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Co-pyrolysis of waste tyre and pine bark: Study of reaction kinetics and mechanisms

Fahima A. Al-Balushi^a, Kiran G. Burra^b, Yue Chai^a, Meihong Wang^{a,*}

^a Department of Chemical and Biological Engineering, The University of Sheffield, Mappin Street, Sheffield, S1 3JD, UK

^b The Combustion Laboratory, Department of Mechanical Engineering, University of Maryland, College Park, MD, 20742, USA

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ABSTRACT

Thermal processing of waste tyre and biomass through pyrolysis and gasification provides a promising pathway to address issues raised by anthropogenic activities including energy security, waste management and environmental sustainability. The study of the kinetics underlying the decomposition of the waste tyre and biomass blend through pyrolysis is an essential step to understand their further reactions in the reforming/cracking stage and to optimize their use. Kinetics analysis of the thermal decomposition of the waste tyre and pine bark with mass blend ratios of 1:0, 3:1, 1:1, 1:3 and 0:1 was investigated using thermogravimetric analysis. Results indicated that the change in heating rates from 10 to 40 K/min with an increment of 10 K/min caused a shift in differential thermogravimetry curves of all the samples to a higher temperature. To evaluate the possible interaction between waste tyre and pine bark in the blended samples, the difference in the weight loss (Δw) was calculated. Occurrence of positive synergetic interaction in terms of increased weight loss between waste tyre and pine bark at different blend ratios varied with the variation in heating rate. Activation energy and pre-exponential factor for different blend ratios were calculated using model fitting method (i.e. Coats-Redfern) and iso-conversional methods (i.e. FWO, KAS and Friedman) as well as combined kinetic analysis. Based on iso-conversional methods and combined kinetic analysis, the single waste tyre has higher activation energy than the single pine bark sample. However, waste tyre and pine bark blend samples with mass ratios of 3:1, 1:1 and 1:3 showed lower activation energy than waste tyre, signifying the benefits of using pine bark in blend samples. The maximum synergetic interaction in terms of lowest activation energy was reported with the use of the waste tyre and pine bark with a mass blend ratio of 3:1. The reaction mechanisms of WT1PB0, WT3PB1, WT1PB1, WT1PB3 and WT0PB1 were evaluated using the Sestak Berggren model and as follows; $\alpha^{-1.866}(1-\alpha)^{1.000}[-\ln(1-\alpha)]^{-2.276}$, $\alpha^{-1.171}(1-\alpha)^{1.000}[-\ln(1-\alpha)]^{-3.007}$, $\alpha^{1.765}(1-\alpha)^{1.000}[-\ln(1-\alpha)]^{-5.381}$, $\alpha^{-2.324}(1-\alpha)^{2.913}[-\ln(1-\alpha)]^{-1.272}$ and $\alpha^{-7.735}(1-\alpha)^{5.658}[-\ln(1-\alpha)]^{5.594}$, respectively. The results of the current study will contribute to the knowledge of expanding waste disposal options and provide essential information for the development of an energy sustainable system.

1. Introduction

1.1. Background

Due to increased consumption of fossil fuels to cover the growing demand for energy including electricity and chemical production [1], there is an increasing concern over the resulting negative environmental impacts. These include increased greenhouse gas emissions and global warming [2]. As a result, this motivated most of the researchers to actively engage in finding clean, renewable and environmentally

sustainable alternatives to replace at least a fraction of fossil fuel.

Among the alternatives, biomass received great attention in recent years. This is because it is (1) a carbon-neutral, as it mainly contributes to natural CO₂ emission which is utilized by plants through photosynthesis [3], and (2) highly abundant and a renewable energy source with the potential to meet 25–30% of energy demand along with the waste by 2050 [4,5]. Therefore, biomass will assist in climate change mitigation.

On the other hand, there is growing production of waste tyre at an annual rate of 3.4 and 4.6 million tons in Europe and USA, respectively [6] which in turn has a great environmental impact due to its nature.

* Corresponding author.

E-mail address: meihong.wang@sheffield.ac.uk (M. Wang).

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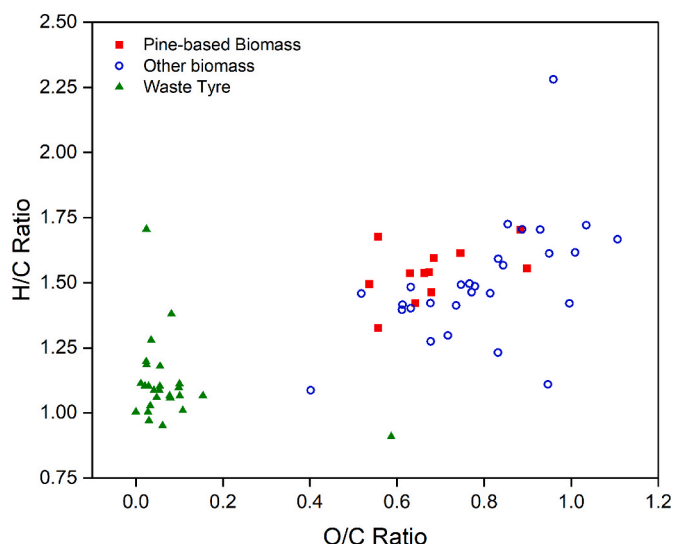


Fig. 1. Van-Krevelen diagram of biomass and waste tyre materials obtained using data from the literature [1,2,5,6,8,9,13–25]

Since waste tyre has an average energy content of 32 MJ/kg [7,8], it is essential to re-direct it from landfilling and incineration [7] to proper utilization for resource and energy recovery.

Thermochemical processing of biomass and waste tyre serves as a promising route to overcome the concerns of energy security and environmental issues associated with overexploitation of petroleum-derived fuels and increased production of waste tyre. This includes pyrolysis and gasification. Pyrolysis, also known as de-volatilization, is the thermal conversion of carbonaceous materials into solid, liquid and gaseous products under an inert atmosphere [9]. It is an integral stage of gasification process.

Co-pyrolysis involves the use of two (most commonly) or more feedstocks during normal pyrolysis process [3]. Co-pyrolysis of biomass and polymeric materials like waste tyre shows positive synergetic effect. It results in enhanced carbon conversion and volatiles yield [10,11], reduces the activation energy [11] and improves the product quality and carbon efficiency [12] compared to the pyrolysis of individual feedstock. This is because these polymeric wastes would compensate for hydrogen deficiency and high oxygen content of biomass.

Fig. 1 presents the Van-Krevelen diagram. It was constructed using ultimate analysis data from the literature for pine-based biomass [2, 13–18], other biomass [1,5,18–25] and waste tyre materials [1,6,8,9,13, 19,21,22,24] and computing H/C and O/C molar ratios. The H/C and O/C ratios represent two main characteristics of the solid fuel including the potential for biofuel production and the heating value. Waste tyre is characterized by low H/C and O/C ratio compared to pine bark. The lower O/C ratio of waste tyre compared to pine bark indicates a higher heating value. However, a lower H/C ratio limits its potential as a source

for biofuel production. Therefore, waste tyre blending with pine-based biomass of high H/C ratio during the thermochemical process would improve the products quality.

Understanding the kinetics underlying the pyrolysis of solid feedstocks, including biomass, waste tyre and their blends, is of high interest to many researchers. This is because it is an essential step in designing, optimizing and scaling up the process and provides essential knowledge of the decomposition mechanism of solid materials [26].

There are several methods to determine the kinetics parameters: activation energy (i.e. E_a) and pre-exponential factor (i.e. A) of solid materials. These methods are classified into two main categories: iso-conversional (also known as model-free) and model fitting methods. Although model fitting method is simple and highly implemented in many studies [27–29], iso-conversional methods were adopted due to associated high accuracy and their independence of reaction model [30–32]. A comparison between the two methods is summarized in Table 1.

1.2. Literature review

Co-pyrolysis of biomass and waste tyre showed positively synergetic effect in terms of (1) increasing bio-oil stability [13,21] and heating value [21,33]; (2) improving product yields and composition [24,34]. Despite the significant experimental research in co-pyrolysis of various biomass materials and waste tyre [12,22,25,34,35], there are few studies on the kinetics analysis of co-pyrolysis of biomass and waste tyre [11,23,31,36–41].

Different kinetics analysis methods were implemented to evaluate the effect of using biomass and waste tyre blends on the minimum energy required for the initiation of the decomposition reaction (i.e. activation energy). These methods include Coats-Redfern [11,36–38,42], Arrhenius [36], FWO [31,38,41], KAS [31,41] and DAEM [23]. Table 2 summarizes the previous studies on the kinetics characteristics of co-pyrolysis of waste tyre and biomass.

Uzun and Yaman [36], Chen et al. [11] and Chen et al. [40] implemented Coats-Redfern method for the calculation of the kinetics parameters, assuming first order reaction. Uzun and Yaman [36] investigated the change in the overall kinetics through the comparison of the average value of the activation energy between single and blend samples. According to International Confederation for Thermal Analysis and Calorimetry (i.e. ICTAC) [43], the existence of multiple peaks and/or shoulders in the DTG curves of the thermal decomposition reflects the presence of multiple reactions during the decomposition. Therefore, drawing a conclusion based on the comparison of overall kinetics values could be unreliable.

Chen et al. [11], Chen et al. [40] and Gao et al. [42] applied the concept of multi-step analysis based on the temperature interval to compare the change in the activation energy at different stages during co-pyrolysis. As a result, they identified the temperature range at which the interaction between the samples is the most synergetic, corresponding to the highest reduction in activation energy. Chen et al. [11]

Table 1

Main categories of methods for analysing solid state reaction kinetics data from TGA [30].

Method	1. Model Fitting	2. Iso-conversional
Principle	Various models are used and the model with best statistical fit in terms of R^2 value is chosen to calculate the kinetics parameters	Requires multiple kinetics curves and the calculation is based on different heating rates for each conversion extent.
Advantages	* Directly determine the kinetics parameters from a single TGA measurement	* Simple and less error associated with the selection of kinetics model
Disadvantages	* Selection of an appropriate model is difficult. * In non-isothermal regime, data usually gives higher values for kinetics parameters	* Allows the estimation of kinetics parameter, E_a , at specific extent of conversion, α_i . * A series of experiments must be carried at different heating rate and under the same conditions like; inert gas flow rate, sample mass, etc.
Types	<i>Isothermal</i> <i>Non-isothermal</i>	<i>Isothermal</i> <i>Non-isothermal</i>
Examples	Conventional Differential Freeman-Carroll Coats-Redfern (CR)	Standard Friedman (FR) Advanced Iso-conversional (AIC) Kissinger-Akahira-Sonuse (KAS)

Table 2
Summary of Kinetics analysis studies of co-pyrolysis of waste tyre and biomass.

