

**Comparison of waste plastics pyrolysis under nitrogen and carbon dioxide atmospheres: A thermogravimetric and kinetic study**

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**Abstract:**

It is important to understand the influence of pyrolysis atmosphere on the thermal degradation of waste plastics. In this study, the decomposition of waste plastics; high and low density polyethylene, polypropylene, polystyrene, and polyethylene terephthalate were investigated from ambient temperature to 500 °C within nitrogen or carbon dioxide atmospheres. The thermal degradation characteristics and kinetic parameters of individual plastics and mixed plastics (household packaging, building construction and agricultural waste plastics) from three different waste treatment plants were investigated under N<sub>2</sub>, CO<sub>2</sub> and N<sub>2</sub>/CO<sub>2</sub> atmospheres. In all atmospheres, only one degradation peak temperature was observed between 250-510 °C. The replacement of N<sub>2</sub> by CO<sub>2</sub> showed different effects on the activation energy. Mixtures of N<sub>2</sub>/CO<sub>2</sub> in the pyrolysis atmosphere resulted to lower activation energy for all plastic samples, with the exception of high density polyethylene, polystyrene and polyethylene terephthalate. The lower activation energy suggested that lower energy was required for the degradation process. However, a mixture of more than 30% of CO<sub>2</sub> may influence the degradation process of plastics due to a higher value of residue obtained after the experiment.

**Keywords:** Waste; plastics; thermogravimetric analysis; carbon dioxide; kinetic

## 1. Introduction

The global plastics production increased every year due to high demand from the industry [1,2]. The large quantity of plastics consumption around the world results in the production of enormous amounts of waste plastics. Global annual commercial plastics production reached 359 million tonnes (Mt) in 2018 [3] and was estimated to double within the next 20 years [4]. It was reported that plastic converters demand in European countries was 51.2 million tonnes, and 29.1 million tonnes of waste plastics were generated in 2018 [3]. The amount of waste plastics will be inevitably further increased in 2020 and after because of the outbreak of COVID-19, as more plastic materials are needed whether in medical areas (especially personal protective equipment like masks) or in daily packing areas (for food hygiene and the increasing of online purchases) [5]. There are growing concerns that the current consumption and disposal of plastics bring substantial problems. A vast unmanaged waste plastics stream which leaks to the environment can be transformed into micro-plastic/nano-plastic, possessing threat to terrestrial and oceanic ecosystem [6,7]. For those collected plastic post-consumer waste, there are three options that are commonly used for disposal, include landfill, energy recovery and recycling. In Europe, though the recycling rate has doubled since 2006, the amount of waste plastics sent to landfill still accounted for 25% [8].

The landfill represents the cheapest and the least environmental harmful, while it requires hundreds of years for degradation and calls for much land place which is unrealistic in land-scarce area [9]. Landfill is facing the shortage of land and pollution of underground water, hence thermal treatment such as chemical depolymerisation, (catalytic) gasification, pyrolysis, and hydrogenation are introduced for converting waste plastics into useful products and energy recovery [10]. Thermo-chemical recycling/pyrolysis/gasification has been seen a promising technology with low carbon footprint for disposing waste plastics. Quite a number of projects have been conducted on chemical recycling/pyrolysis of waste plastics to produce liquid fuels [11]. Gasification of waste plastics for producing hydrogen or syngas has also been widely studied [12-16]. It is often suggested that large quantities of waste plastics are available and can be used to produce significant amounts of hydrogen. Polyethylene, including high density polyethylene (HDPE) and low density polyethylene (LDPE), is one of the main types of waste plastics [17]. Researchers have focused on the thermal decomposition of plastics and their results are indicative of the viability of using plastics to produce hydrogen [12-14,18]. In the thermo-chemical conversion of waste plastics to produce hydrogen, catalysts play a key role of maximizing hydrogen production. Also, two-stage pyrolysis-catalysis systems are more controllable than one-stage catalysis processes, because they separate the pyrolysis residues containing contaminants from catalysts [17]. From previous studies, nickel-based catalysts are the most common catalysts used for hydrogen production from plastics by thermal processing, mainly because of their high thermal stabilities and hydrogen selectivity [12,15,17]. Many types of Ni-based catalysts have been investigated such as Ni/Al<sub>2</sub>O<sub>3</sub>[19], Ni-Mg-Al catalyst [17] and Ni/MgO catalysts [20].

Combination of pyrolysis and gasification process is one of the option for energy recovery of waste plastics. Pyrolysis reaction normally take place at 300 – 800 °C, while the gasification at higher temperature of 700 – 1100 °C [21]. The addition of steam into the gasification process seems to give promising results [13], however the reaction yields some amount of greenhouse gas CO<sub>2</sub>. Dry (CO<sub>2</sub>) reforming reaction, which has been studied for decades [22] is an ideal approach for transforming waste plastics into environmentally promising energy recovery. Synthesis gas, including hydrogen and carbon monoxide are produced from the main reaction between methane (hydrocarbon) and CO<sub>2</sub>. Suelves et al. [23] in their research on dry reforming of methane with 65 wt%Ni/silica and alumina catalyst found that at 700 °C, hydrogen concentration was approximately 80%, quite similar to theoretical equilibrium value. The catalyst activity maintained even after 8 h on stream at a space-time of 1 s. In other studies, Rahman et al. [24] discovered that the activation energy of dry reforming of methane under 5 wt%Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was 46 kJ/mol. Therefore, dry reforming of waste plastics is a promising approach due to its high hydrocarbon content [25].

Although pyrolysis and gasification of waste plastics have been studied by many researchers, there are many challenges still exist, in the product homogeneity from mixed feedstock, optimization of product quality, minimization of handling cost, before such technology being accepted and widely applied for waste plastics. There is still room to further understanding the thermal behaviour of the waste plastics due to the complexity of the reaction and the in-homogeneity of the waste materials. Also, the simultaneous conversion and utilization of CO<sub>2</sub> and plastics into useful fuels/chemicals has accompanied many benefits, such as reducing greenhouse gas effects, as effective and clean energy resources, less dependence on non-renewables and sustainable pollution, and waste plastics management practices [26]. Therefore, this work presents thermogravimetric analysis (TGA) and kinetic-pyrolysis of each individual plastic normally found in the municipal waste treatment plant in two different sets of experiment. The waste plastics including HDPE, LDPE, polystyrene (PS), polypropylene (PP) and polyethylene terephthalate (PET). The first set of experiment was to investigate the effect of N<sub>2</sub> or CO<sub>2</sub> as a carrier gas in the pyrolysis process from ambient temperature up to 500 °C. The investigation continued with a set of experiments where the plastics are heated to a higher final temperature 900 °C, which investigated the effect of N<sub>2</sub> to CO<sub>2</sub> ratios on the thermal degradation of the waste plastics. 100% N<sub>2</sub> and 70%/30% of N<sub>2</sub>/CO<sub>2</sub> mixtures were investigated which represented the N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3. Mixed plastics from household packaging, building construction and agricultural waste treatment plant (MP<sub>HP</sub>, MP<sub>BC</sub>, and MP<sub>AGR</sub>) were also investigated to understand the thermal degradation characteristics of real-world waste plastics.

