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# Research into fine powder and large particle tyre pyrolysis

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This paper investigates the kinetics of the pyrolysis of scrap tyre using thermogravimetry and a small batch laboratory-scale externally heated fixed-bed. Five particle sizes (20–40, 40–60, 60–80, 80–100, 100–200 mesh) and five heating rates (5, 10, 15, 20, 40 K min<sup>-1</sup>) were investigated. The results show that there is no obvious distinction on weight loss for different sizes. With increasing heating rate the weight loss regions shift to a higher temperature range and the weight loss rate increases. The activation energy ( $E$ ) and pre-exponential factor constant ( $A$ ) were calculated using the Arrhenius type kinetic model. The heat value of pyrolysis gases is in the range of 12 to 22 MJ Nm<sup>-3</sup>. The yields of solid, liquid and gas of pyrolysis scrap tyre and tyre cube at 800 °C were investigated, the ratio of pyrolysis production composition of scrap tyre and tyre cube for gas, oil and char is found to be 35 : 23 : 42 and 10 : 31 : 59, respectively.

**Keywords:** Pyrolysis, scrap tyres, thermobalance, kinetic parameters, wmr 1299-5

## Introduction

Increasing numbers of discarded tyres have caused many environmental and economical problems in many countries. The world production of waste tyres amounts to  $5 \times 10^6$  tonnes year<sup>-1</sup>,  $2 \times 10^6$  tonnes year<sup>-1</sup> of which is produced in Europe,  $2.5 \times 10^6$  tonnes year<sup>-1</sup> in North America and  $0.5 \times 10^6$  tonnes year<sup>-1</sup> in Japan. China is the biggest consumption country of rubber, which is about  $4.2 \times 10^6$  tonnes in 2004 (Shen *et al.* 2007). Tyres are made from different materials: organic materials of a polymeric type, such as natural or synthetic rubber, inorganic ones and metals (Aylón *et al.* 2007). The most common method of waste tyre disposal is dumping them in open storage or in landfill sites. Landfilling of waste tyres for disposal purposes is relatively cheap and easy to achieve, but the physical properties of tyres give rise to problems when landfill disposal is used. This method of disposal occupies large spaces as the tyres are not compressed, presents an eyesore, causes potential health and environmental hazards and poses a potential danger because of the possibility of accidental fires with high emissions of hazardous gases. It also illustrates the wastage of valuable energy and recyclable resource (Seneca *et al.* 1999; Sharma *et al.* 2000; Laresgoiti *et al.* 2004). Waste tyres have highly volatile and fixed carbon contents

with a heating value greater than that of coal (Berruenco *et al.* 2005). Thermo-chemical technology may be a fine way to dispose of waste tyres. Pyrolysis, incineration, and gasification processes are considered to be more attractive and practicable methods for recovering energy from scrap tyres (Leung & Wang 1998).

Pyrolysis is an endothermic process (i.e. thermal degradation of materials caused by heating in an oxygen-free or oxygen-deficient atmosphere) offering an environmentally attractive method of reducing the world waste tyre backlog (Sharma *et al.* 2000). Pyrolysis techniques have been widely studied for years. By pyrolysis, waste tyres become a potential source of fuel and recovery products. The main products are solid carbon residues, condensable fractions and gases (Murena *et al.* 1996, Chen *et al.* 2007). The solid phase contains the mineral matter initially present in the tyre, which represent an approximately 40% yield, and this solid char may be used either as smokeless fuel, carbon black or activated carbon (Rodriguez *et al.* 2001, Murillo *et al.* 2004). The liquid by-products of tyre pyrolysis are a complex mixture of C5–C20 organic compounds with a very high proportion of aromatics (Berruenco *et al.* 2005). Finally, the gas fraction, which could

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Table 1: Composition of samples.

Ultimate analysis	Present paper		Senneca <i>et al.</i> (1999)	Díez <i>et al.</i> (2005)	Dai <i>et al.</i> (2001)	Galvagno <i>et al.</i> (2002)	Laresgoiti <i>et al.</i> (2004)	Conesa <i>et al.</i> (1998)
	Scrap tyre	Tyre cube						
Carbon	83.22	79.10	86.7	89.5	82.8	85.16	74.2	83.5
Hydrogen	7.09	6.80	6.9	7.3	7.6	7.27	5.8	7.8
Nitrogen	0.50	0.10	0.3	0.3	0.5	0.38	0.3	0.39
Sulfur	1.34	1.55	1.9	1.9	1.3	2.30	1.5	9.5
Ashes	2.08	6.55	3.3	7.1	3.3	4.36	13.5	8.2
Oxygen	7.76	5.90	0.9	0.8	4.5	0.54	4.7	6.8

also be useful as fuel, contains a mixture of light hydrocarbons and carbon dioxide. The fraction yields and compositions depend on the reaction conditions and the experimental system (Williams & Taylor 1993).

Many authors have investigated the thermal degradation of scrap tyres using the common thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) measurements. The maximum degradation rates reported (for heating rates of 5 to 100 K min<sup>-1</sup>) are to be found in the temperature range of 375 °C for natural rubber (NR), 445 °C for styrene butadiene rubber (SBR) and 465 °C for butadiene rubber (BR) (Seidelt *et al.* 2006). Bouvier *et al.* (1987) found that rubber degradation is a one-step mechanism and proposed to be a first-order reaction. Senneca *et al.* (1999) investigated that the primary and secondary pyrolysis stages take place at small heating rates (5–100 K min<sup>-1</sup>). At large heating rates (900 K min<sup>-1</sup>), however, the phenomenon is no longer observed and only a single peak exists in the pyrolysis rate. Many authors have proposed sets of formal kinetic parameters for the different rubber types. These studies were mainly performed with microbalance in which only small samples with fine particle materials were investigated. However, the pyrolysis behaviour of large tyre particle samples may be closer to the true pyrolysis process.