Type of biomass blended	Heating rate (K/min)	Kinetics analysis method	E_a of the blend compared to WT	E_a changes with α	Reaction mechanism	Ref.
Offshore oil sludge	15	CR (1st order reaction model with two consecutive stages)	Decreased from 51.31 to 44.86 kJ/mol as the fraction of waste tyre decreased from 75 to 25 wt%	N/A ^a	Assumed first order reaction model	[42]
Torrefied bagasse	20	1st order reaction model with two consecutive stages	Varies between 110.69 and 111.05 kJ/mol for 30 wt% waste tyre in the blend compared to 61.78–76.02 kJ/mol for single waste tyre over two stages	N/A ^a	D1 (at lower temperature) and O2 (at higher temperature)	[37]
Tobacco stalk	10	1st order reaction model with multiple consecutive stages	Decreased from 91.40 and 65.21 to 18.233 and 40.41 kJ/mol at temperature range of 324–395 and 395–490 °C, respectively, as the fraction of waste tyre reduced by 50 wt%	N/A ^a	Assumed first order reaction model	[11]
Tobacco stalk	10, 20 and 30	1st order reaction model with multiple consecutive stages	Decreased from 56.25 to 29.24 kJ/mol as the fraction of waste tyre decreased from 80 to 20 wt% compared to 70.66 kJ/mol for single waste tyre	E_a varied with conversion	Assumed first order reaction model	[40]
Wood	10, 20 and 40	FWO (single-step process)	Decreased from 189.68 to 136.72 kJ/mol as the fraction of waste tyre reduced by 50% on mass basis	N/A ^a	Assumed nth order reaction model for pre-exponential factor	[31]
		KAS (single-step process)	Decreased from 273.64 to 196.86 kJ/mol as the fraction of waste tyre reduced by 50% on mass basis			
Micro-algae		FWO (single-step process)	Decreased from 189.68 to 160.85 kJ/mol as the fraction of waste tyre reduced by 50% on mass basis			
		KAS (single-step process)	Decreased from 273.64 to 230.64 kJ/mol as the fraction of waste tyre reduced by 50% on mass basis			
Kitchen waste	10, 20 and 30	FWO and KAS (single-step process)	Decreased from 212.34 to 198.78 kJ/mol as the fraction of waste tyre decreased from 75 to 50 wt% and then increased to 249.89 kJ/mol with waste tyre mass fraction of 25 wt%. Similar values and trend were obtained with KAS.	N/A ^a	N/A ^a	[41]
Eucalyptus sawdust	2, 5, and 10 2, 5, and 10	FWO (single-step process) FR (single-step process)	150.29 kJ/mol with 50 wt% waste tyre 147.84 kJ/mol with 50 wt% waste tyre	Increase in E_a between α of 0.1–0.5 and then decreased until α value of 0.8 and then increased	First order reaction model based on CR	[38]
J. regia shell	5, 10, 15 and 20	Arrhenius method	A minimum value of 33.87 kJ/mol at heating rate of 5 K/min and waste tyre mass fraction of 25 wt% compared to 669.71 kJ/mol for single waste tyre at same heating rate	N/A ^a	Assumed first order reaction model	[36]
		CR	A minimum value of 29.3 kJ/mol at heating rate of 5 K/min and waste tyre mass fraction of 25 wt% compared to 68.59 kJ/mol for waste tyre at same heating rate			

^a N/A: Not Addressed and described as a function of change in temperature.

and Azizi et al. [31] followed the recommendation of the ICTAC to overcome the limitations of model fitting methods which induce a variation in the activation energy of up to 33% as observed in Uzun and Yaman [36].

Despite the limitations of different kinetics analysis methods, the type of feeding materials found to play an important role in the co-pyrolysis process affecting differently the decomposition pattern and reaction kinetics. Wang et al. [23] investigated the effect of co-pyrolysis of rice straw, poplar wood and waste tyre on kinetics parameters and they measured a higher conversion rate indicating positive synergetic effect. However, Azizi et al. [31] studied kinetics analysis of co-pyrolysis of micro-algae, wood and waste tyre. Inhibitive effect was observed based on the comparison of weight loss between individual and blended feedstock.

According to Azizi et al. [31] and Gao et al. [42], using a blend of biomass and waste tyre showed a synergetic interaction by lowering the E_a of waste tyre decomposition for up to a certain blending ratio. For example, the E_a values for co-pyrolysis of scrap tyre with wood and microalgae separately were 197 and 231 kJ/mol, respectively compared to 274 kJ/mol for sole scrap tyre [31]. Similarly, Chen et al. [11] reported a positive effect during co-pyrolysis of tobacco stalk and scrap tyre in terms of reducing the yield of solid residue, increasing the yield of gaseous products and decreasing the activation energy. However, Keliona et al. [37] emphasized the negative effect of torrefaction of biomass as pre-treatment process on the kinetics parameters during co-pyrolysis process. They found that the use of torrefied biomass with waste tyre resulted in higher E_a and lower A compared to sole materials. Since the interaction between different biomass and waste tyre is not clear as a result of the variation in the decomposition mechanism of each material, it is not possible to draw consolidated conclusion on the existence of neither positive nor negative synergetic effect.

As of author's knowledge none of the previous studies on kinetics analysis of co-pyrolysis of biomass and waste tyre addressed the identification of possible reaction mechanisms and their importance in the calculation of activation energy through combined kinetics analysis. Since pyrolysis is an integral part of pyrolysis/reforming reaction systems, so understanding the underlying reaction kinetics and mechanisms and possible synergetic interaction is important. This would make theoretical contribution towards the proper utilization of solid fuels as well as the development of energy efficient, large-scale facilities.

1.3. Motivation

Interest in co-pyrolysis of waste tyre and biomass has arisen due to the high availability of such polymeric material in waste streams; especially in developing countries. In general, barks have high global production rate of nearly 400 million cubic meters in a year [44]. Despite the high ash content and low energy density of pine bark, the ash is potentially high in inorganic fractions especially Calcium, Magnesium and Sodium [44]. These inorganic alkali and alkaline earth metals are known to pose catalytic effect during thermochemical process [19,45]. Therefore, the use of pine bark in current study would enhance the decomposition of blended waste tyre.

On the other hand, passenger car waste tyre was used, which accounts for around 90% of an annual tyre sale worldwide [46]. In addition, passenger car tyre has a single re-treading potential, meaning that shorter wear time than truck tyre [47]. This will contribute to the increased dumping and/or incineration of such type of tyre as waste without proper utilization. In addition, co-pyrolysis of waste tyre and biomass shows positive synergetic effect, influencing the decomposition reactions, which further affects the product yield and distribution.

According to Brebu et al. [16], biomass is carbon and hydrogen deficit material which could be balanced during thermal co-processing with synthetic polymers like waste tyre and plastics which are acting as hydrogen source. Therefore, this study will provide a theoretical framework of the possible synergetic effect of pine bark and waste tyre.

Table 3

Proximate and ultimate analysis of waste tyre and pine bark [35,48].

	Waste tyre	Pine bark
Proximate Analysis, wt%		
Volatile matter	62.51	63.86
Fixed carbon	27.88	26.19
Ash	8.92	4.77
Moisture	0.69	5.18
Ultimate Analysis, wt%		
C	81.85	50.37
H	6.66	4.20
N	1.70	1.61
S	1.37	0.03
O	9.80	43.81

Table 4

Weight percentage of waste tyre (WT) and pine bark (PB) in the blend samples.

Sample ID	Weight Percentage (wt%)	
	Waste tyre	Pine bark
WT1PB0	100	0
WT3PB1	75	25
WT1PB1	50	50
WT1PB3	25	75
WT0PB1	0	100

1.4. Aim of the study

The aim of the current study is to (1) analyse the thermal decomposition behaviour of waste tyre, pine bark and their blends and the existence of synergetic effect in terms of weight loss at different blend ratios and heating rate, (2) determine the kinetics parameters underlying the decomposition of waste tyre, pine bark and their blends based on TGA data and evaluate the effect of co-pyrolysis on activation energy and (3) examine the variation in the kinetics parameters derived using different methods. This will be addressed by implementing the concept of multi-step reactions using Coats-Redfern and iso-conversional methods (i.e., KAS, FWO and Friedman method) then compared with combined kinetic analysis. Combined kinetics analysis provides a comprehensive analysis of the possible reaction mechanism followed by the feedstock during the thermal degradation regardless the variation in heating rate.

The current study will help in understanding the influence of the composition of feeding materials (i.e., waste tyre, biomass and their blends) on the reaction rates during co-pyrolysis process.

1.5. Novel contribution of this study

The novel contribution of the current study could be summarized as follows:

- 1) To the best of author's knowledge, there are no previous studies reported in the literature on the kinetics analysis of co-pyrolysis of waste tyre and pine bark. This will provide basic knowledge regarding the potential synergetic in terms of weight loss and activation energy and improve the available kinetics database of co-pyrolysis process.
- 2) The available studies on kinetics analysis of co-pyrolysis of waste tyre and biomass focused on the overall kinetics either assuming nth order reaction model or neglecting the reaction model. Therefore, the current study would be the first of its kind considering the study of possible reaction mechanism and the estimation of activation energy. This will provide comparative evaluation of the kinetics from different methods. Therefore, the findings of the current study will provide useful theoretical background for the potential reaction

Table 5
Mathematical expressions of solid state reaction functions; $f(\alpha)$ and $g(\alpha)$, of different reaction mechanisms [26,51–54].

Reaction Mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Reaction Order			
First	O1	$(1 - \alpha)^n$	$-\ln(1 - \alpha)$
Second	O2	$(1 - \alpha)^n$	$(n - 1)^{-1}(1 - \alpha)^{(1-n)}$
nth order	O3	$(1 - \alpha)^n$	$(n - 1)^{-1}(1 - \alpha)^{(1-n)}$
Nucleation and Growth			
Power law	P1–P4	$n(\alpha)^{1-1/n}$	$\alpha^n; n = 3/2, 1/2, 1/3, 1/4$
Exponential law	E1	$\ln(\alpha)$	α
Avrami-Erofeev	N1–N4	$n[(1 - \alpha)[-\ln(1 - \alpha)]^{1-1/n}$	$[-\ln(1 - \alpha)]^{1/n}; n = 1, 2, 3, 4$
Diffusional			
1-D	D1	$(1/2)\alpha$	α^2
2-D	D2	$[-\ln(1 - \alpha)]^{-1}$	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
3-D (Jander)	D3	$[3(1 - \alpha)^{2/3}]/[2(1 - (1 - \alpha)^{1/3})]$	$[1 - (1 - \alpha)^{1/3}]^2$
3-D (Ginstling-Brounshtein)	D4	$3/[2((1 - \alpha)^{-1/3} - 1)]$	$1 - (2/3)\alpha - (1 - \alpha)^{2/3}$
Contracting Geometry			
Contracting area ($n = 2$)	C1	$2(1 - \alpha)^{1/n}$	$1 - (1 - \alpha)^{1/n}$
Contracting volume ($n = 3$)	C2	$3(1 - \alpha)^{2/n}$	$1 - (1 - \alpha)^{1/n}$
Sesták-Berggren function	SB	$\alpha^m(1 - \alpha)^n[-\ln(1 - \alpha)]^p$	–

mechanism during the co-pyrolysis process of waste tyre and pine bark.