## **2. Materials and Methods**

### **2.1 Materials**

The individual plastics: HDPE, PS and (PP were provided from Regain Polymers Ltd., UK while PET and LDPE were obtained from Sigma-Aldrich Company Ltd., UK. The mixed plastic from household

packaging waste (MP<sub>HP</sub>) was collected and recycled from Fost Plus in Belgium. The 5.0 mm sized flakes of MP<sub>HP</sub> were obtained from a low density fraction through the air separation process. In addition, mixed plastics from building construction waste (MP<sub>BC</sub>) and mixed plastics from agriculture waste (MP<sub>AGR</sub>) were also studied which were supplied from University of Pannonia, Hungary. In this study, all samples were grinded and dried in an oven heated to 110 °C overnight prior to the analysis, hence no moisture content in the TGA plots was detected on the waste materials between the temperature of 20 to 100 °C. The ultimate and proximate analysis of individual plastic waste (HDPE, PP, PS, PET and LDPE) and mixed plastic waste (MP<sub>BC</sub>, MP<sub>HP</sub> and MP<sub>AGR</sub>) are shown in Table 1. The highest composition element is carbon for all of the samples. There is not too much oxygen content in all of the plastic samples except PET which has the highest amount of oxygen of 32.59%.

*Table 1 The ultimate and proximate analysis of individual plastic waste (HDPE, PP, PS, PET and LDPE) and mixed plastic waste (MP<sub>BC</sub>, MP<sub>HP</sub> and MP<sub>AGR</sub>).*

Sample	N Wt. %	C Wt. %	H Wt. %	O Wt. %	S Wt. %	Ash Wt. %	Volatile Wt. %	Moisture Wt. %	Fixed Carbon Wt. %
HDPE	0.02	85.39	14.23	0.37	0.23	0.38	99.27	0.72	0
PP	0.04	78.85	12.74	8.38	0.23	0.39	95.00	5.68	0
PS	0.11	89.91	8.14	1.84	0.23	5.23	98.25	1.72	0
PET	0.03	63.04	4.34	32.59	0.18	1.20	85.64	0.06	13.10
LDPE	0	86.32	14.43	0	0.21	0.08	99.95	0.01	0
MP <sub>HP</sub>	0.16	82.90	13.37	3.57	0.23	1.74	99.15	0.90	0
MP <sub>BC</sub>	0.14	80.91	12.22	6.74	0.22	0.81	99.02	0.49	0
MP <sub>AGR</sub>	0.89	79.08	12.91	7.12	0.26	0.99	99.06	1.26	0

## 2.2 Thermogravimetric Analysis

The first study is to investigate the influence of atmosphere on pyrolysis of individual component of waste plastics. Approximately 8-9 mg of raw material in a flake size was placed in the alumina pan. The sample was heated in a TGA-50 Shimadzu with a ramp rate of 10 °C min<sup>-1</sup> from room temperature and kept at 500 °C for 30 min. The N<sub>2</sub> or CO<sub>2</sub> flow rate used was 50 ml min<sup>-1</sup>. The second study was carried out to investigate the influence of N<sub>2</sub> and CO<sub>2</sub> mixture in the pyrolysis process. The non-isothermal degradation of each raw material was performed in a thermogravimetric analyser (STA449F3, NETZSCH). Approximately 4-6 mg of sample in powder form was placed in an alumina pan, and heated from room temperature to 900 °C at 10 °C min<sup>-1</sup>. Three different flow gases were used with different ratios for HDPE pyrolysis, including 100% of N<sub>2</sub>, 100% of CO<sub>2</sub>, N<sub>2</sub>/CO<sub>2</sub> of 70/30%, N<sub>2</sub>/CO<sub>2</sub> of 50/50% and N<sub>2</sub>/CO<sub>2</sub> of 30/70% ( N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0, 0:1, 7:3, 1:1 and 3:7). For the rest of the plastic samples,

two flow gas mixture ratios were investigated, which were 100 % of N<sub>2</sub> and 70/30% N<sub>2</sub>/CO<sub>2</sub> (N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3). The total flow rate of gas for each analysis was consistently at 100 ml min<sup>-1</sup>.

### 2.3 Kinetic analysis calculation

A modified Coats-Redfern technique [27] was used to obtain the values of activation energy of decomposition of each plastic sample. The technique has been reported and discussed by many researchers [28-31]. All kinetic studies presented in this work utilized the basic rate equation of conversion  $\alpha$  for the thermal degradation under a N<sub>2</sub> or CO<sub>2</sub> atmosphere and are presented as the following:

$$\ln \frac{-\ln(1-\alpha)}{T^2} = \ln \frac{AR}{\beta E} - \frac{E}{RT} \quad (\text{Equation 1})$$

The left side of Equation 1 was plotted against 1/T by considering  $\alpha$  as the conversion of the waste plastics.

$\alpha$  is defined as the following:

$$\alpha = \frac{m_0 - m}{m_0 - m_f} \quad (\text{Equation 2})$$

where  $m_0$  is the initial sample weight;  $m$  is the sample weight at time  $t$ , and  $m_f$  is the final sample weight. The slope of the resultant straight line from the plotted data represents the activation energy ( $-E/R$ ) of the thermal degradation of the waste plastics. In this work, a reaction order of  $n=1.0$  was used to calculate the kinetic parameters.

## 3. Results and discussion

### 3.1 Influence of nitrogen or carbon dioxide atmosphere on the pyrolysis of individual component of waste plastics.

#### 3.1.1. Thermogravimetric characteristics

Figure 1 and Figure 2 show the weight loss profile and decomposition rate of five different individual plastics (HDPE, LDPE, PS, PP and PET) under N<sub>2</sub> or CO<sub>2</sub>. As shown in Figure 1 and Figure 2, the overall shapes of the weight loss and degradation graph profiles were similar for all the plastics. It can be observed that there was only one degradation peak for each individual plastic, which started at temperatures higher than 300 °C. The pyrolysis degradation of PS, PP, and PET in either N<sub>2</sub> or CO<sub>2</sub> atmospheres occurred with a gentler slope while the degradation of both LDPE and HDPE took place more rapidly. Ahmad et al. [32] suggested that heating rate was an important parameter affecting the degradation of samples. They have reported that two degradation peaks were observed for the pyrolysis of PS under N<sub>2</sub> atmosphere with a heating rate lower than 10 °C min<sup>-1</sup>, and only one peak was found at higher heating rate. They concluded that, there are certain limitations on the degradation of product, in which at some point, the product may not get sufficient time to condense with each other. The starting degradation temperature of pure PS in their studies was observed between 300 and 400 °C. They have also cited other researchers which suggested that the degradation of PS producing mainly styrene

monomer, benzene, toluene, some dimers and trimers as volatile products and cross-linked residue above 400 °C.