In the present study, a common thermobalance and a laboratory scale pyrolysis plant were used to investigate the decay performance of fine powder and large tyre particles. Samples of tyres, made of SBR and NR elastomers, of known composition, were studied by TGA. The gaseous products of the pyrolysis were then analysed by gas chromatography (GC). The influence of particle size, heating rate, and temperature was studied by thermobalance. A kinetic study of the TGA data allowed the determination of the kinetic parameters of the process. A weight loss comparison of large particle size and fine particle were studied on a common balance and a laboratory-scale thermobalance, respectively. Finally, the yield, heat value, composition of char, oil and gases were investigated.

## Experimental

### Raw materials

The original material (scrap tyres and tyre cube) used for the pyrolysis was obtained from Shandong Jinlun Co. Ltd in China. The steel thread and the textile netting had previously been removed. The proximate and ultimate analyses are shown in

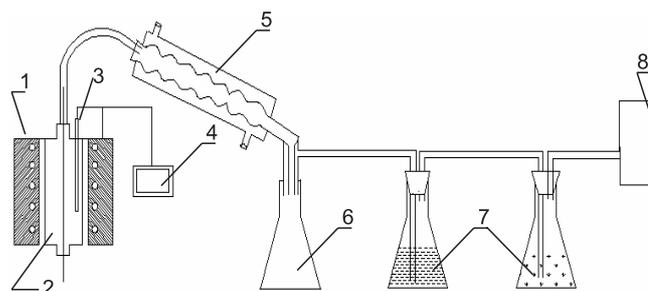


Fig. 1: Experimental device of tyre pyrolysis: 1. electric heater; 2. pyrolysis tube; 3. flame couple; 4. temperature controller; 5. condenser; 6. oil collector; 7. purification device; 8. collection chamber.

Table 1. The results show similar values to those obtained by other authors. The only significant difference that should be noted when comparing different samples was the oxygen content. Scrap tyre samples were shredded, crumbed and sieved from the sidewall rubber of scrap tyres to produce five different sizes: 0.833–0.35 mm (20–40 mesh), 0.35–0.246 mm (40–60 mesh), 0.246–0.198 mm (60–80 mesh), 0.198–0.165 mm (80–100 mesh) and 0.165–0.074 mm (100–200 mesh).

The experiments were carried out by three methods of measurement: the first method involved the use of a small batch laboratory-scale, externally heated, fixed-bed apparatus. Figure 1 shows a schematic diagram of the fixed-bed pyrolysis reactor and temperature control system. The second was thermogravimetric measurement, which was carried out with a thermobalance (Beijing Optical Apparatus Co. Ltd, thermogravimetric analyser model WCT-1C); and the third type used a laboratory-scale thermobalance to investigate the weight loss of large particle sizes in the pyrolysis process (see Figure 2).

### Thermogravimetry equipment

The kinetic study by thermogravimetry was carried out in a WCT-1C thermobalance, consisting of a 1 mg precision microbalance and an alumina oven with graphite resistance of 0.1 K precision, which allowed continuous data registration. The operating method consists of subjecting the sample (approximately 5–10 mg) to a heating ramp from room temperature to 1073 K in a nitrogen purge gas flow of 30 mL min<sup>-1</sup> for all experiments, and the temperature was controlled by a type-K chromel–alumel thermocouple wire placed about 1–2 mm

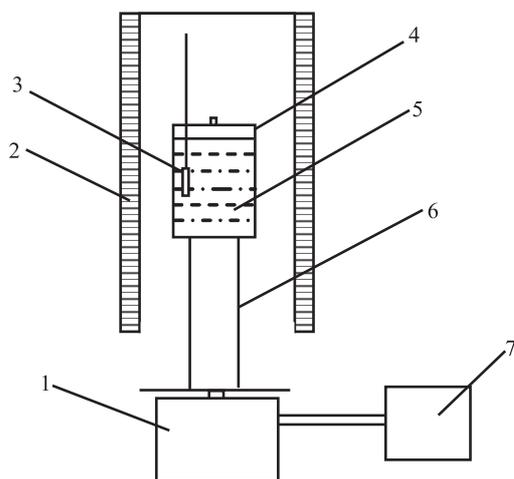


Fig. 2: A laboratory-scale thermobalance scheme: 1. electronic balance; 2. heating apparatus; 3. thermal couple; 4. reactor; 5. pyrolysis sample; 6. tie strap; 7. data collector.

below the platinum crucible. Heating rates of 5, 10, 15, 20 and 40 K min<sup>-1</sup> with particle sizes of about 5–10 mg were applied. The total analysis time was approximately 60 min. To verify the validity of the data, all experiments were performed twice.