2. Materials and methods

2.1. Materials

In this study, waste tyre and pine bark were used as feeding materials. Goodyear winter radial passenger car used tyre was used as waste tyre whereas pine bark was collected from local nursery. Proximate and ultimate analysis of these materials are given in Refs. [35,48] and provided in Table 3.

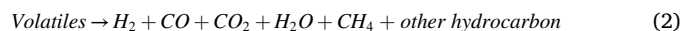
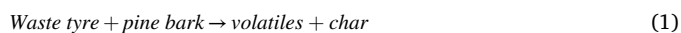
The blend samples of waste tyre and pine bark were named as following WT_xPB_y, where WT and PB refer to waste tyre and pine bark, respectively. x and y represent the weight ratio of waste tyre and pine bark, respectively. The labels of the blend samples are defined in Table 4.

2.2. TGA/DTG analysis

Thermal decomposition of pine bark, waste tyre and their blends were carried out in TGA, STD-Q600 analyzer under an inert atmosphere of Ar with a flow rate of 100 ml/min. Sample size about 2.0 mg was used in each experimental run. The process was conducted under non-isothermal condition where the temperature increased from room temperature to 1173 K. Four heating rates of 10, 20, 30 and 40 K/min was considered. Further details of the experimental procedure are provided in Ref. [48].

2.3. Kinetics study

The overall decomposition reaction taking place during co-pyrolysis of waste tyre and pine bark could be summarized in Equations (1) and (2) [30,48,49].



The reaction rate of single step process (i.e. da/dt) is expressed as [26,43]

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (3)$$

where $k(T)$ and $f(\alpha)$ represent the temperature dependence of the reaction rate and the process rate dependence on the conversion, α , respectively. $f(\alpha)$ also refers to the differential reaction model.

The extent of reaction or known as conversion (α) is used for the calculation of kinetics parameters for solid state reactions and defined as [28,50]:

$$\alpha = \frac{w_o - w_t}{w_o - w_\infty} \quad (4)$$

where w_o , w_t and w_∞ are the sample weight at the start time, time equals to t and the end of the measurements, respectively.

$k(T)$ is represented by Arrhenius equation as follows;

$$k(T) = A \exp^{-E_a/RT} \quad (5)$$

where A , E_a , R and T are pre-exponential factor (min^{-1}), activation energy (J/mol), gas constant (8.3145 J/mol K) and temperature (K), respectively [28].

Combining Equations (3) and (5), it will result in an equation for the differential kinetic model as following;

$$\frac{d\alpha}{dt} = A \exp^{-E_a/RT} \cdot f(\alpha) \quad (6)$$

Under non-isothermal condition at constant heating rate (i.e., $\beta = \frac{dT}{dt}$), then Equation (6) will become;

$$\beta \frac{d\alpha}{dT} = A \exp^{-E_a/RT} \cdot f(\alpha) \quad (7)$$

By integrating Equation (7) with respect to temperature at constant heating rate, then

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(\frac{-E_a}{RT}\right) \cdot dT \quad (8)$$

where, $g(\alpha)$ is the integral form of reaction model, $f(\alpha)$.

Table 5 summarizes the expression of $f(\alpha)$ and $g(\alpha)$ for different reaction mechanisms.

For the calculation of kinetics parameters, E_a and A , for solid state reactions, various methods are available in the literature including CR, FWO, KAS, etc. The applicability of the method depends on the experimental operating conditions (isothermal, non-isothermal, single or multiple heating rates). Both model fitting and iso-conversional (i.e., model free) methods used in the current study are discussed in sections 2.3.1–2.3.4. Coats-Redfern was used as model fitting method whereas FWO, KAS and Friedman are used as iso-conversional methods.

2.3.1. Coats-Redfern (CR)

Coats-Redfern method is based on the integral form of reaction models and used to evaluate kinetics parameters from the TGA data using Equation (9) for different reaction order, n [36,38,51];

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E_a}\left[1 - \frac{2RT}{E_a}\right]\right) - \frac{E_a}{RT} \quad (9)$$

In the current study, the selection of the reaction order is investigated by using n values ranging between 0 and 3 with an increment of 0.5. The best reaction order was decided based on the highest correlation coefficient, R^2 , indicating its ability to fit well with the experimental data as assumed by the literature [11,28]. The results are provided in section 3.2.1. For the estimation of kinetics parameters, conversion, α ,

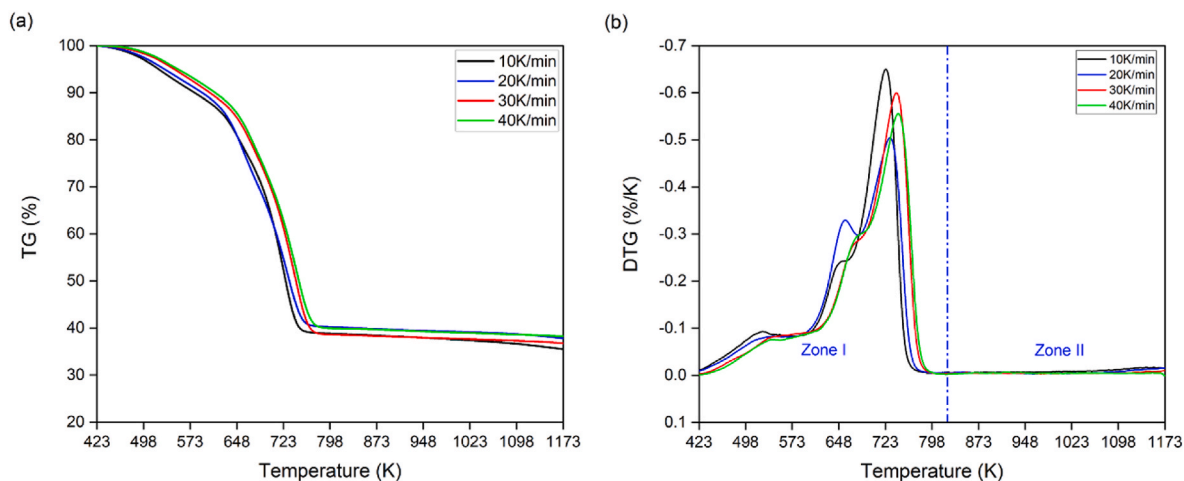


Fig. 2. (a) TG and (b) DTG curves of pyrolysis of waste tyre at 10, 20, 30 and 40 K/min.

was calculated first for the TGA data using Equation (4). Then, the value for the left-hand side of Equation (9) was calculated and plotted against $1/T_\alpha$ where T is in K. Activation energy, E_a , and pre-exponential factor, A , were calculated for each blend ratio using the plot and maintaining the best linear correlation coefficient.

2.3.2. Flynn-Wall-Ozawa (FWO)

FWO method allows the estimation of apparent E_a using the slope of $\ln(\beta)$ versus $1/T_\alpha$ as expressed in Equation (10) for a given value of conversion (α) [30]. T_α refers to the temperature at specific reaction extent.

$$\ln \beta = \ln \left(\frac{AE_a}{Rg(\alpha)} \right) - 5.3305 - 1.052 \left(\frac{E_a}{RT_\alpha} \right) \quad (10)$$

2.3.3. Kissinger-Akahira-Sunose (KAS)

KAS method is based on Equation (11) where the apparent E_a is estimated from the slope of $\ln\left(\frac{\beta}{T_\alpha^2}\right)$ versus $1/T_\alpha$ for different conversion value (α) for different blend samples [30].

$$\ln \left(\frac{\beta}{T_\alpha^2} \right) = \ln \left(\frac{A_a R}{E_a g(\alpha)} \right) - \left(\frac{E_a}{RT_\alpha} \right) \quad (11)$$

2.3.4. Friedman method

Friedman method is the differential form of iso-conversional method and expressed in Equation (12). It is widely used and more accurate

method because it is independent of any mathematical approximation like other methods [54]. The slope of left-hand side of Equation (12) against $1/T_\alpha$ provides an estimation for the value of E_a .

$$\ln \left(\beta \frac{d\alpha}{dT} \right) = \ln[A.f(\alpha)] - \frac{E_a}{RT_\alpha} \quad (12)$$

2.3.5. Generalized master plot method

The reaction mechanism that best describes the solid-state reaction process can be identified using Criado et al. [52] procedure. This is achieved through a comparison between the experimental curves and pre-defined set of plots known as theoretical master plots. Theoretical master plots are independent of reaction kinetics. Each theoretical master plot is unique to a specific reaction mechanism. The expressions of reaction mechanisms listed in Table 5 are used to develop the theoretical master plots using $y(\alpha)$ function as expressed in Equation (13) [52].

$$y(\alpha) = f(\alpha)/f(\alpha)_{0.5} \quad (13)$$

Equation (14) is used to construct the experimental curve [50].

$$y(\alpha) = \frac{(d\alpha/dt) \cdot \exp(E/RT_\alpha)}{(d\alpha/dt)_{0.5} \exp(E/RT)_{0.5}} \quad (14)$$

Activation energy values obtained using Friedman method are used for the calculation of experimental $y(\alpha)$ function.

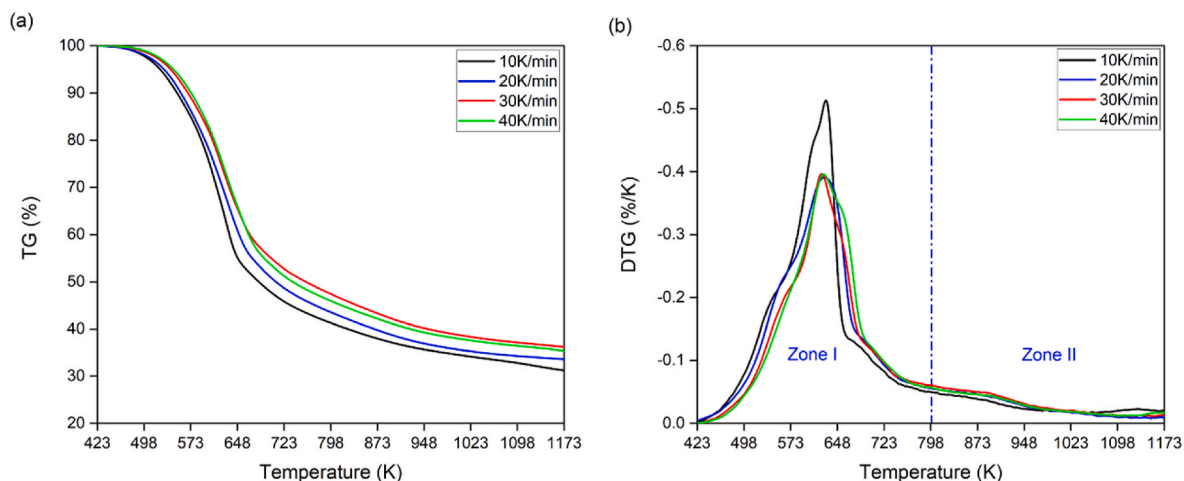


Fig. 3. (a) TG and (b) DTG curves of pyrolysis of pine bark at 10, 20, 30 and 40 K/min.

