peaks in DTG curves (not seen for the 40 °C/min heating rate) (Fig. 1b). The formation of the peaks could be attributed to multiple and complex reactions involved in the thermal decomposition of WT (Miranda et al., 2013; Vyazovkin et al., 2011).

The pre-exponential factor (A) was calculated from the intercept of the line in Fig. 5 with the x-axis. The order of reaction was first calculated with the aid of MP (n-MP) and once the model was fixed, n was analytically recalculated (n-analytical) and showed remarkably good agreement between the two results. The results of all the parameters are presented in Table 3. Despite the previously discussed difference in DTG and TG behavior, changes in the heating rate induced minimal variance in the values of A and n , consistent with a common single step reaction. It can therefore be concluded that a possible mechanism for the pyrolysis of WT was an n^{th} order reaction model with a possible form of $f(x)$ for the pyrolysis of WT of:

$$f(x) = (1-x)^{3.055} \quad (14)$$

This third-order reaction model suggests that the chemical reactions during pyrolysis of the WT are the rate limiting steps to this thermochemical conversion, rather than diffusion or phase boundary reactions. While the pyrolysis of cellulosic biomasses often are diffusion or nucleation limited (Celaya and Goldfarb, 2014), carbonaceous wastes with higher activation energies (and stronger bonds) such as plastics tend towards power law and higher reaction order mechanisms (Aboukaskas et al., 2010), as observed here.

3.6. Evaluation of kinetic parameters

Fig. 6 shows calculated ($x_{\text{calculated}}$) versus experimental ($x_{\text{experimental}}$) conversion curves for WT at different heating rates,

Table 3

Kinetic parameters calculated for different heating rates.

Heating rate (β) (°C/min)	n	A (s^{-1})	R^2
5	3.03	1.41E+17	0.9796
10	3.05	9.40E+16	0.9745
20	3.06	1.32E+17	0.9811
40	3.08	1.27E+17	0.9863

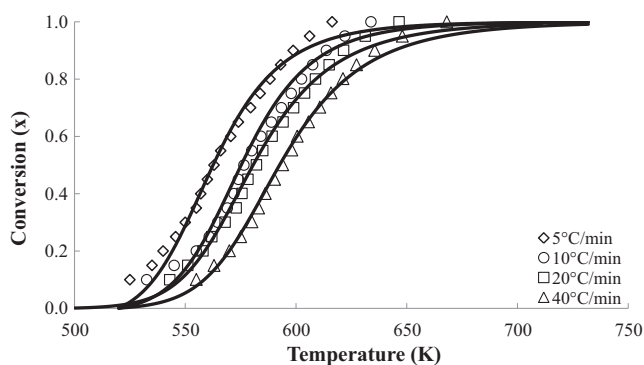


Fig. 6. Experimental data and Master-Plots prediction results (solid lines) for the nonisothermal pyrolysis of WT at different heating rates.

obtained assuming a one-step thermal decomposition reaction. The theoretical calculations slightly underestimate the conversion at a given temperature for conversions between 0.00 and 0.20, and above 0.80. However, for the conversion between 0.20 and 0.80, the theoretical curves are in a good agreement with the experimental data. The variation below 0.20 and above 0.80 could be attributed to a change in the reaction model. Such trends in theoretical-experimental data agreement at conversion levels above 0.20 are common in the literature (Aboukaskas et al., 2010), suggesting that these models are quite suitable for describing the continuing degradation and activation energy barriers once the initial depolymerization reaction begins, and when the concentration of ash/inorganics is relatively low compared to the volatile carbon content. The obtained kinetic parameters (Table 3), i.e., activation energy, pre-exponential factor, and reaction model, remained almost constant for all the analyzed heating rates. This indicates that the decomposition of WT is independent of the heating rate, at least at heating rates mimicking slow pyrolysis, such that this study did not encounter any inter- and intra-particle transport limitations.

4. Conclusions

Pyrolysis of waste tires has been previously demonstrated as a possible management solution for this globally imperative waste stream. In order to design appropriate thermal conversion units to transform this solid waste to energy and chars, we need a full understanding of the reaction kinetics and mechanisms. In this work, we find activation energies of pyrolysis ranging from 128.9 kJ mol⁻¹ to 192.9 kJ mol⁻¹ with average activation energy of 162.8 ± 23.2 kJ mol⁻¹, in strong agreement with literature values. This is the first study that probes the applicability of various reaction models to pyrolytic decomposition of waste tire. Using the Master Plots method, it was determined that a third order reaction model best fit the data, suggesting that the chemical reactions of pyrolysis themselves are the rate-limiting step, as compared to diffusion of phase boundary limitations often seen for cellulosic biomasses. This is attributed to the heterogeneous, strongly bonded nature of the waste tire.

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