#### Laboratory-scale pyrolysis plant

A cylindrical stainless-steel atmospheric pressure reactor was used for laboratory-scale pyrolysis experiments. The main part of this apparatus is a quartz tube 200 mm long and 57 mm in diameter, which was loaded with the sample. A diagram of this system can be seen in Figure 1. The oven was heated electrically and the system was heated at a rate of 10–20 K min<sup>-1</sup> to the desired temperature, and maintained there for 30 min. The pyrolysis products (gas and liquids) evolving from the reactor passed through a heat-exchange system. To clean the gas and separate it from the condensable fraction, three stages of traps were set up. First, the gases leaving the reactor made direct contact with a countercurrent water-cooled heat exchanger, and then passed through an oil-collecting vial and a water-scrubbing flask, to be finally filtered through a tube packed with cotton and silica gel. For the sake of gas purity, the gases were collected using a gas-bag only after 3 min of pyrolysis; the aim was to exhaust the oxygen remaining in the pyrolysis tube to the utmost extent. Throughout the study, it was considered that the little oxygen remaining in the reactor had no obvious influence on the pyrolysis reaction.

In order to compare the influence on the pyrolysis of large and fine particle sizes a laboratory-scale thermobalance was designed, as can be seen in Figure 2. The scrap tyre and tyre cube samples were loaded into the reactor, the heating apparatus worked at a rate of 20 K min<sup>-1</sup> and the electronic balance recorded the weight loss simultaneously.

To determine the characteristic of pyrolysis oil, a digital pH meter (PHS-3c) was employed to measure the pH value of the oil and the gross calorific value of the pyrolysis oil was measured by means of an oxygen bomb calorimeter.

#### Analysis

The derived gases were collected through a gas syringe and analysed off-line by gas chromatography. The gas fraction composition, mainly H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>, was identified using a gas chromatograph with a thermal conductivity detector and a double injector connected to two 5 m length, 3 mm diameter 5 A 100:120 columns with helium as the carrier gas, and with one column being carboxen and the other a porapak column. The weight of gas collected was determined by subtracting the weight of liquid and char from that of the tyre sample.

#### Numerical treatment

A thermal decomposition of scrap tyres using nitrogen can be given a global reaction as



The rate equation of conversion factor  $\alpha$  is expressed in an Arrhenius relation in the form of (Chen *et al.* 2001)

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

where  $\alpha = (m_0 - m_t)/(m_0 - m_\infty)$ ;  $k = A \exp(-E/RT)$ ; and  $t$  is time (s),  $A$  is a pre-exponential factor (min<sup>-1</sup>),  $E$  is the activation energy (J mol<sup>-1</sup>),  $T$  is the temperature of reaction (K),  $R$  is the universal gas constant (= 8.314 J mol<sup>-1</sup> K),  $m_t$  is the mass of the sample at time  $t$ , and  $m_0$  and  $m_\infty$  are the initial and final masses of the sample, respectively.

The functional form of  $f(\cdot)$  in equation (2) is assumed to be the  $n^{\text{th}}$  order of the unreacted material according to

$$f(\alpha) = [-\ln(1 - \alpha)]^3$$

Rearranging equation (2), the scrap tyre pyrolysis reaction equation may be expressed as following formula:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} [-\ln(1 - \alpha)]^3 \exp(-E/RT) \quad (3)$$

where  $\beta = dT/dt$ .

According to the approximate expression of Coats–Redfern method (single heating-rate integral method), and for a constant heating rate,  $\beta = dT/dt$  during pyrolysis, rearranging equation (3) and integrating gives:

$$\ln \left[ -\frac{1}{2} \frac{1 - (1 - \alpha)^{-2}}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (4)$$

for most temperature regions and  $E$  of pyrolysis reaction,

$\frac{E}{RT} \gg 1$ ,  $\left( 1 - \frac{2RT}{E} \right) \approx 1$  so equation (4) can be simplified as

$$\ln \left[ -\frac{1}{2} \frac{1 - (1 - \alpha)^{-2}}{T^2} \right] = \ln \left( \frac{AR}{\beta E} \right) - \frac{E}{RT} \quad (5)$$

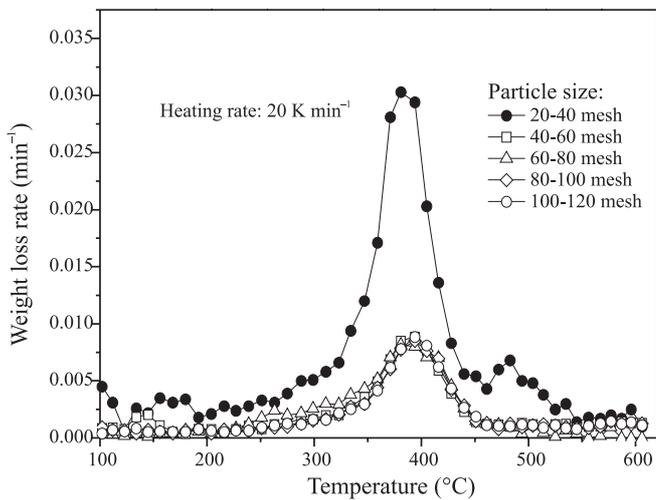


Fig. 3: DTG profiles of different particle sizes samples at heating rate of 20 K min<sup>-1</sup>.

Equation (5) gives a plot of  $\ln\left[-\frac{11 - (1 - \alpha)^{-2}}{T^2}\right]$  versus  $T^{-1}$

for various heating conditions should yield a straight line, whose slope is  $-E/R$  and  $Y$  intercept is  $\ln[(AR)/(\beta E)]$ . The value of  $\alpha$ ,  $d\alpha/dt$  and  $T$  at any time could be obtained from the experimental TGA and DTG curves. Thus, the apparent activation energy  $E$  and the pre-exponential factor  $A$ , could be determined from the above method.