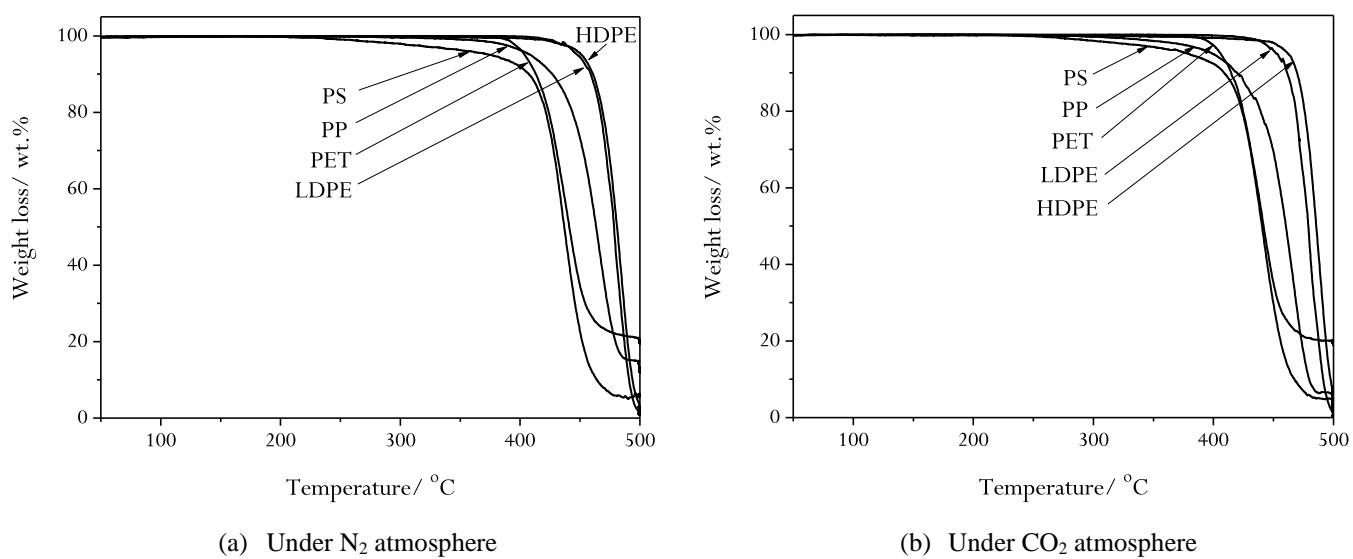


Figure 1 Weight loss profile of individual plastic (HDPE, LDPE, PS, PP and PET) over N<sub>2</sub> (a) or CO<sub>2</sub> (b) atmosphere.

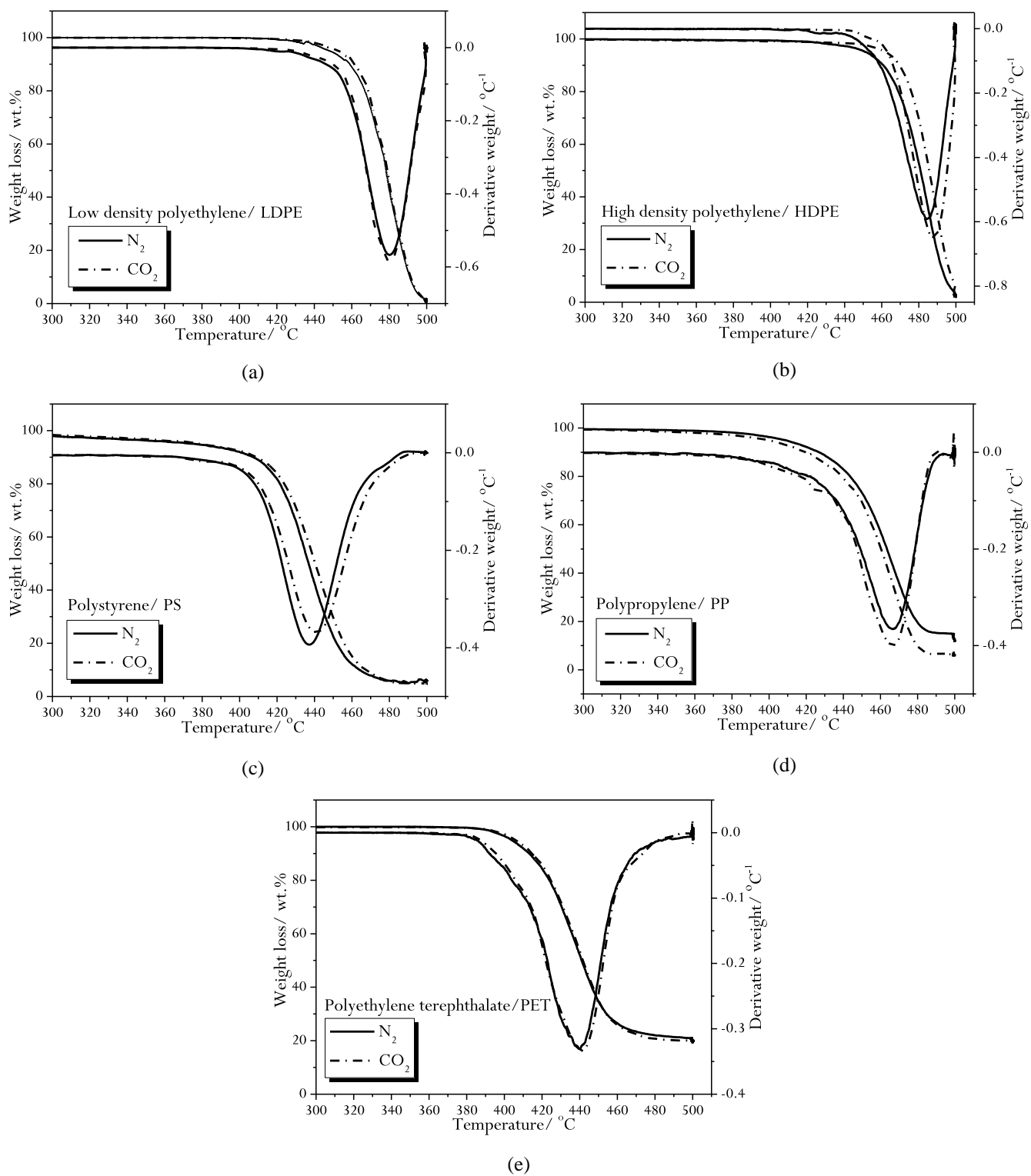


Figure 2 TGA and DTG plots of LDPE (a), HDPE (b), PP (c), PS (d) and PET (e) over  $\text{N}_2$  or  $\text{CO}_2$  atmosphere.

The characteristics of the thermal decomposition of the plastic materials should be known to describe the possible reaction kinetics of pyrolysis. Characteristic data of each raw material is shown in Table 2. The initial temperature ( $T_i$ ) is defined as the temperature where the plastic started to degrade, while the end temperature ( $T_f$ ) represents the final degradation temperature. The peak temperature ( $T_m$ ) is related to the chemical structure of the material, that longer chain or higher molecular weight material will have the higher peak temperature. Experiments using the TGA system were very reproducible, and any changes in decomposition temperature were attributed to the change in the TGA purge gas.

*Table 2 Characteristic data of each individual plastic in  $N_2$  and  $CO_2$  atmospheres.*

Plastic samples	$T_i$ (°C)		$T_f$ (°C)		$T_m$ (°C)		Residue (wt. %)	
	$N_2$	$CO_2$	$N_2$	$CO_2$	$N_2$	$CO_2$	$N_2$	$CO_2$
HDPE	464	465	497	500	487	490	2.16	1.86
PP	441	435	483	481	466	466	11.91	5.89
PS	420	417	452	462	435	440	5.91	4.78
PET	414	418	456	453	436	441	19.66	18.97
LDPE	457	462	495	497	480	474	1.25	0.00

$T_i$ =initial temperature,  $T_f$ =final temperature,  $T_m$ = peak temperature.