Table 6

Thermal decomposition characteristics of waste tyre and pine bark in main pyrolysis zone (i.e., Zone I) at different heating rates.

Sample ID	β (K/min)	Sub-zones	Temperature (K)			Weight loss (%)
			T_i	T_{max}	T_f	
WT1PB0	10	Stage a	423.0	524.8	577.9	9.8
		Stage b	577.9	651.7	664.7	13.3
		Stage c	664.7	723.7	775.2	37.9
	20	Stage a	423.0	533.2	582.6	9.1
		Stage b	582.6	658.2	679.3	19.7
		Stage c	679.3	730.6	795.0	30.9
	30	Stage a	423.0	539.5	596.9	9.3
		Stage b	596.9	674.1	690.7	17.1
		Stage c	690.7	740.9	806.2	35.1
40	Stage a	423.0	542.2	615.6	10.2	
	Stage b	615.6	675.4	696.1	17.0	
	Stage c	696.1	743.9	811.2	32.9	
WT0PB1	10	Stage a	423.0	–	566.7	13.5
		Stage b	566.7	629.7	661.5	33.8
		Stage c	661.5	–	745.3	8.5
	20	Stage a	423.0	–	578.3	15.1
		Stage b	578.3	627.0	674.2	30.3
		Stage c	674.2	–	752.8	8.3
	30	Stage a	423.0	–	583.1	13.2
		Stage b	583.1	622.8	682.9	29.4
		Stage c	682.9	–	763.3	7.8
	40	Stage a	423.0	–	590.6	13.9
		Stage b	590.6	625.9	694.3	31.5
		Stage c	694.3	–	774.3	7.2

2.3.6. Combined kinetic analysis

Rearranging Equation (12) to account for the reaction model, it can be expressed as Equation (15) [43,55];

$$\ln \left(\beta \frac{\frac{d\alpha}{dT}}{f(\alpha)} \right) = \ln[A] - \frac{E_a}{RT_\alpha} \tag{15}$$

Like the iso-conversional methods, plotting $\ln \left(\beta \frac{d\alpha/dT}{f(\alpha)} \right)$ against the reciprocal of the temperature at specific reaction extent results in straight line in which the activation energy and the pre-exponential factor can be obtained from the slope and intercept, respectively. However, this requires the knowledge of proper reaction mechanism which is proposed based on Sestak-Berggren expression.

Sestak-Berggren (i.e. SB) empirical expression is characterized by better flexibility in fitting various reaction models through the estimation of unknown parameters; m , n and p , providing a better estimation of $f(\alpha)$ [43,53]. This is expressed as Equation (16) [43,53];

$$f(\alpha) = \alpha^m (1 - \alpha)^n [-\ln(1 - \alpha)]^p \tag{16}$$

Parameters m , n and p are evaluated using optimization functions ‘lsqcurvefit’ and ‘lsqnonlin’ in MATLAB R2021b software with minimization of least square difference as an objective function.

3. Results and discussion

The framework of the current research is as follow. First, thermogravimetric analysis results of waste tyre, pine bark and their blends were discussed. Then, the synergetic interaction between waste tyre and pine bark was evaluated in terms of variation in weight loss between single and blend samples. To do so, difference in weight loss was used as an index. Further, the kinetics characteristics of co-pyrolysis of waste tyre and pine bark are investigated through model fitting and iso-conversional methods. In addition, the effect of co-pyrolysis on the activation energy of the reaction was discussed. This is important to identify the proper blend ratio from reactor design and reaction engineering perspective. Finally, the proper reaction mechanisms were identified through master plot method as well as fitting with Sestak-Berggren empirical equation. The derived reaction mechanisms, $f(\alpha)$, were used for the accurate estimation of kinetics parameters, E_a and A .

3.1. TG and DTG analysis

3.1.1. Thermal decomposition of single feedstock

Thermal degradation of a single feedstock of waste tyre (WT1PB0) and pine bark (WT0PB1) was investigated at four different heating rates of 10, 20, 30 and 40 K/min. TG and DTG curves of waste tyre and pine bark decomposition are presented in Figs. 2 and 3, respectively. It can be clearly seen from DTG curves that the decomposition of waste tyre and pine bark occurred over two stages excluding moisture removal. These stages are named as Zone I and Zone II.

Waste tyre showed three main decomposition peaks in Zone I around temperatures of 538, 657 and 729 K. Thermal decomposition of tyre is highly influenced by the type of the rubber and other contents contained in the waste tyre [38]. The first peak in Zone I is associated with the release of volatiles contained in the additives used for waste tyre manufacturing including oils, plasticisers and others [56,57]. However, the last two peaks are ascribed to the decomposition of natural rubber and butadiene and styrene-butadiene rubber, respectively [57]. Waste tyre pyrolysis was completed at a temperature of 801 K at which nearly constant weight loss was recorded.

On the other hand, pine bark degradation extended over wide temperature range with a single shoulder and peak shown in Zone I. The

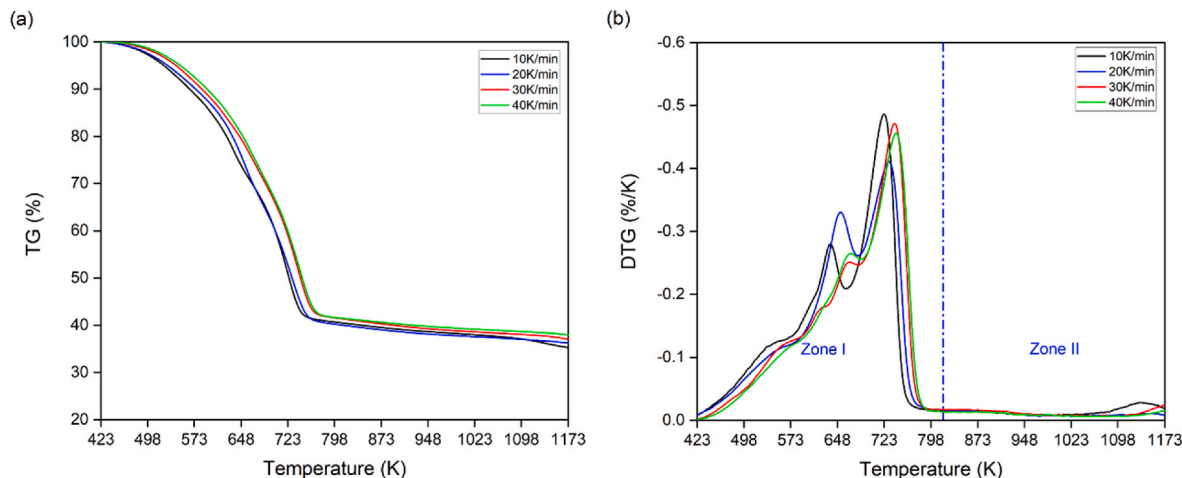


Fig. 4. (a) TG and (b) DTG curves of co-pyrolysis of waste tyre and pine bark at 10, 20, 30 and 40 K/min for WT3PB1.

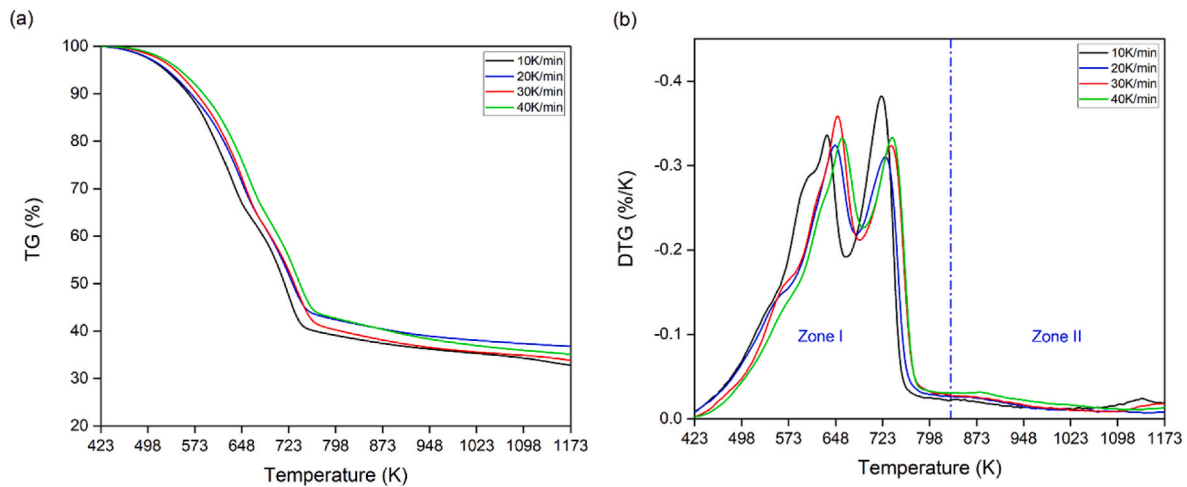


Fig. 5. (a) TG and (b) DTG curves of co-pyrolysis of waste tyre and pine bark at 10, 20, 30 and 40 K/min for WT1PB1.