## Results and discussion

### Thermobalance analysis

#### Particle size influence

Figure 3 shows the typical DTG curves for the pyrolysis of various sizes of scrap tyre particles at a heating rate of 20 K min<sup>-1</sup>. The sample particle sizes were divided into five groups: 20–40, 40–60, 60–80, 80–100 and 100–200 mesh. The TG curve of the scrap tyre pyrolysis is shown in Figure 4. It should be noted that the DTG curve exhibits three different normalized weight loss rate regions over a temperature range of 100–600 °C. The reasons of this phenomenon may be associated with the main constituents of the tyre material used in this study, which were either NR, SBR, BR or the mixture of oils, moisture, plasticizers and other additives (Leung & Wang 1998). Different materials lose their weights at different rates and in different temperature regions. The first peak corresponds to the thermal decomposition of the mixture of oils, moisture, plasticizers and other additives; the second and third peaks are due to the thermal decomposition of NR, BR and polybutadiene–styrene, which are the main components of tyres (Berruoco *et al.* 2005).

In these experiments there are three transport processes that may have influenced the global rate: intraparticle transport, which is affected by particle size; particle-to-fluid transport, which in turn depends upon nitrogen flow rate and particle size; and the interparticle transport, which depends upon the number of layers of particles in the sample basket (Enci-

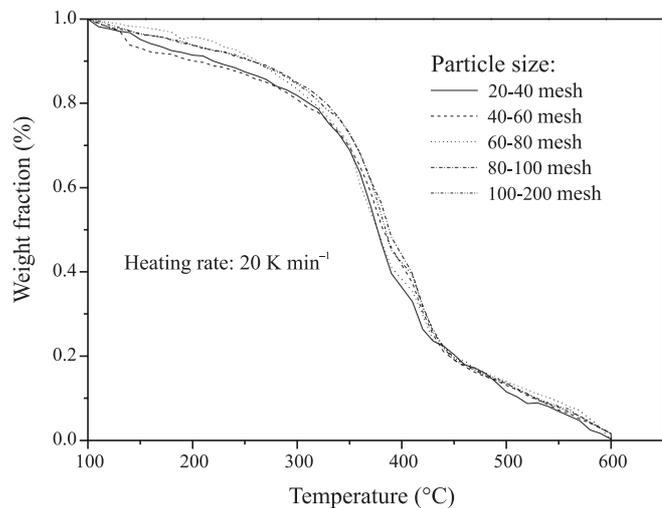


Fig. 4: Weight loss profiles of different particle size samples at heating rates of 20 K min<sup>-1</sup>.

nar *et al.* 2000). Some authors have observed that particle sizes between 0.1 and 0.2 mm was used for determining the kinetic parameters to minimize internal diffusion (Murillo *et al.* 2004). An increase in particle size causes greater temperature gradients inside the particles for heat and mass transfer in thermo-balance.

Five runs with different particle sizes (20–40, 40–60, 60–80, 80–100 and 100–200 mesh.) were carried out. Figure 4 shows the weight loss versus temperature at 20 K min<sup>-1</sup> and similar curves were obtained for all the runs. The experiments showed a weight loss of around 18–22% in the temperature range of 100–320 °C, 57–63% in the range 320–470 °C and 15–22% in the range 470–600 °C. Furthermore, it was observed that there was no obvious difference of weight loss for different particle sizes in TGA.

#### Heating rate influence

The pyrolysis experiments were carried out at four heating rates, namely 5, 10, 15 and 40 K min<sup>-1</sup>. Figures 5 and 6 display the variations of fractional mass (TGA curves) and derivative mass-change (DTG curves), respectively, against the reaction temperature  $T$  at the above-mentioned heating rates for scrap tyres. Figure 5 shows that in the temperature range of 100–380 °C, the weight loss decreased with the heating rate. However, in the temperature range of 450–572 °C, the weight loss increased with the heating rate. These two reverse dependences shifted gradually in the temperature range of 380–450 °C. A likely explained of this phenomenon is that in the transition temperature range (380–450 °C) the degradation of NR gradually turned to SBR.

Figure 6 shows that the increasing heating rate led to greater weight loss rates in the range 300–500 °C. As the heating rate increased from 5 to 40 K min<sup>-1</sup>, the maxima of the DTG curves were shifted rightward and the highest weight loss rate increased significantly in the temperature range of 280–480 °C. The respective peak corresponding to the maxi-

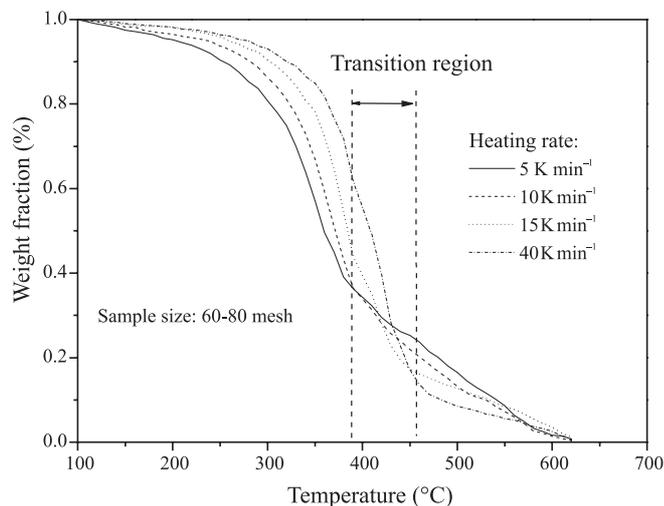


Fig. 5: Comparison profiles at different heating rates of 60–80 mesh samples.