As shown in Table 2, there is only a slight difference on the degradation temperature range (from  $T_i$  to  $T_f$ ) for both  $N_2$  and  $CO_2$  atmospheres. The decomposition of PP, PS, and PET started at lower temperature in both  $N_2$  and  $CO_2$  atmospheres as compared to both LDPE and HDPE. The lowest initial degradation temperature was observed at PET in  $N_2$  atmosphere while in  $CO_2$  atmosphere, PS started to degrade earlier than other plastics. The highest initial degradation temperature was observed at HDPE in both atmospheres. According to Hujuri et al. [33], the linear polymers (HDPE and LDPE) decompose at higher temperatures in  $N_2$  atmosphere than substituted/branched polymers such as PP or PET. These results show that PP, PS, and PET were easily degraded into oil product. In comparison, HDPE in  $CO_2$  atmosphere required the highest temperature to degrade as shown in Table 2. Albeit the decomposition temperature difference between each individual plastic was not substantial, it can be summarized that the degradation of plastics started earlier in  $N_2$  for HDPE, PET, and LDPE while in  $CO_2$  atmosphere, PP and PS started to decomposed earlier than in  $N_2$  atmosphere. This could due to PP and PS start decomposing at relatively lower temperature between 417-441 °C compare with HDPE and LDPE start decompose at higher temperature between 414-465 °C, that char formation would be earlier during PP and PS decomposition which could react with  $CO_2$  [34], correspondingly promotes the decomposition of these two plastics. However, PET started decomposing at relative lower temperature in both  $N_2$  and  $CO_2$  atmospheres, which are 414 and 418 °C, respectively, but it started decomposing early in  $N_2$  rather than  $CO_2$ , this could due to the high oxygen content in PET as shown in Table 1, that char already reacted



with oxygen content to form CO<sub>2</sub> [35]. The degradation of individual plastics reach their maximum slightly higher in CO<sub>2</sub> atmosphere for HDPE, PS, and PET. In contrast, the temperature at peak maximum decreased slightly for LDPE and was remained the same for PP in CO<sub>2</sub> atmosphere compared to N<sub>2</sub> atmosphere. In summary, based on the degradation peak temperature, the decomposition rate of each plastic was in the order of: PET<PS<PP<LDPE<HDPE in both N<sub>2</sub> and CO<sub>2</sub> atmospheres.

A study by Chen et al. [36] of pyrolysis and gasification of 8 different combustible solid wastes, including PE and PS summarized that degradation of both plastics reached their maximum peak value at 477 and 417 °C, respectively in a N<sub>2</sub> atmosphere, while in a CO<sub>2</sub> atmosphere, the maximum degradation temperature decreased slightly to 473 and 413 °C, respectively. They also reported that the starting and finishing degradation temperature of PE was higher than that of PS similarly as reported in this study. The residue obtained after the TGA experiments is also shown in Table 2. It can be observed that the residue of each individual waste plastic was higher in the N<sub>2</sub> than in the CO<sub>2</sub>. As discussed by Irfan [37] for coal pyrolysis-gasification in N<sub>2</sub>/O<sub>2</sub>/CO<sub>2</sub> atmospheres, these differences may be due to the density difference and transport properties of these two gases in which the mass of the CO<sub>2</sub> molecule is different from that of N<sub>2</sub>. Overall, both LDPE and HDPE were nearly fully decomposed at 500 °C, hence producing a low mass of residue. In contrast, PET produced a high residue value compared to other plastics in both N<sub>2</sub> and CO<sub>2</sub> atmospheres.

### 3.1.2 Kinetic parameters

The activation energies, overall rate constants, and other kinetic reaction parameters of material degradation were obtained based on the weight loss decomposition curves from thermogravimetric analysis. In this study, the kinetic calculation was focused on a first order parallel reaction due to the fact that only one degradation peak was observed in all plastics as mentioned above. Table 3 summarizes the resultant activation energy, pre-exponential factor, and correlation coefficient using the modified Coats-Redfern method for the purpose of comparison the results between N<sub>2</sub> and CO<sub>2</sub> atmospheres. It was found that slightly higher activation energy was required for thermal decomposition of the plastics in a CO<sub>2</sub> atmosphere than in the N<sub>2</sub> atmosphere for HDPE, LDPE, and PET. In contrast, PS and PP showed marginally higher activation energy in the experiments in N<sub>2</sub> atmosphere compared to CO<sub>2</sub> atmosphere. Chen et al. [36] also observed a slight decrease in the activation energy of PS under CO<sub>2</sub> atmosphere compared to N<sub>2</sub> atmosphere by using the discrete distributed activation energy method (DAEM) kinetic analysis. Wang et al. [38] described in details on the morphological characteristic of PE and PP pyrolysis in N<sub>2</sub> atmosphere. They discovered that the decomposition process of PP started and completed earlier than that of PE. This result is in agreement with results from our studies, which also observed from the activation energy value that PE required more energy (446 kJ mol<sup>-1</sup>) to initiate the reaction than PP (274 kJ mol<sup>-1</sup>). The relationship between activation energy and initial degradation temperature between N<sub>2</sub> and CO<sub>2</sub> atmosphere can be concluded as a lower initial degradation temperature of waste plastics resulted in lower activation energy and vice versa. The activation energy of each individual waste plastic

increases in the following order LDPE>HDPE>PS>PP>PET in N<sub>2</sub> atmosphere and HDPE>LDPE >PET>PP>PS in CO<sub>2</sub> atmosphere.

*Table 3 Kinetic parameters of individual plastic sample from Arrhenius model; activation energy (E), pre-exponential factor (A) and correlation coefficients (R<sup>2</sup>).*

Sample	Condition	Temperature (°C)	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>
HDPE	N <sub>2</sub>	467-494	445.9	5.27x10 <sup>30</sup>	0.99
	CO <sub>2</sub>	468-497	472.1	2.40x10 <sup>33</sup>	0.99
PP	N <sub>2</sub>	444-480	274.2	1.47x10 <sup>19</sup>	0.99
	CO <sub>2</sub>	438-478	264.8	3.44x10 <sup>18</sup>	0.99
PS	N <sub>2</sub>	423-449	283.4	3.47x10 <sup>20</sup>	0.99
	CO <sub>2</sub>	420-459	260.3	5.03x10 <sup>18</sup>	0.99
PET	N <sub>2</sub>	417-453	273.2	5.84x10 <sup>19</sup>	0.99
	CO <sub>2</sub>	421-450	281.2	2.20x10 <sup>20</sup>	0.99
LDPE	N <sub>2</sub>	460-492	446.7	7.61x10 <sup>30</sup>	0.99
	CO <sub>2</sub>	465-494	467.0	1.83x10 <sup>32</sup>	0.99

### 3.2 Influence of nitrogen and carbon dioxide ratio on the pyrolysis of waste plastics

#### 3.2.1. Thermogravimetric characteristics

The weight loss and rate of degradation curves of HDPE over five different N<sub>2</sub>/CO<sub>2</sub> ratios; 1:0, 7:3, 1:1, 3:7, and 0:1 were carried out and the results are shown in Table 4 and Figure 3. As shown in Table 4, N<sub>2</sub>/CO<sub>2</sub> ratio of 1:1 showed the highest initial degradation temperature and final degradation temperature, starting at 407 °C to 501 °C. Furthermore, only one peak of plastic degradation was observed in all given ratios as shown in Figure 3 (b), and the maximum peak degradation temperature (480 °C) was observed at N<sub>2</sub>/CO<sub>2</sub> ratio of 3:7. This indicates the ratio N<sub>2</sub> to CO<sub>2</sub> ratio has no significant effect on the degradation of HDPE in terms of degradation rate.