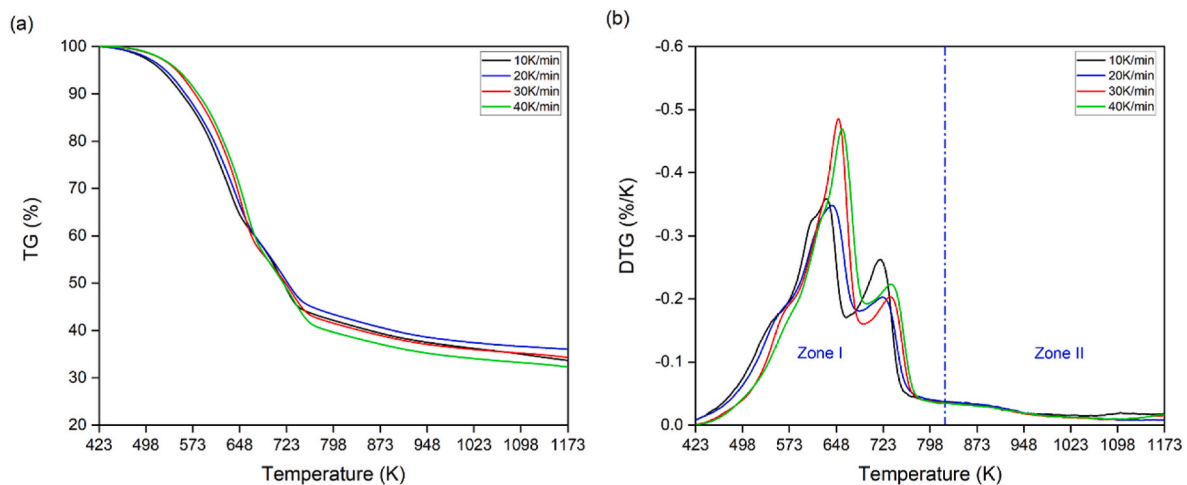


Fig. 6. (a) TG and (b) DTG curves of co-pyrolysis of waste tyre and pine bark at 10, 20, 30 and 40 K/min for WT1PB3.

presence of shoulder at lower temperature of around 553 K is associated with the decomposition of hemicellulose [58]. Azizi et al. [31] reported the appearance of hemicellulose as shoulder rather than a clear peak during the decomposition of wood. Maximum weight loss occurred at a temperature of around 626 K. Similar observation was reported by Singh et al. [28]. This could be attributed to the breakdown of cellulose [3,20]. However, the decomposition of lignin as a constituent of biomass extends over wider temperature range (473–823 K) [20,58] which could coincide with the decomposition of hemicellulose and cellulose. The pyrolysis process was continued to a final temperature of 1173 K. The weight loss of pine bark continued throughout the selected temperature range whereas there was almost no significant change in the weight of waste tyre at around 791 K with a total residue of 37 and 32 wt% for waste tyre and pine bark, respectively. High fraction of solid residue is associated with fixed carbon and ash content of both materials [23,32] as calculated by proximate analysis and given in Table 2. In addition, the use of carbon black during tyre manufacturing contributes to high yield of char [59].

In comparison between thermal degradation characteristics of waste tyre and pine bark, waste tyre starts the decomposition at higher temperature than biomass and is represented by more than one decomposition peaks. Similar observation was noticed by Wang et al. [23] during pyrolysis of rice straw, poplar wood and waste tyre separately in which rice straw and poplar wood started the decomposition at approximately 473 K compared to 653 K for waste tyre. The maximum degradation rate

of waste tyre and pine bark occurred over the temperature range of 724–744 K and 623–630 K with an average value of 0.58 and 0.42 wt %/K, respectively.

Thermal decomposition characteristics of the single feedstocks at different heating rate are summarized in Table 6, where T_i , T_{max} and T_f refer to initial temperature, the maximum temperature at which the DTG peaks occur and the final temperature, respectively. For both samples, the highest weight loss of more than 50 wt% occurred at Zone I. Therefore, Zone I is considered as main pyrolysis zone and used for the kinetics analysis.

3.1.2. Thermal decomposition of waste tyre and pine bark blends

Figs. 4–6 show TG and DTG curves of the waste tyre and pine bark blend samples. Like single feedstocks, TG and DTG curves of the waste tyre and pine bark blends were divided into two zones. It can be noticed clearly that the pyrolysis of the waste tyre was promoted to some extent with the addition of pine bark. As the fraction of pine bark in the blend increases, the value of the mass loss rate associated with the first peak increased in comparison to single waste tyre while the second peak decreased. This is attributed to the release of free radicals during the degradation of pine bark. Since biomass has lower thermal stability due to presence of unstable o-containing bonds, it decomposes at lower temperature [23] and release free radicals including O-radical, OH-radical and other O-containing radicals [17]. These reactive free radicals in turn will enhance the decomposition of waste tyre through

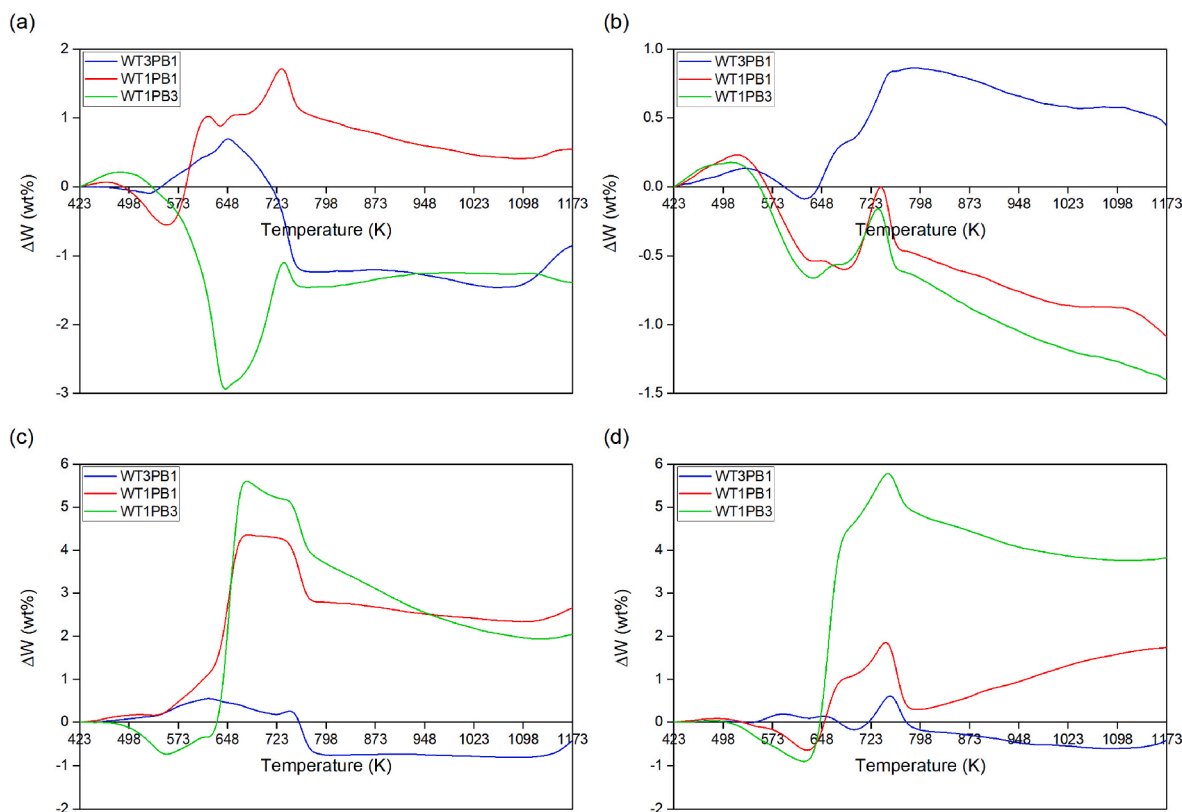


Fig. 7. Variation in the difference of weight loss (ΔW) for waste tyre and pine bark blends at (a) 10, (b) 20, (c) 30 and (d) 40K/min.

chain scission of rubber components [60]. Therefore, higher degradation is noticed at lower temperatures for blended samples compared to waste tyre.

3.1.3. Effect of heating rate on the decomposition of waste tyre, pine bark and their blends

Table 6 highlights the effect of the heating rate on the decomposition characteristics of waste tyre and pine bark. A shift in the peak temperature of TGA curves of all the samples including the blends (results are not shown here) to higher values was observed because of an increase in heating rate. Similar observation was reported by Williams and Besler [59] and others [18,31,36]. It was attributed to increased thermal lag induced by limited heat diffusion and the change in the decomposition kinetics of the feedstocks at higher heating rates.

The synergetic effect between the feedstocks used is considered as one of the main factors that play a key role in the improvement in the quality and quantity of the products during co-pyrolysis. The existence of synergetic interaction between waste tyre and pine bark during co-pyrolysis in response to the change in heating rate and blend ratio as operating conditions was evaluated using the difference in weight loss (ΔW) as an index [37]. Difference in weight loss is defined as [37];

$$\Delta W = W_{exp} - W_{cal} \tag{17}$$

Where W_{exp} and W_{cal} are the weight loss experimentally measured and theoretically calculated, respectively. W_{cal} is calculated using Equation (18);

$$W_{cal} = (x_{WT} \times W_{WT}) + (x_{PB} \times W_{PB}) \tag{18}$$

Where x_{WT} and x_{PB} refer to the weight fraction of waste tyre and pine bark in the blend, respectively, and W_{WT} and W_{PB} are weight loss in wt% when only single feed of waste tyre and pine bark, respectively, is used for pyrolysis.

Negative ΔW values indicate the occurrence of inhibiting effect

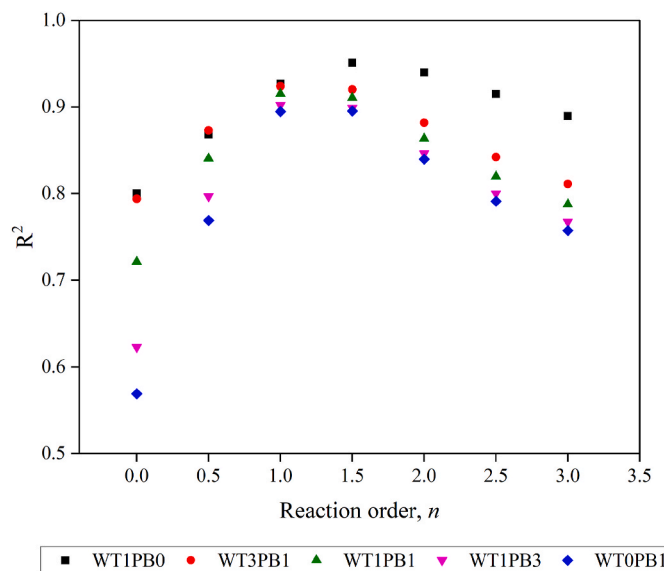


Fig. 8. Correlation coefficient (i.e. R^2) versus reaction order, n , for different blend ratios based on Coats-Redfern method.

while the positive values correspond to the promoting effect. This was examined at heating rate of 10, 20, 30 and 40 K/min as shown in Fig. 7. It can be seen clearly that the change in heating rate affected differently the difference in weight loss, ΔW , for each sample with different waste tyre to pine bark mass ratios. The use of heating rate of 10, 30 and 40 K/min in the decomposition of WT3PB1 blend sample resulted in negative values of ΔW indicating the occurrence of lower experimental weight loss, whereas the most inhibitive interaction took place under heating rate of 10 K/min at temperature higher than 723 K. However, promoting

Table 7
Reaction kinetics parameters of the pyrolysis of single and blended feedstocks in Zone I.