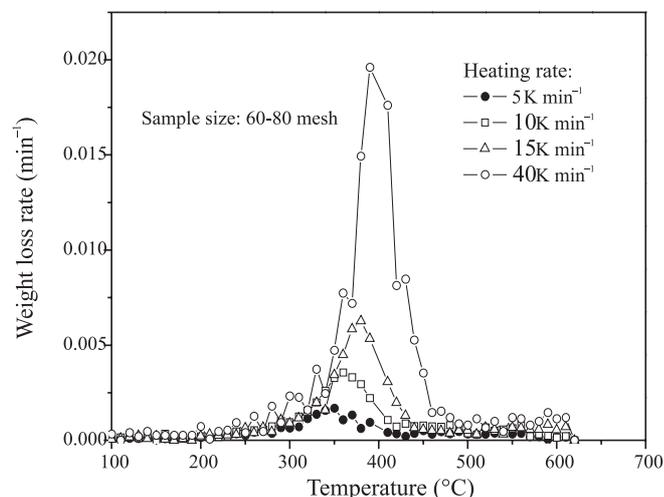


Fig. 6: DTG profiles at different heating rates of 60–80 mesh samples.

imum weight loss rate for each heating rate occurred at approximately 349 °C at 5 K min<sup>-1</sup>, 360 °C at 10 K min<sup>-1</sup>, 381 °C at 15 K min<sup>-1</sup> and 390 °C at 40 K min<sup>-1</sup>. The DTG curves also show that these peaks shifted rightward as the heating rate increased. The explanation of these findings may be that the constituents of the tyres, such as NR, BR, SBR, or their combination, tars, carbon black and other trace materials (such as additives, plasticizers, vulcanizing agents), have different rates of weight loss and the weight loss occurs over different temperature ranges (González *et al.* 2001).

**Pyrolysis comparison of fine and large particle size**

Figure 7 shows a TGA comparison of large and fine particle size samples at the heating rate of 20 K min<sup>-1</sup>. The scrap tyre was shredded to 1 cm × 1 cm pieces and the pyrolysis experiments were carried out using a laboratory-scale thermobalance (see Figure 2). As can be seen in Figure 7, two curves show the TGA results of the common thermobalance and a laboratory-scale thermobalance, respectively. The pyrolysis

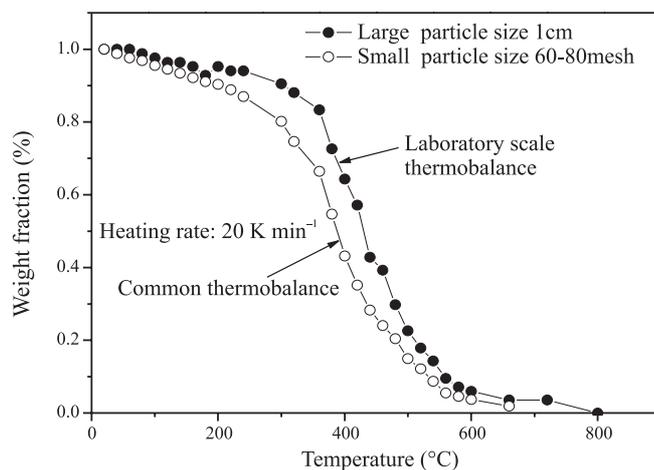


Fig. 7: Weight loss profiles at different particle size samples at heating rates of 20 K min<sup>-1</sup>.

weight loss of the scrap tyres on the latter was apparent below the former. There was a fast weight loss zone at about 300–530 °C on the two curves. After this main fall in the weight loss, the solid continued to decompose smoothly up to 800 °C. The reason is that mass diffusion and calorific transfer need a period of time during the pyrolysis process. Large particle sizes have a pyrolysis reaction retardancy in comparison with the fine ones.

**Kinetic approach**

The kinetic parameters of scrap tyre pyrolysis for different particle sizes and heating rates were obtained according to equation (5). The activation energy (*E*) and the pre-exponential factor (*A*) were determined by performing experiments with five particle sizes (20–40, 40–60, 60–80, 80–100 and 100–200 mesh) and five heating rates (5, 10, 15, 20 and 40 K min<sup>-1</sup>). The activation energies and the pre-exponential factors were calculated by the common Arrhenius representation, yielding the values shown in Tables 2 and 3; only the second degradation process (at about 300–465 °C) parameters was calculated. It can be seen from Table 2 that the activation energy of various particle sizes lies in the range 244.74–268.43 kJ mol<sup>-1</sup>. At different heating rates the activation energy of fine powder tyres was in the range 223.38–267.18 kJ mol<sup>-1</sup>. It was shown that the activation energy increased as the heating rates increased. However, with the changing particle sizes, the trend of activation energy showed regularity; this may be caused by the slight difference of heat and mass transfer in the reaction processes. Yang *et al.* (1993) reported the activation energy of NR, BR and SBR degradation at a heating rate of 10 K min<sup>-1</sup> to be 207, 215 and 152 kJ mol<sup>-1</sup>. Chen *et al.* (1997) reported the SBR activation energy in nitrogen as an inert gas with different oxygen contents to be 211 and 153 kJ mol<sup>-1</sup>. The values reported in the literature are slightly different from the present result.