Table 4 Characteristic data of HDPE in different mixtures of  $N_2$  and  $CO_2$ .

$N_2/CO_2$	$T_i$ (°C)	$T_f$ (°C)	$T_m$ (°C)	Residue at 500 °C (wt.%)	Residue at 900 °C (wt.%)	Weight loss at 900 °C (wt.%)
1:0	397	500	475	5.5	4.4	95.6
7:3	393	500	475	4.9	4.2	95.8
1:1	407	501	476	9.6	8.9	91.1
3:7	402	499	480	7.7	6.8	93.2
0:1	402	495	476	7.6	7.2	92.8

$T_i$ =initial temperature,  $T_f$ =final temperature,  $T_m$ = peak temperature.

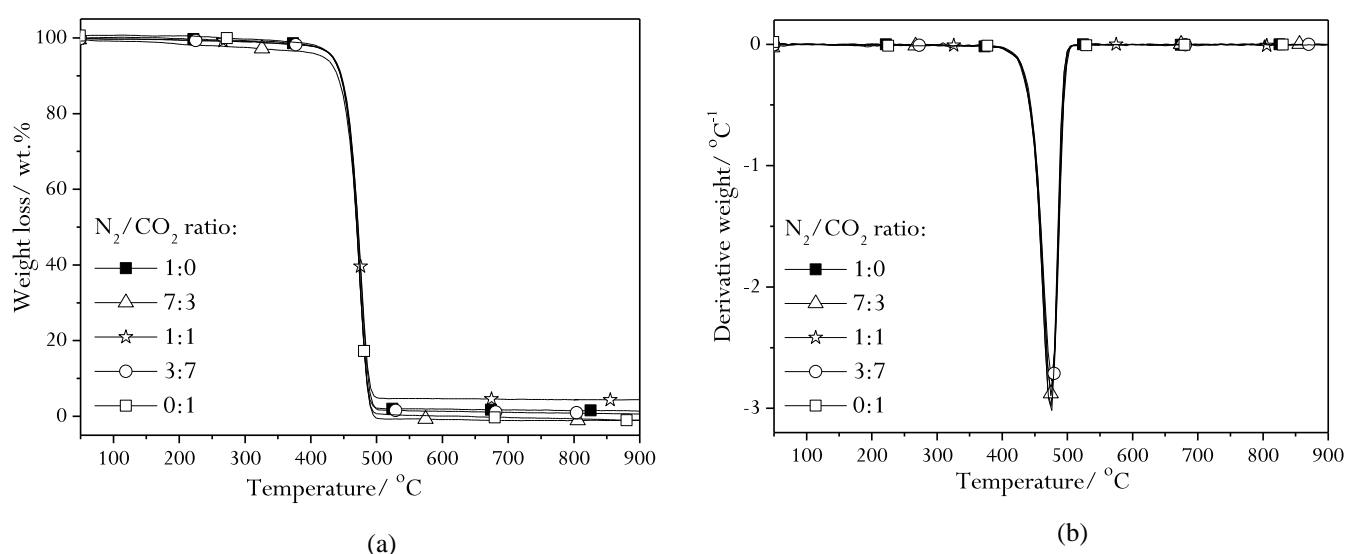


Figure 3 (a) TGA and (b) DTG thermographs of HDPE in different  $N_2/CO_2$  ratio; 100%  $N_2$  (1:0), 70%  $N_2/30\%$   $CO_2$  (7:3), 50%  $N_2/50\%$   $CO_2$  (1:1), 30% $N_2/70\%$   $CO_2$  (3:7) and 100%  $CO_2$  (0:1).

As shown in Figure 3 (b), the mass decomposition curves for all  $N_2/CO_2$  ratios showed a similar degradation rate. However, there were slight differences in terms of the residual mass as shown in Figure 3 (a). The addition of  $CO_2$  increased the residual mass with the highest at the  $N_2/CO_2$  ratio of 1:1 at 8.9 wt.%. This result was different from the results reported by Lai et al. [39], who observed a decrease of residual mass with the increase in  $CO_2$  addition for the thermal decomposition of municipal solid waste (MSW) due to the char gasification at high temperatures. However, the mass loss from the residue at 500 to 900 °C as shown in Table 4 confirmed that char gasification occurred since the residual mass was further reduced at high temperatures. In the case of the study here, the non-stable residual mass losses in regards to the increase of  $N_2/CO_2$  ratios may be caused by the characterisation of HDPE decomposition may also affect the residual mass. The  $CO_2$  may react with the surface of the plastics during the pyrolysis

heat-up. A principal component analysis (PCA) of waste HDPE plastics reported by Aguado et al. [40] suggested a five lump kinetic scheme for thermal pyrolysis between 550 to 650 °C as follows: (i) waxes, C<sub>11</sub><sup>+</sup> hydrocarbons are the primary products derived from raw polymer cracking; (ii) gaseous products, C<sub>1</sub>-C<sub>4</sub> are the primary or secondary products depending on the reaction; (iii) non-aromatic C<sub>5</sub>-C<sub>9</sub> hydrocarbons are the primary or secondary products; (iv) aromatic products are the secondary products; (v) char is the tertiary product derived from polyaromatic products. In addition, Al-Salem and Lettieri [41] summarized the activation energy of each primary lumped products from the thermal degradation of HDPE as; 26.7, 44.1, 124.3, 98.9, and 282.0 kJ mol<sup>-1</sup> for waxes (> C<sub>11</sub>), char, liquids (non-aromatics C<sub>5</sub>-C<sub>10</sub>), rich gases (C<sub>1</sub>-C<sub>4</sub>), and aromatics (single ring structures), respectively. Based on the residual mass observation, the addition of more than 30% of CO<sub>2</sub> in the gas mixture may affect the thermal degradation process of HDPE; hence high residual mass was obtained.

### 3.2.2 Kinetic parameters

Figure 4 and Table 5 show the kinetic parameters of the thermal degradation of HDPE in five different N<sub>2</sub>/CO<sub>2</sub> ratios; 100% N<sub>2</sub> (1:0), 70% N<sub>2</sub>/30% CO<sub>2</sub> (7:3), 50% N<sub>2</sub>/50% CO<sub>2</sub> (1:1), 30%N<sub>2</sub>/70% CO<sub>2</sub> (3:7), and 100% CO<sub>2</sub> (0:1). The results show that the values of activation energy increased with the increase of N<sub>2</sub>/CO<sub>2</sub> ratio, from 317.5 kJ mol<sup>-1</sup> under 100% N<sub>2</sub> to 345.9 kJ mol<sup>-1</sup> under 100% CO<sub>2</sub>. It should be noted that the addition of CO<sub>2</sub> does not produce a significant impact on the degradation peak temperature. Based on the comparison obtained the analysis for HDPE, two different ratios of N<sub>2</sub>/CO<sub>2</sub> were chosen for the following study; 1:0 and 7:3 due to its lowest residual mass and lowest activation energies.