Sample ID	Stage	Temperature (K)	α range	E_a (kJ/mol)	A (min ⁻¹)	R ²
WT1PB0	a	423–561	0.01–0.13	57.3	2.66E+06	0.9928
	b	590–700	0.17–0.57	111.7	3.88E+09	0.9975
	c	714–760	0.66–0.95	292.4	9.26E+21	0.9811
WT3PB1	a	417–568	0.02–0.16	61.9	8.86E+06	0.9919
	b	578–679	0.18–0.54	109.9	6.41E+09	0.9933
	c	691–760	0.58–0.92	195.9	1.24E+15	0.9910
WT1PB1	a	419–575	0.04–0.21	60.0	3.52E+06	0.9932
	b	596–678	0.26–0.59	119.8	4.47E+10	0.9951
	c	696–753	0.66–0.89	186.3	2.34E+14	0.9893
WT1PB3	a	415–564	0.05–0.21	63.5	9.89E+06	0.9917
	b	582–684	0.26–0.68	97.5	6.75E+08	0.9935
	c	703–745	0.73–0.85	188.9	3.07E+14	0.9832
WT0PB1	a	423–560	0.06–0.21	74.5	1.09E+08	0.9935
	b	599–669	0.36–0.69	86.5	7.75E+07	0.9926
	c	734–816	0.80–0.87	122.4	1.20E+09	0.9928

interaction occurred at heating rate of 20 K/min. In addition, WT3PB1 blend sample showed the lowest degree of variation in the change of weight loss regardless of being positive or negative. Since waste tyre is known as thermally high stable material and contains high fraction of fixed carbon, there is less impact from the addition of 25 wt% of pine bark on its decomposition as represented by nearly constant change in ΔW , at higher temperatures.

Waste tyre and pine bark blend sample with the mass ratio of 1:1 showed almost promoting interaction at all heating rates except at 20 K/min in which the promoting interaction was only up to a temperature of 573 K.

In contrast, WT1PB3 blend sample showed positive interaction only at high heating rate of 30 and 40 K/min. The results indicate that the maximum synergetic effect occurred over a temperature range of 648–748 K which coincides with the degradation of synthetic rubber, cellulose and lignin [20,57]. This is confirmed by higher peaks at higher heating rate as shown in Fig. 6. At heating rate of 10 and 20 K/min the difference in weight loss showed an inhibitive turning point at a temperature of 520 and 571 K.

The positive synergetic interaction in terms of weight loss at low heating rate compared to higher heating rate is attributed to the longer heating time required to achieve the desired final temperature in TGA analysis. Therefore, low heating rate will allow better heat diffusion, promoting the decomposition reactions. However, the promoting interaction at higher heating rate could be attributed to more rapid temperature increase of the sample and the high temperature gradient within the sample [61].

3.2. Kinetics analysis

The kinetics characteristics of pyrolysis process of individual and blended feedstocks were investigated and the effect of different blend ratios on the kinetics parameter; E_a was discussed. From DTG curves of waste tyre, pine bark and their blends shown in section 3.1, it can be clearly pointed out that multiple reactions are necessary to describe the kinetics of the pyrolysis/co-pyrolysis process. Details on how the kinetics are determined using both model fitting and iso-conversional methods are discussed in the following sections.

3.2.1. Overall kinetics analysis of pyrolysis/Co-pyrolysis of waste tyre and pine bark using model-fitting methods

Since the decomposition of waste tyre and pine bark blends showed different synergetic interaction at different heating rate as well as due to space limitation, the results of TGA of waste tyre, pine bark and their blends at single heating rate of 20 K/min was used for kinetics analysis using Coats-Redfern method. This is to calculate the global kinetics parameters assuming single step process. First, the curves of $\ln\left[\frac{g(\alpha)}{T^2}\right]$

against $1/T$ were developed for different blend ratios. This is accomplished using $g(\alpha)$ expressions of different reaction orders mentioned in Table 4 to propose the reaction order that best describes the process based on the highest correlation coefficient. The results are shown in Fig. 8. It can be clearly noticed that first order reaction is the best to fit the experimental data for all the samples except waste tyre (i.e. $n = 1.5$) which confirms the assumption made by others in the literature [11,28]. For the simplicity of the calculation, all the kinetics analysis based on Coats-Redfern method was made using reaction order of 1 for all the samples.

In the calculation of kinetics parameters, the main decomposition region, named as zone I, was considered for each sample. The kinetic curves of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ against $1/T$ were constructed assuming single step process as shown in Fig. S1 in the supplementary document. It can be observed that there is a non-linear trend indicating that the pyrolysis process of waste tyre, pine bark and their blends constitute multiple first order reactions. Therefore, the obtained curves were broken down into segments of different temperature ranges corresponding to the shoulders and peaks in the main pyrolysis zone as shown in Fig. S2 (in the supplementary document).

The apparent activation energy (E_a) and pre-exponential factor (A) were calculated from the slope and intercept, respectively, of the regression line for each curve. The results are summarized in Table 7.

Waste tyre showed higher E_a than pine bark at a temperature higher than 590 K. This is contributed to higher thermal stability of waste tyre constituents including natural and synthetic rubbers [11]. Therefore, materials with lower E_a values tend to initiate the reaction more effectively showing higher pyrolysis feasibility [42] which is the case with pine bark.

The variation in the values of apparent activation energy for the different temperature range is associated with the compositional differences of the feedstocks. DTG curves of waste tyre and pine bark given in 3.1 support the findings of apparent activation energy values provided in Table 7. According to Akubo et al. [20] and Yeo et al. [54] hemicellulose consists of branched polysaccharides which are known to easily degrade at lower temperature during thermal process than cellulose. The latter has higher thermal stability than hemicellulose due to its β (1 \rightarrow 4) linked D-glucose units [20]. This supports the findings of TGA analysis as well as the kinetics data in which the shoulder as associated with hemicellulose decomposition has lower E_a value than the peak (i.e., cellulose). According to the literature, the activation energy of hemicellulose and cellulose decomposition varies in the range of 77.93–137.9 kJ/mol and 132.2–354.4 kJ/mol [14,15,49,54], respectively. Lignin is composed of alkyl-benzene structure with three-dimensional linkages [54]. This structure results in higher thermal stability of lignin compared to other biomass constituents. Therefore, the highest E_a value (122 kJ/mol) was calculated at higher

Table 8

Average E_a values for single feedstocks (i.e., WT1PB0 and WT0PB1) obtained by Iso-conversional methods.

Sample ID	Conversion (α)	E_a (kJ/mol)		
		FWO	KAS	Friedman
WT1PB0	0.10	102.1	98.2	100.3
	0.15	117.0	113.3	131.6
	0.20	159.9	157.9	198.9
	0.25	205.9	206.0	237.7
	0.30	231.6	232.8	265.0
	0.35	264.3	267.0	317.4
	0.40	309.8	314.6	365.9
	0.45	343.3	349.7	372.9
	0.50	350.7	357.3	353.7
	0.55	343.5	349.6	330.6
	0.60	332.2	337.6	314.1
	0.65	321.8	326.6	302.8
	0.70	312.9	317.1	295.2
	0.75	305.8	309.5	290.8
	0.80	300.1	303.5	287.9
	0.85	295.5	298.5	285.5
	0.90	291.5	294.3	284.7
Average	269.9	272.6	278.5	
WT0PB1	0.10	169.5	169.3	174.2
	0.15	179.1	179.2	192.5
	0.20	196.1	196.8	217.5
	0.25	216.4	217.9	239.3
	0.30	233.1	235.4	252.4
	0.35	244.6	247.3	260.6
	0.40	251.7	254.7	262.9
	0.45	254.6	257.6	257.9
	0.50	251.2	253.9	239.6
	0.55	238.3	240.2	204.7
	0.60	217.0	217.6	168.0
	0.65	194.6	193.9	148.8
	0.70	177.2	175.5	153.3
	0.75	172.8	170.7	192.8
	0.80	188.8	187.1	202.4
	0.85	198.2	196.6	204.2
	0.90	213.9	212.4	247.7
Average	211.6	212.1	212.9	

temperatures.

On the other hand, Waste tyre consists of additives used in the tyre manufacturing process and are known to be volatiles so they will decompose more easily [61] at temperature lower than 573 K showing the lowest E_a (57 kJ/mol). Similarly, Lah et al. [61] reported low value of E_a of 33.5 kJ/mol for the volatiles. Natural rubber decomposes at lower temperature with a peak around 658K compared to synthetic rubber. Apparent activation energy at Stage b corresponding mainly to the decomposition of natural rubber is lower than the stage c which is 112 kJ/mol compared to 292 kJ/mol. Williams and Besler [59] reported that natural rubber has slightly higher activation energy of 199.9 kJ/mol than styrene butadiene rubber (i.e. 195.2 kJ/mol) but lower than polybutadiene rubber (i.e. 223.8–244.4 kJ/mol) at heating rate of 20 K/min. Therefore, higher activation energy of waste tyre at stage c compared to b could be contributed to the fact that it contains higher fraction of polybutadiene rubber than styrene butadiene rubber.

According to the results of activation energy reported in Table 7 for blend samples, an increase in the mass fraction of pine bark in the blend to 75 wt% had negligible effect on the activation energy of stage a in comparison to waste tyre. This could be attributed to high E_a value of pine bark in the same stage which is associated with the devolatilization of extractives as well as a fraction of hemicellulose. However, the activation energy of decomposition reaction decreased by a maximum of 13% at stage b with a temperature range of 573–673 K and 35% at stage c with temperature higher than 700 K compared to single waste tyre. This means that the energy requirement for the decomposition of fixed carbon fraction and synthetic rubber component of tyre is lowered due to addition of biomass. Similarly, Uzun and Yaman [36] found that the addition of biomass to scrap tyre decreased the activation energy from

Table 9

Average E_a values for blend feedstocks (i.e., WT3PB1, WT1PB1 and WT1PB3) obtained by Iso-conversional methods.