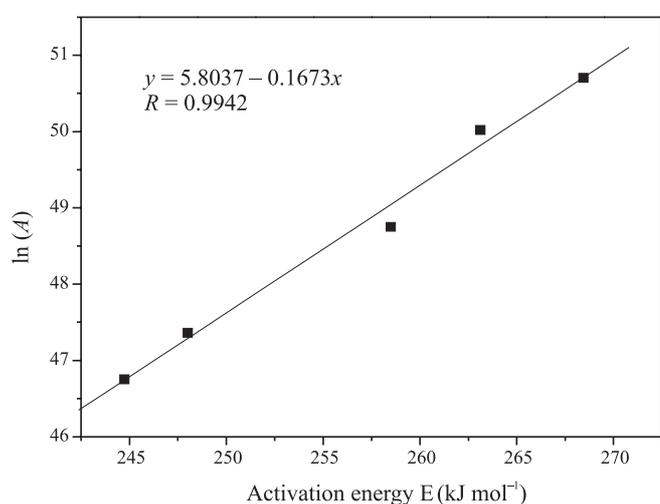
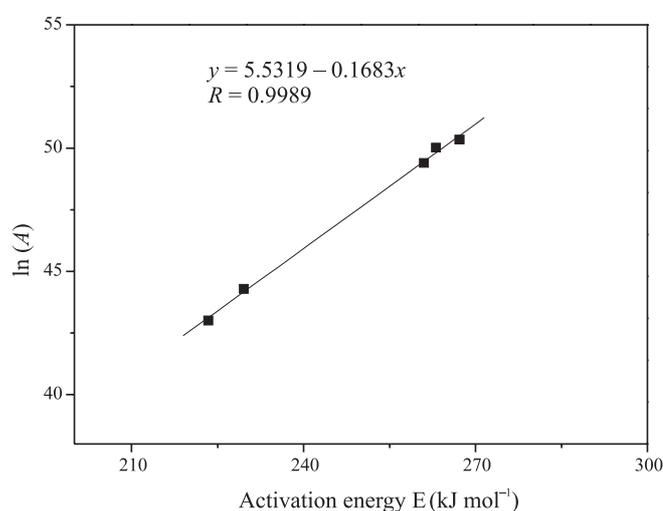
By using equation (5), the values of activation energy *E* versus logarithm of pre-exponential factor ln(*A*) were plot-

Table 2: Kinetic parameters of pyrolysis scrap tyre for different particle sizes.

Particle size	Temperature range (°C)	Activation energy (kJ mol <sup>-1</sup> )	Pre-exponential factor (s <sup>-1</sup> )	Correlation coefficient (R)
20–40 mesh	305–455	244.74	$2.02 \times 10^{20}$	0.9793
40–60 mesh	315–465	268.43	$1.05 \times 10^{22}$	0.9786
60–80 mesh	300–450	263.11	$5.29 \times 10^{21}$	0.9795
80–100 mesh	315–465	248.00	$3.71 \times 10^{20}$	0.9792
100–200 mesh	310–460	258.49	$1.49 \times 10^{21}$	0.9698

Table 3: Kinetic parameters of pyrolysis fine powder scrap tyre for different heating rates.

Heating rate	Temperature range (°C)	Activation energy (kJ mol <sup>-1</sup> )	Pre-exponential fact (s <sup>-1</sup> )	Correlation coefficient (R)
5 K min <sup>-1</sup>	280–430	223.38	$4.77 \times 10^{18}$	0.9507
10 K min <sup>-1</sup>	285–435	229.58	$1.73 \times 10^{19}$	0.9641
15 K min <sup>-1</sup>	295–445	261.01	$2.85 \times 10^{21}$	0.9667
40 K min <sup>-1</sup>	310–460	267.18	$7.33 \times 10^{21}$	0.9685

Fig. 8:  $E$ - $\ln(A)$  plot of different particle size samples at heating rates of 20 K min<sup>-1</sup>.Fig. 9:  $E$ - $\ln(A)$  plot of different heating rates for 60–80 mesh samples.

ted, as shown in Figures 8 and 9. The plot indicates a clear linear relation. Different particle sizes and heating rates gave different  $E$ - $\ln(A)$  plots, therefore, theoretically, if two particle sizes and heating rates are used, a series of  $E$  values can be calculated from the slopes of the straight lines. The plotted  $E$  versus  $\ln(A)$  straight line was found with a correlation coefficient ( $R$ ) that was greater than 0.9942 and 0.9989.

### Fixed-bed batch reactor results

#### Composition of gaseous products

The gas composition is presented in Figures 10 and 11. Figure 10 shows the scrap tyre pyrolysis gases, and Figure 11 that of tyre cube. Detailed analysis of the gases produced from the pyrolysis process revealed that the main components consisted of H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>, etc. It can be seen that the gaseous products displayed an

approximate trend with the temperature increase in the pyrolysis process. The presence of CO<sub>2</sub> and CO from pyrolysis of scrap tyres and tyre cube may derive from the decarbonylation and decarboxylation reactions of oxygenated compounds, such as stearic acid, extender oils, which are used in tyre manufacture, or secondary oxidation reactions of carbon in which CO is formed from reactions in the gas phase between CO<sub>2</sub> and hydrocarbons or from other cracking reactions (González *et al.* 2001, Díez *et al.* 2004, Ucar *et al.* 2005, Ayllón *et al.* 2006). With increasing reaction temperature, the concentration of methane, ethane, ethene and propane decreased gradually. This may be because most carbon-carbon double chains of the original rubber molecule were consumed in the further pyrolysis stage. Ayllón *et al.* (2006) have reported that the organic compounds have maximum values at different temperatures; for example, C<sub>2</sub>H<sub>6</sub> at 450 °C, C<sub>2</sub>H<sub>4</sub> at 750 °C and C<sub>2</sub>H<sub>2</sub> at 400 °C. High temperatures favour the