*Table 5 Kinetic parameters of high density polyethylene at different N<sub>2</sub>/CO<sub>2</sub> ratios from Arrhenius model; activation energy (E), pre-exponential factor (A) and correlation coefficients (R<sup>2</sup>).*

N <sub>2</sub> /CO <sub>2</sub>	Temperature (°C)	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>
1:0	429 – 490	317.5	1.03 x 10 <sup>22</sup>	0.99
7:3	434 – 495	320.4	1.66 x 10 <sup>22</sup>	0.99
1:1	433 – 491	331.5	9.48 x 10 <sup>22</sup>	0.99
3:7	435 – 494	345.2	8.53 x 10 <sup>23</sup>	0.99
0:1	433 – 491	345.9	1.06 x 10 <sup>24</sup>	0.99

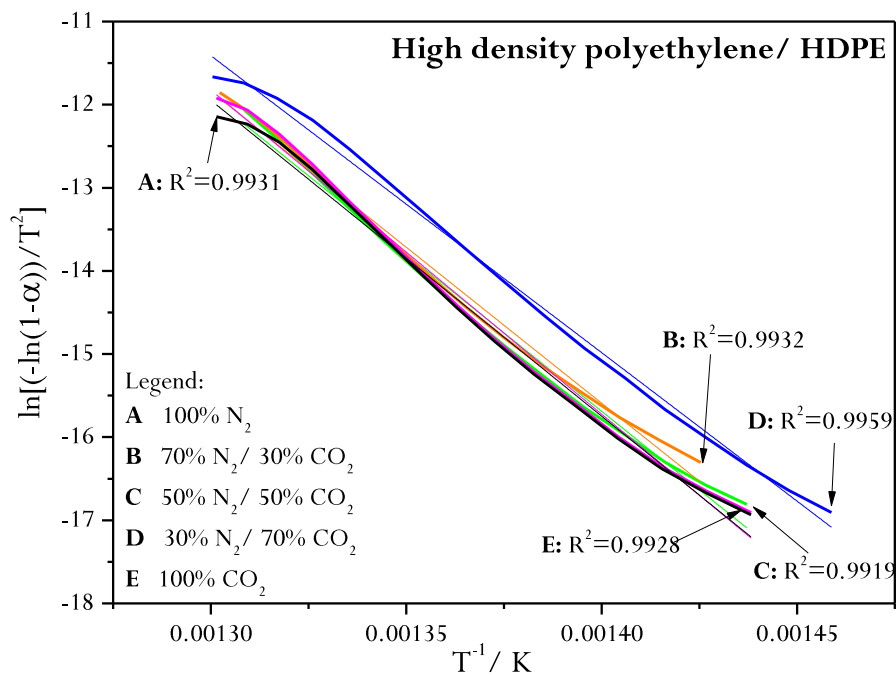


Figure 4 Plot of  $\ln[-\ln(1-\alpha)/T^2]$  versus  $1/T$  of HDPE in different N<sub>2</sub>/CO<sub>2</sub> ratio; 100% N<sub>2</sub> (1:0), 70% N<sub>2</sub>/30% CO<sub>2</sub> (7:3), 50% N<sub>2</sub>/50% CO<sub>2</sub> (1:1), 30%N<sub>2</sub>/70% CO<sub>2</sub> (3:7) and 100% CO<sub>2</sub> (0:1).

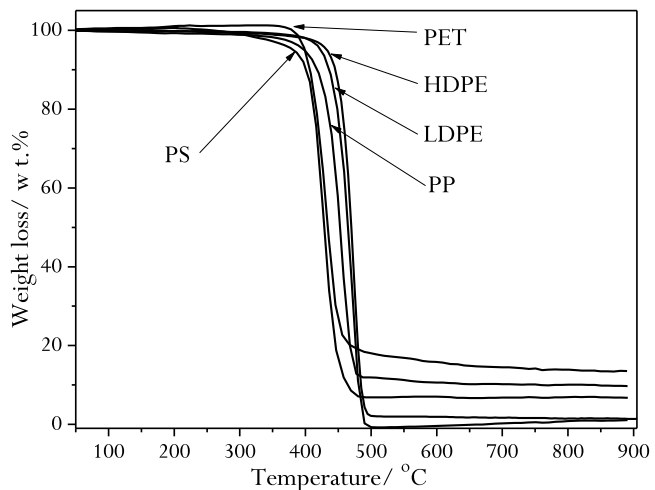
### 3.3. Thermogravimetric characteristic and kinetic analysis for individual plastics and mixed plastics at N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3

The TGA and DTG thermographs of each plastic in N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3 are shown in Figure 5 and the characteristic data of each raw material in both conditions is shown in Table 6. In general, the degradation peak of each plastic was higher in the experiments with mixture of N<sub>2</sub> and CO<sub>2</sub> compared to only N<sub>2</sub>. The highest increment of degradation peak temperature from the experiment with only N<sub>2</sub> compared to a mixture of N<sub>2</sub> and CO<sub>2</sub> was observed for PET with an increase of 1.15 %, followed by PS, PP, LDPE, and HDPE. The decomposition rate in both conditions showing a degradation peak temperature trend of PS>PET>PP>LDPE>HDPE. No significant further decomposition of plastics occurred when temperature was higher than 500 °C.

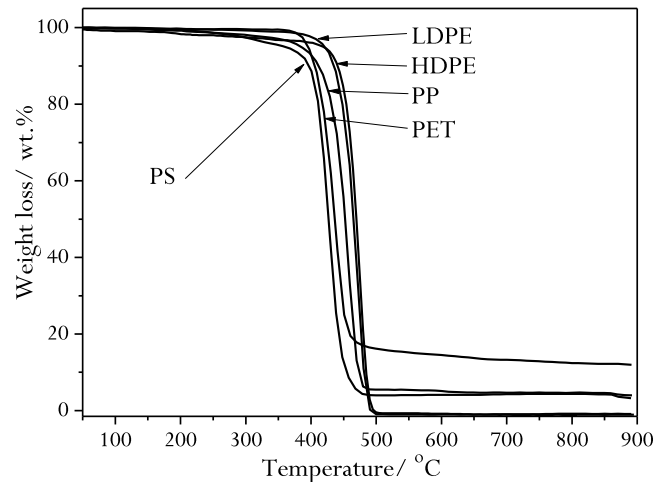
Table 6 Characteristic data of raw materials in N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3.

Plastic samples	T <sub>i</sub> (°C)		T <sub>f</sub> (°C)		T <sub>m</sub> (°C)		Residue at 900 °C (wt.%)		Weight loss (wt.%)	
	1:0	7:3	1:0	7:3	1:0	7:3	1:0	7:3	1:0	7:3
	HDPE	397	393	500	500	475	475	4.4	4.2	95.6
PP	349	340	488	480	458	460	9.7	6.9	90.3	93.1
PS	273	275	492	479	426	429	7.9	7.3	92.1	92.7
PET	369	367	579	509	436	441	14.7	15.9	85.3	84.1
LDPE	359	378	500	500	480	480	2.2	3.2	97.8	96.8
MP <sub>HP</sub>	274	263	497	509	479	479	4.8	5.0	95.2	95.0
MP <sub>BC</sub>	340	330	489	499	469	470	7.3	7.2	92.7	92.8
MP <sub>AGR</sub>	298	286	499	501	480	481	5.0	3.8	95.0	96.2

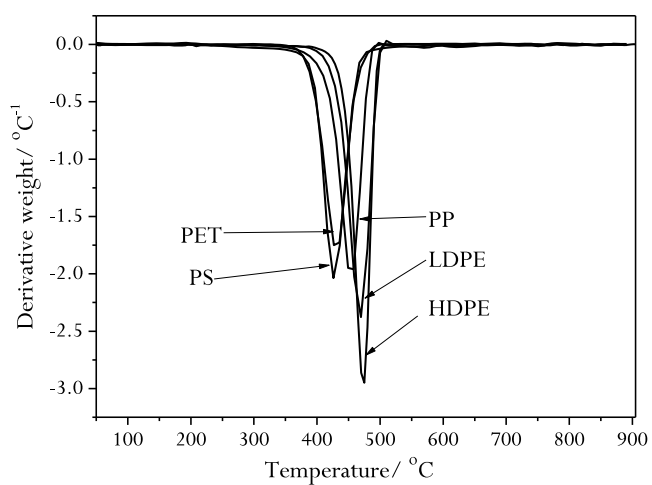
T<sub>i</sub>=initial temperature, T<sub>f</sub>=final temperature, T<sub>m</sub>= peak temperature.