Sample ID	Conversion (α)	E_a (kJ/mol)		
		FWO	KAS	Friedman
WT3PB1	0.10	127.6	125.2	129.3
	0.15	137.0	134.7	144.8
	0.20	153.0	151.1	168.4
	0.25	170.0	168.7	183.1
	0.30	179.6	178.5	185.2
	0.35	180.0	178.7	174.3
	0.40	177.7	176.1	179.8
	0.45	188.4	187.1	221.5
	0.50	218.8	218.9	265.7
	0.55	252.2	253.9	293.6
	0.60	275.4	278.1	303.2
	0.65	286.7	289.8	302.1
	0.70	291.4	294.6	300.2
	0.75	293.8	297.0	300.7
	0.80	295.5	298.8	302.4
	0.85	297.5	300.7	305.7
	0.90	300.8	304.1	314.4
Average	225.0	225.7	239.7	
WT1PB1	0.10	160.6	159.9	172.0
	0.15	175.5	175.2	184.6
	0.20	178.2	177.7	172.8
	0.25	173.4	172.5	165.0
	0.30	172.2	170.9	172.2
	0.35	175.3	174.0	183.4
	0.40	183.3	182.3	200.3
	0.45	192.6	191.9	209.4
	0.50	202.5	202.1	228.7
	0.55	229.7	230.6	290.6
	0.60	287.0	290.6	345.7
	0.65	335.9	341.9	366.8
	0.70	351.3	357.8	353.0
	0.75	343.6	349.5	333.8
	0.80	331.3	336.5	318.3
	0.85	319.0	323.4	303.7
	0.90	303.6	307.0	278.1
Average	242.1	243.8	251.7	
WT1PB3	0.10	113.1	110.0	121.4
	0.15	124.5	121.6	136.1
	0.20	137.7	135.2	155.9
	0.25	155.0	153.2	180.1
	0.30	172.0	170.9	194.7
	0.35	183.0	182.3	197.6
	0.40	191.9	191.5	212.9
	0.45	205.9	206.1	240.9
	0.50	225.6	226.6	274.8
	0.55	254.1	256.5	330.4
	0.60	316.2	321.6	476.7
	0.65	248.9	250.7	300.1
	0.70	-39.4	-52.8	-8.6
	0.75	233.0	233.4	323.1
	0.80	748.4	775.4	662.9
	0.85	602.5	621.7	543.1
	0.90	588.4	606.6	711.9
Average	262.4	265.3	297.3	

78.7 to 63.8 kJ/mol using scrap tyre and scrap tyre/biomass blend with 1:1 mass ratio, respectively. According to Wang et al. [23] biomass plays a role in activating the decomposition process of waste tyre during co-pyrolysis process. This is attributed to low thermal stability of biomass compared to polymeric wastes like waste tyre and the formation of free radicals [32], lowering the activation energy of the blend samples. This indicates positive synergetic effect during co-pyrolysis process. The lowest activation energy and thus highest synergetic interaction occurred with WT1PB3 compared to single waste tyre. Although WT1PB3 showed lowest E_a value for stages b and c compared to other blend samples, the comparison between experimentally obtained average E_a and theoretically calculated showed maximum synergetic interaction with WT3PB1 blend sample.

The experimental and theoretical average activation energy (i.e.

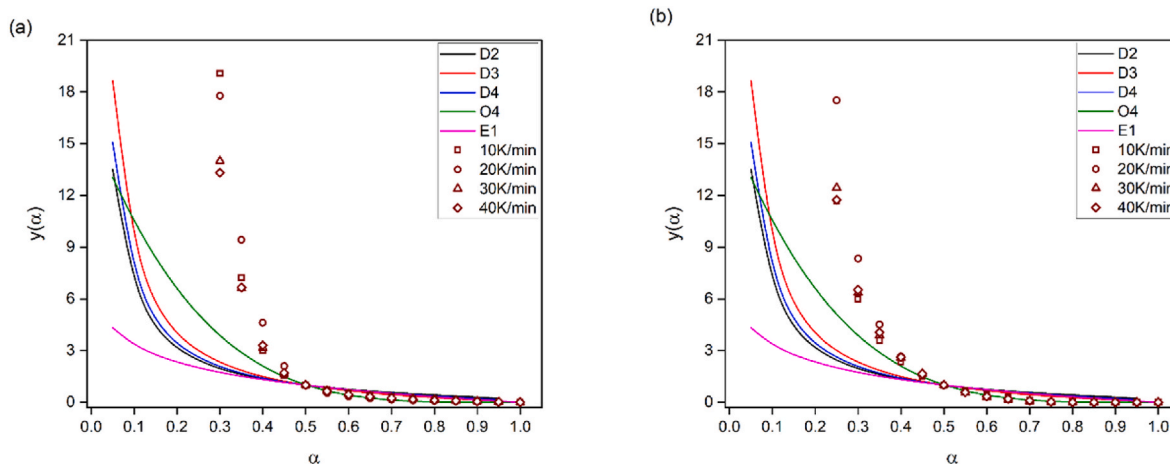


Fig. 9. Comparison of theoretical master plots and experimental data for (a) WT1PB0 and (b) WTOPB1 at different heating rates.

$\bar{E}_{a,exp}$ and $\bar{E}_{a,cal}$ are calculated using Equations (19) and (20), respectively [40].

$$\bar{E}_{a,exp} = \left(\sum_{i=1}^N \alpha_i E_{a,i} \right) / \sum_{i=1}^N \alpha_i \quad (19)$$

$$\bar{E}_{a,cal} = (x_{WT} \times \bar{E}_{WT}) + (x_{PB} \times \bar{E}_{PB}) \quad (20)$$

where, α_i and $E_{a,i}$ refer to conversion and activation energy values at each temperature range, respectively, and x_{WT} and x_{PB} refer to the weight fraction of single waste tyre and pine bark in the blend, respectively. \bar{E}_{WT} and \bar{E}_{PB} are experimental average activation energy for single waste tyre and pine bark samples, respectively, in kJ/mol.

The theoretical \bar{E}_a of all blend samples were higher than the experimental one, indicating that promoting positive interaction took place. The $\bar{E}_{a,cal}$ values for WT3PB1, WT1PB1 and WT1PB3 were as follow; 147.9, 127.9 and 107.9 compared to $\bar{E}_{a,exp}$ values of 136.7, 126.5 and 105.3 kJ/mol, respectively. The highest percent difference between $\bar{E}_{a,exp}$ and $\bar{E}_{a,cal}$ of 7.9% was reported for WT3PB1.

Using Coats-Redfern method with reaction order of 1 showed high correlation coefficients (>0.98) for different blend samples as shown in Table 7. Despite the best fitting of Coats-Redfern with the experimental data, using first order reaction model does not necessarily provide an accurate representative of the reaction mechanism. Therefore, attempts were made to define the reaction mechanism underlying the pyrolysis of waste tyre, pine bark and their blends as will be discussed in sections 3.2.3 and 3.2.4.

3.2.2. Determination of overall kinetics parameters using iso-conversional method

The determination of apparent activation energy of all the blend samples was conducted by linear fit of left-hand side of the equations representing iso-conversional methods against $1/T_\alpha$. The conversion ranges from 0.1 to 0.9 with a step size of 0.05 was considered. In addition, the fitting of experimental data using the iso-conversional methods for the four heating rates showed low correlation coefficient. Therefore, experimental data of three heating rates (i.e., 10, 30 and 40 K/min) were considered which still satisfy the recommendation made by ICTAC [43]. Correlation coefficients were higher than 0.9 for each method which signifies that they were better fitted with experimental data except for WT3PB1 and WTOPB1 for the conversion values higher than 0.55. Tables 8 and 9 summarizes the values of E_a for different blend samples using different iso-conversional methods at heating rate of 10, 30 and 40 K/min. Comparing the overall variation in activation energy values with conversion for single sample, the difference between each

sample is observed. This is contributed to the differences in the molecular structure of waste tyre compared to pine bark.

As seen in Table 8, the lowest activation energy value was obtained at the lowest conversion value of 0.1 and it was higher for waste tyre compared to pine bark. However, as the conversion value increased to 0.5 and 0.45, the activation energy increased to a maximum value of higher than 350 and 250 kJ/mol for waste tyre and pine bark, respectively. A decrease in activation energy was noticed at conversions higher than 0.5 for waste tyre. However, E_a of pine bark is fluctuated at conversions higher than 0.45. This indicates the occurrence of multiple decomposition reactions. Similar observation was reported by Yeo et al. [54] for the decomposition of hemicellulose and lignin where the E_a values highly varied as a function of conversion. According to Wang et al. [55], the decrease in E_a could be attributed to in-situ catalytic effect of metals contained in the ash of either biomass, waste tyre or both and the enhanced diffusion of volatiles into porous char material making the reaction easier (lower E_a).

Like pine bark, the variation in E_a values with the change in conversion and temperature for the blend samples is large. This could be associated with the overlapping of the decomposition temperature of waste tyre and pine bark constituents including cellulose, hemicellulose, etc. [37] and the possible interactions taking place between the devolatilization products. Devolatilization products here refer to the reactive free radicals, which released throughout devolatilization (i.e., pyrolysis). The thermal decomposition mechanism of both waste tyre and pine bark and the release of such reactive compounds is a function of pyrolysis conditions including temperature and the composition of these materials [9,12,59]. Therefore, the variation in activation energy is ascribed to the difference in the composition of both waste tyre and pine bark and their fraction in the blends which results in different reactivity as the temperature changes [62]. This variation was also reported in other studies of waste tyre and biomass constituents [54,55,59,61]. It is noteworthy that the average activation energy values of the blend samples were lower than the single waste tyre sample as provided in Table 9. The highest reduction of 14–17% in activation energy was achieved with waste tyre to pine bark mass blend ratio of 3:1. Although the activation energy values for all the blend samples differ from the one calculated using CR method, the visual comparison shows agreement in terms of WT3PB1 requiring the lowest energy input compared to WT1PB0.