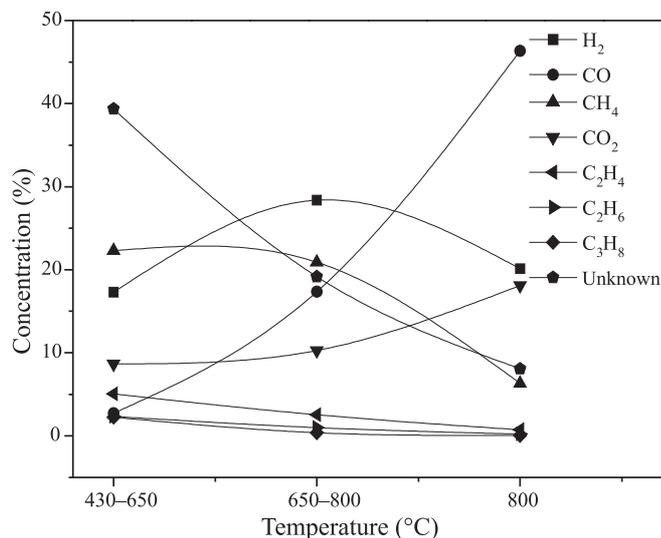


Fig. 10: The composition of the gaseous products of tyre pyrolysis at different temperature ranges.

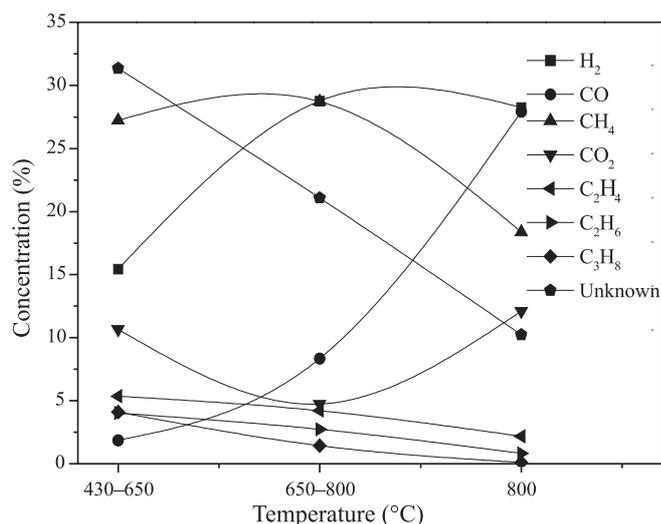


Fig. 11: The composition of the gaseous products of tyre cube pyrolysis at different temperature ranges.

production of H<sub>2</sub> and CH<sub>4</sub>. The total concentrations of hydrogen and methane reached 39.59% at 430–650 °C, 49.27% at 650–800 °C and 26.44% at invariable 800 °C. Some authors considered that hydrogen and methane were mainly derived from secondary aromatization reactions that produce aromatic hydrocarbons and molecular hydrogen may be formed as a primary stable product from branched alkenes (Abbot & Wojciechowski 1988, Williams & Taylor 1993, Ucar *et al.* 2005). With increasing temperature the heavier hydrocarbons and large molecular weight materials are cracked generating lighter ones, methane and hydrogen (Dai *et al.* 2001).

Figure 12 presents the gaseous fraction low heating value (LHV) of two samples that underwent the pyrolysis process at the final temperature of 800 °C. It can be observed that the heating value of the gases produced from scrap tyre and tyre cube pyrolysis increased with increasing temperature for tem-

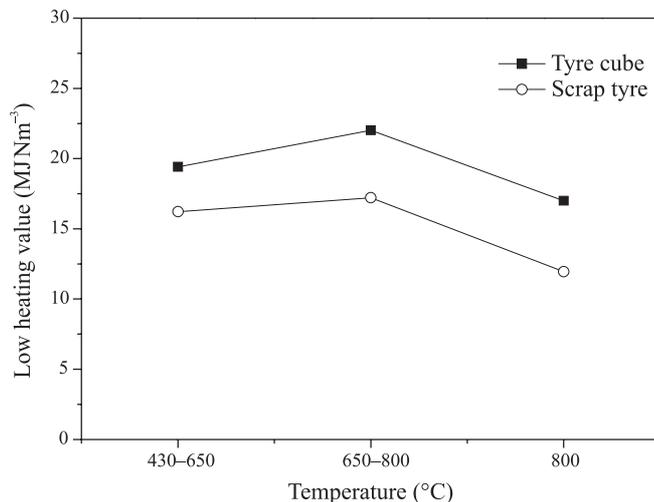


Fig. 12: Low heating values of pyrolysis gases at different temperature ranges.

peratures below 800 °C. When the temperature was stabilized at 800 °C, the LHV of the gases decreased. The LHV of the gases varied between 11.96 and 17.22 MJ Nm<sup>-3</sup> for scrap tyres and between 16.17 and 22.02 MJ Nm<sup>-3</sup> for tyre cube. The LHV of the gas fraction was lower than the value reported in the literature (Bouvier *et al.* 1987, Chen *et al.* 1997, Aylón *et al.* 2007).