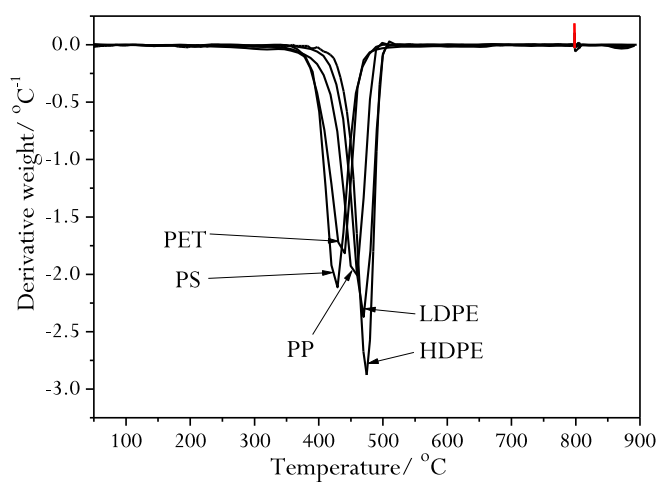
(a)  $N_2/CO_2$  ratio of 1:0



(c)  $N_2/CO_2$  ratio of 7:3



(b)  $N_2/CO_2$  ratio of 1:0



(d)  $N_2/CO_2$  ratio of 7:3

Figure 5 TGA weight loss thermographs of each individual plastic in  $N_2/CO_2$  ratio of 1:0 (a) and 7:3 (c); DTG results of each individual plastic in  $N_2/CO_2$  ratio of 1:0 (b) and 7:3 (d).

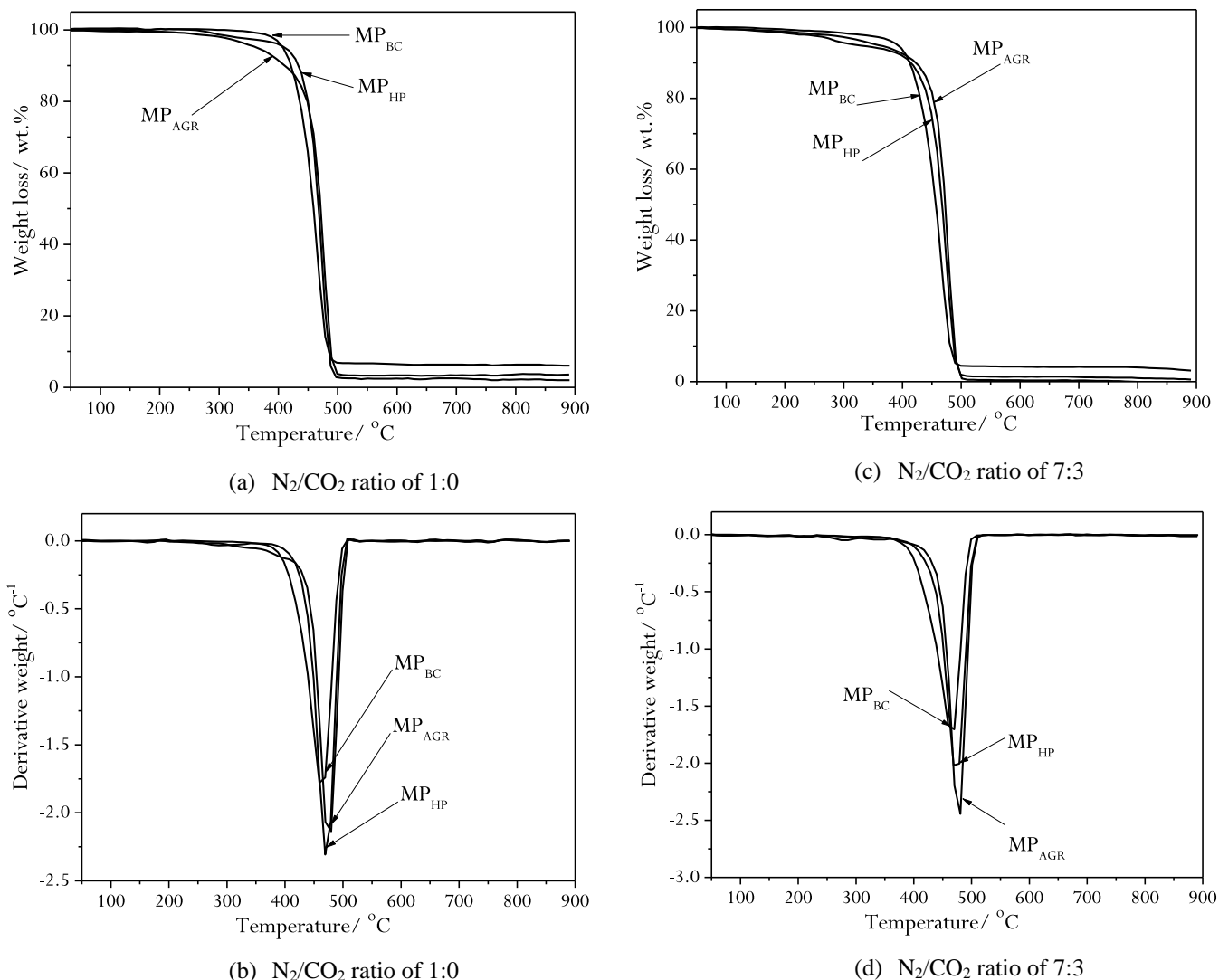


Figure 6 TGA thermographs of mixed plastics ( $MP_{BC}$ ,  $MP_{HP}$  and  $MP_{AGR}$ ) from different waste treatment plants in  $N_2/CO_2$  ratio of 1:0 (a) and 7:3 (c); DTG thermographs of mixed plastics ( $MP_{BC}$ ,  $MP_{HP}$  and  $MP_{AGR}$ ) from different waste treatment plants in  $N_2/CO_2$  ratio of 1:0 (b) and 7:3 (d).

Figure 6 presents the weight loss curves and thermal degradation temperature peaks of mixed plastics collected from three different waste treatment plants; household packaging ( $MP_{HP}$ ), building construction ( $MP_{BC}$ ), and agricultural ( $MP_{AGR}$ ) in  $N_2/CO_2$  ratios of 1:0 and 7:3. Only one decomposition peak was observed for these samples as shown in Figure 6 (b) and (d). As shown in Figure 6 (a) and (c), the weight loss peak of these three different mixed plastics appeared to be more or less in the same temperature range in both conditions. The highest degradation peak temperature in both conditions was obtained from mixed plastic obtained from agricultural waste treatment plant ( $MP_{AGR}$ ); 479.8 °C and 480.6 °C in  $N_2/CO_2$  ratio of 1:0 and 7:3, respectively. By referring to Table 5 and Figure 6 (b) and (d), the degradation peak temperature remain the same for  $MP_{HP}$ , but increased of 1 °C for  $MP_{BC}$  and  $MP_{AGR}$  with 100%  $N_2$



compare to 70% N<sub>2</sub>/30% CO<sub>2</sub> ratio. From the degradation data for individual plastic as shown in Table 5, Figure 5 (a) and (c) and mixed plastics as shown in Figure 6 (a) and (c), it is recommended that the mixed plastics contains mostly HDPE and LDPE. MP<sub>HP</sub> and MP<sub>AGR</sub> may also contain PS since they both started to degrade a bit earlier in both conditions.