3.2.3. Master plot method for $f(\alpha)$

Theoretical master plots are constructed separately for each kinetic model given in Table 5 by calculating $y(\alpha)$ function and they were plotted against α . Master plots of the experimental data are built individually for each sample at different heating rate. To do that, $y(\alpha)$

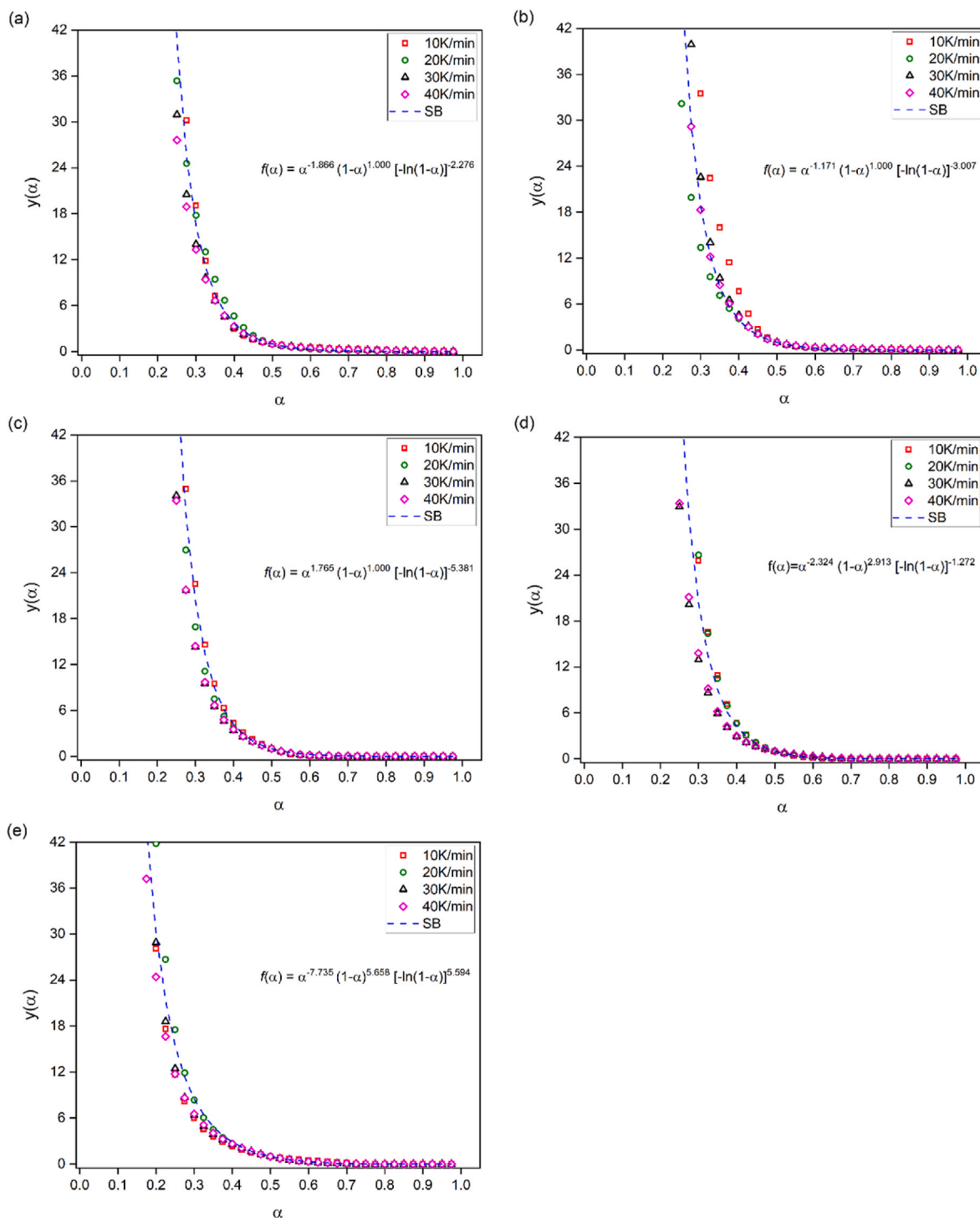


Fig. 10. Combined kinetics analysis for normalized reaction mechanism, $y(\alpha)$ of (a) WT1PB0, (b) WT3PB1, (c) WT1PB1, (d) WT1PB3 and (e) WTOPB1.

Table 10

Values of optimum parameters, activation energy and pre-exponential factor for different blend samples obtained through combined kinetic analysis.

Sample ID	m	n	p	E_a (kJ/mol)	A (min^{-1})	R^2
WT1PB0	-1.8660	1.0000	-2.2755	241.4	8.36E+17	0.942
WT3PB1	-1.1314	1.0000	-3.0069	232.6	4.59E+17	0.978
WT1PB1	1.7654	1.0000	-5.3813	236.5	7.68E+18	0.990
WT1PB3	-2.3241	2.9130	-1.2720	255.0	9.27E+20	0.990
WTOPB1	-7.7352	5.6576	5.5944	182.1	1.91E+15	0.985

function was calculated for each sample using Equation (14), considering the average value of apparent activation energy obtained from Iso-conversional Friedman method. Plots of WT1PB0 and WTOPB1 are shown as an example in Fig. 9. Even though it was difficult to determine the possible reaction mechanism based on the comparison with the theoretical master plots, it can be noticed that the decomposition reactions of both waste tyre and pine bark are either following power law, diffusional, high order reaction mechanism, or combination of them. According to Fig. 9, pyrolysis of waste tyre and pine bark follow high order reaction mechanism (i.e. O4) for α value between 0.40 and 0.95 and diffusional reaction mechanism (i.e. D2, D3 and D4) for the range

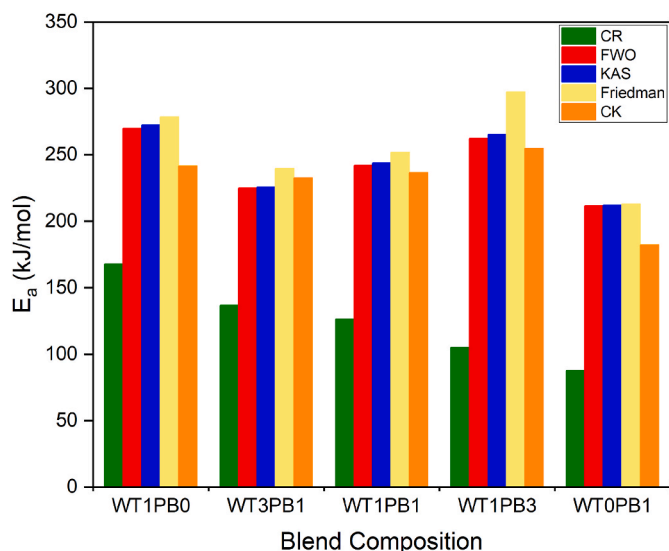


Fig. 11. Comparison in E_a values for different samples obtained using model fitting (CR), integral model free (FWO and KAS) and differential model free (Friedman) methods.

$0.05 < \alpha < 0.95$. Therefore, a combined kinetic analysis was carried out and discussed in the following section to identify the reaction mechanism with better accuracy using the results of master plot method as reference.

3.2.4. Kinetic triplets through combined kinetic analysis

Experimental data of all the samples was fitted with Sestak-Berggren function and optimized to obtain the best parameters (i.e., m , n and p) of the empirical function shown in Equation (16). The fitting results of the main decomposition zone, Zone I, for all the blend samples at different heating rates are provided in Fig. S3 (in the supplementary material). The slope and the intercept of the linear fit line was used to calculate the E_a and A . Based on combined kinetics analysis, the reaction mechanisms followed by waste tyre, pine bark and their blends are depicted in Fig. 10 and the results are summarized in Table 10. High R^2 value (i.e. > 0.94) of linear fitting indicates that pyrolysis process of waste tyre, pine bark and their blends can be described through SB model. According to Hidayat et al. [63] and Wang et al. [55], the parameters m , n and p refer to power law, reaction order and nucleation reaction mechanism, respectively. It can be clearly observed that the decomposition of waste tyre, pine bark and their blends is a combination of different mechanisms including nucleation, diffusion, and power law in addition to reaction order. As per the results reported in Table 10, negative and high value of m parameters reflects that the decomposition of both single and blend samples follows 1-dimensional diffusion and power law reaction mechanisms [55,63]. In addition, high values of p parameter for all the blend samples signify the contribution of nucleation mechanism during the decomposition of these samples. Several studies suggested that waste tyre decomposition follows random bond scission model involving free radicals formation, hydrogenation and recombination [46,60]. However, the combined kinetic analysis results indicate the difference. In reference to the values of SB parameters shown in Table 10, random nucleation and growth of nuclei through different nucleation and nucleus growth (i.e., $n \neq 1$) and diffusion are the rate-limiting steps for waste tyre decomposition. Perejon et al. [60] emphasized that diffusion of primary degradation species at lower operating temperature has significant effect during polymer degradation.

Although the results of combined kinetic analysis signify that WT1PB0, WT3PB1 and WT1PB1 follow 1st order reaction model, the comparison of $y(a)$ profiles of waste tyre, pine bark and their blends revealed that they resemble the plot of high order reaction model with

$n \geq 7$ (The results are not shown here). This indicates the complexity of the decomposition reaction mechanism followed by these materials. The shape of the normalized $y(a)$ of pine bark looks similar to the one for lignin which was reported in Wang et al. [55] and Yeo et al. [54]. This is attributed to the heterogenous, complex composition of lignin and the presence of aromatic benzene ring compounds [55]. According to Diez et al. [64] and Phyllis database for biomass and waste [65] lignin made up 40–50 wt% of pine bark composition. It is important to emphasize that the kinetics analysis performed by several authors [11,36,37,42], assuming 1st order reaction model, would not be suitable for pyrolysis of waste tyre, pine bark and their blends.

In short, thermal degradation of waste tyre, pine bark and their blends follow combined degradation mechanism due to heterogenous composition and complex structure of reacting feedstocks. Thermal degradation behaviour of waste tyre, pine bark and their blends is highly affected by the contents of these materials [38].

Fig. 11 shows a comparison of the average activation energy values obtained from different methods. It is worth noting that the values vary from one another due to the difference in the mathematical approximation used in each of them [66]. FWO and KAS showed the least variation in E_a for all the samples since they do not depend on the assumption of reaction mechanism, $f(\alpha)$. Friedman method has better accuracy in the determination of activation energy [55] and the activation energy value obtained by this method is higher than model fitting method as well as integral iso-conversional methods. Even though all the methods showed variation in the value of activation energy excluding Coats-Redfern, they all showed similar pattern in terms of the change in activation energy with the variation in mass blend ratio. Since the activation energy values obtained using combined kinetics analysis method incorporate proper reaction mechanism as well as the use of weight loss data from different heating rate, it is considered as the best and the most accurate [53–55,63].

4. Conclusion

Co-pyrolysis of waste tyre and pine bark was investigated to understand the synergetic interaction between the materials in terms of mass loss and kinetics analysis. Based on the comparison of DTG curves, use of waste tyre blended with pine bark caused a change in the degradation rate peak and the corresponding temperature. Waste tyre and pine bark showed positive synergetic interaction to some extent as represented by the difference in weight loss. Blending waste tyre and pine bark at different mass ratios showed positive synergetic interaction by lowering the activation energy of the blends compared to single waste tyre. Waste tyre and pine bark blend with mass ratio of 3:1 resulted in lowest activation energy than sole waste tyre with all the kinetics analysis method including Coats-Redfern. Although Coats-Redfern method has its own disadvantages, it could be used as visual evaluation tool to assess the possible change in activation energy. Waste tyre, pine bark and their blends showed complex decomposition behaviour and most probably due to followed reaction mechanism with a combined effect of nucleation, growth, and diffusion. Despite high reaction activation energy of waste tyre, waste tyre and pine bark blends could work in developing feed flexible thermal processing unit with low energy input as both showed similar reaction mechanism.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.biombioe.2022.106654>.

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