#### Oil composition

The condensation method was applied to collect pyrolysis oil. The gross calorific value and pH value of the pyrolysis oil of scrap tyres and tyre cube are presented in Table 4. The oil was a dark brown-coloured, sticky fluid, which resembled petroleum fractions. It can be seen that the gross calorific value (GCV) was very high (35.44 and 38.37 MJ kg<sup>-1</sup> for the pyrolysis oil of scrap tyres and tyre cube, respectively), which is almost coincident with the results reported by González *et al.* (2001) and Rodriguez *et al.* (2001). As the GCV was even higher than certain commercial fuel oils, tyre pyrolysis oils, as a whole, can be considered rather good liquid fuel, with the potential for use as heating fuels (González *et al.* 2001, Rodriguez *et al.* 2001). The pH values of pyrolysis oil were 9.02 and 8.25, the oil liquid exhibited slight alkalinity. The oil contains some organo-alkali compounds such as aniline and sodium phenolate, which cause the oils to have a pH of between 8.0 and 9.0. The pH values of the pyrolysis liquid products are in the range 8.25 to 9.02 for pyrolysis oil from scrap tyres and tyre cube, respectively. These pH values are just opposite to biomass pyrolysis oil whose pH value lies in the range 2.0 to 4.5 (Tsai *et al.* 2006).

Table 4: The characteristic of pyrolysis oil.

Sample	GCV (MJ kg <sup>-1</sup> )	pH value
Scrap tyre	35.44	9.02
Tyre cube	38.37	8.25

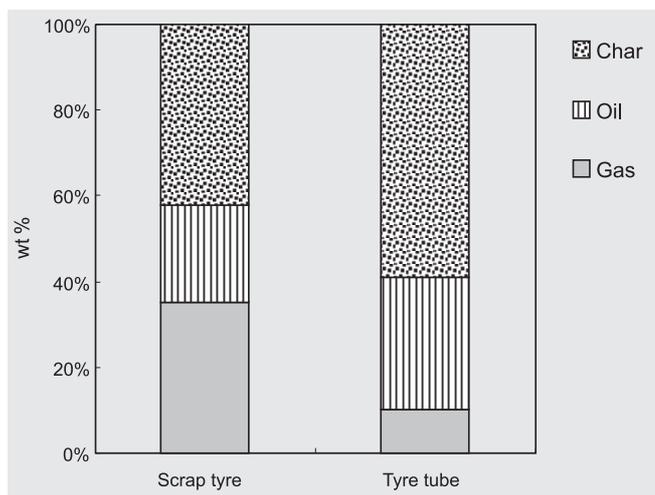


Fig. 13: Composition of production obtained from pyrolysis of two type samples.

#### Yield of char, oil and gas

The solid, liquid and gas yields (wt.%) obtained in the tyre pyrolysis experiments carried out at 800 °C are presented in Figure 13. It can be seen that at 800 °C, the pyrolysis production composition of gas, oil and char for scrap tyres was 35, 23 and 42%, respectively, and the yields of char, oil and gas were 10, 31 and 59% for tyre cube. Similar yields have been reported by other authors (Miguel *et al.* 1998, Sharma *et al.* 2000, González *et al.* 2001). The solid yields obtained from scrap tyres at 800 °C are higher than the yield from tyre cube under the same working conditions. However, the gas produced from scrap tyres was only 10%, which is less than the amount of gas achieved from tyre cubes (35%).

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#### Conclusions

In this paper, the pyrolysis kinetics of scrap tyres in nitrogen were investigated thermogravimetrically for the particle sizes of 2–40, 40–60, 60–80, 80–100 and 100–200 mesh. The result shows that there is a significant difference in the curves of weight loss at different sizes. It should be noted that the DTG curve exhibits three different normalized weight loss rate regions over the temperature range of 100–600 °C. The weight loss of large tyre particles was less than that of the fine ones. The main reason was the retardancy between samples that existed in the pyrolysis reaction. The heating rate had a significant effect on the pyrolysis process. With increasing heating rate, the weight loss regions shifted to a higher temperature range and the weight loss rate was increased. For the range 100 to 380 °C, the weight loss decreased as heating rates increased; however, a reverse trend then appeared and the weight loss increased gradually as heating rates increased over the range 380 to 450 °C, and it is displayed as heating rate increasing, the weight loss also increases in 450–572 °C. The kinetics of the thermal decomposition of the scrap tyre material using thermogravimetric methods was studied. The activation energy of various particle sizes was in the range 244.74 to 268.43 kJ mol<sup>-1</sup> and at different heating rates the values for the activation energy of this work were also in the range 223.38 to 267.18 kJ mol<sup>-1</sup>. The main components derived from scrap tyre pyrolysis included H<sub>2</sub>, CO, CH<sub>4</sub>, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>, etc. Its low heating value was in the range of 12 to 22 MJ Nm<sup>-1</sup>. The GCV of pyrolysis oil varied in the range 35.44 to 38.37 MJ kg<sup>-1</sup>. The ratio of pyrolysis production composition of gas, oil and char was 35 : 23 : 42 for scrap tyre, and 10 : 31 : 59 for tyre cube.

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