### 3.3.1. Kinetic analysis.

The kinetic parameters of each individual plastics and mixed plastics are shown in Table 7 and Figure 7. In accordance with the aforementioned TGA and DTG thermograph of each individual plastics and mixed plastics, thermal decomposition of all samples could be simulated in a first order parallel reaction. The correlation coefficients of each sample were greater than 0.90, supporting the credibility of the kinetic model.

*Table 7 Kinetic parameters of individual plastics and mixed plastics at N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3 from Arrhenius model; activation energy (E), pre-exponential factor (A) and correlation coefficients (R<sup>2</sup>).*

Sample	N <sub>2</sub> /CO <sub>2</sub> ratio	Temperature (°C)	E (kJ mol <sup>-1</sup> )	A (min <sup>-1</sup> )	R <sup>2</sup>
HDPE	1:0	429 – 490	317.5	1.03 x 10 <sup>22</sup>	0.99
	7:3	434 – 495	320.4	1.66 x 10 <sup>22</sup>	0.99
PP	1:0	410 – 468	228.3	1.17 x 10 <sup>16</sup>	0.98
	7:3	408 – 470	155.7	5.38 x 10 <sup>10</sup>	0.94
PS	1:0	397 – 469	203.1	3.99 x 10 <sup>14</sup>	0.97
	7:3	401 – 468	207.1	8.28 x 10 <sup>14</sup>	0.96
PET	1:0	398 – 467	210.2	1.13 x 10 <sup>16</sup>	0.96
	7:3	398 – 460	234.3	7.25 x 10 <sup>16</sup>	0.99
LDPE	1:0	429 – 490	293.4	2.88 x 10 <sup>20</sup>	0.99
	7:3	428 – 490	287.9	1.05 x 10 <sup>20</sup>	0.99
MP <sub>HP</sub>	1:0	429 – 488	248.4	1.37 x 10 <sup>17</sup>	0.98
	7:3	418 – 499	200.1	4.43 x 10 <sup>13</sup>	0.97
MP <sub>AGR</sub>	1:0	438 – 499	236.6	1.75 x 10 <sup>16</sup>	0.97
	7:3	429 – 491	224.4	1.88 x 10 <sup>15</sup>	0.95
MP <sub>BC</sub>	1:0	408 – 479	207.4	2.28 x 10 <sup>14</sup>	0.99
	7:3	408 – 480	189.3	1.13 x 10 <sup>13</sup>	0.99

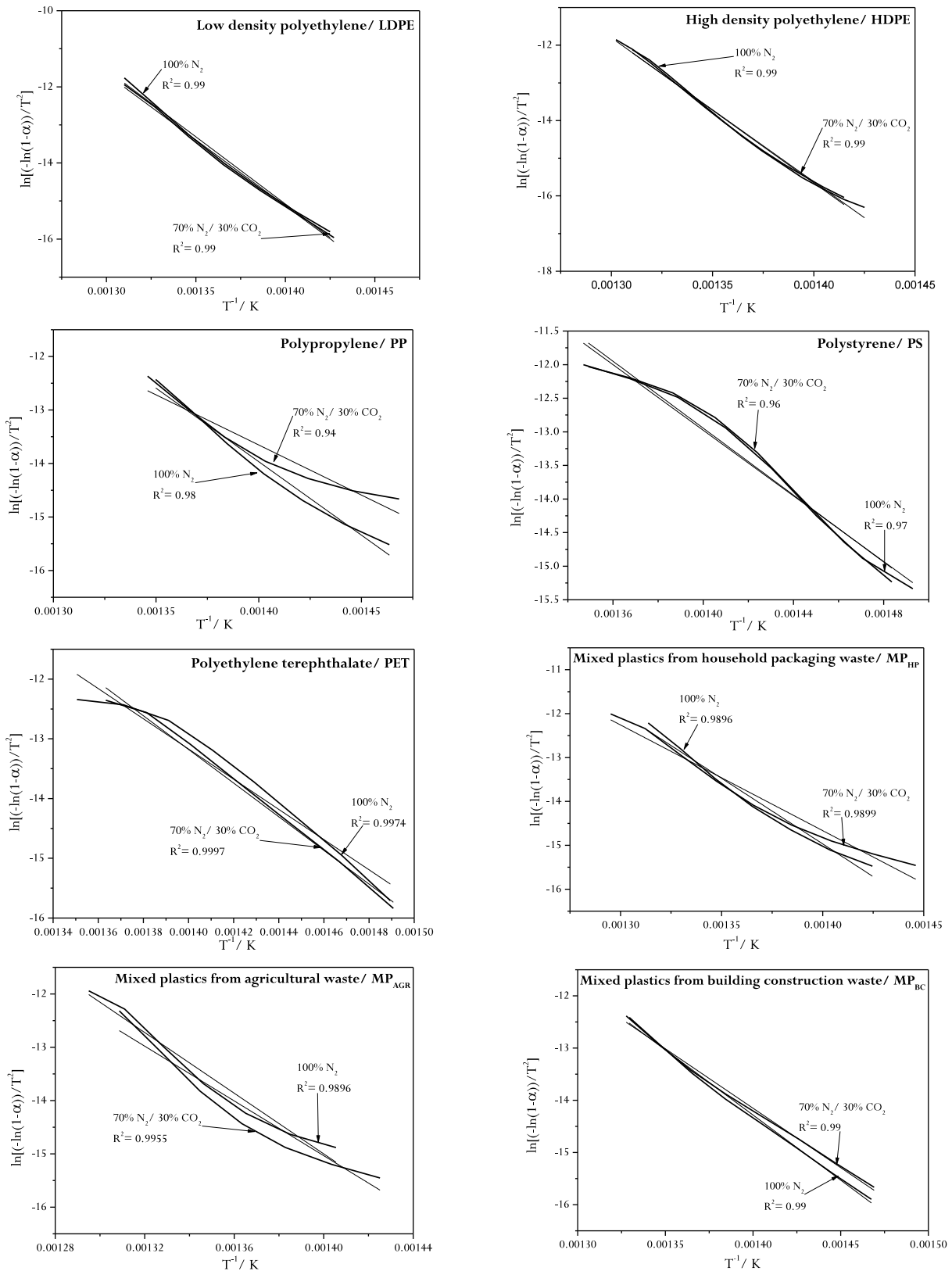


Figure 7 Plot of  $\ln[-\ln(1-\alpha)/T^2]$  versus  $1/T$  of individual plastics and mixed plastics at N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3.

As shown in Figure 7, the results indicated that there were slight influences on the activation energy value of each individual plastic and mixed plastics. The values decreased in almost all samples at the N<sub>2</sub>/CO<sub>2</sub> ratio of 7:3 compared to 1:0 except for HDPE, PS, and PET which showed very small increments in the activation energy. HDPE required more energy to activate the reaction in both conditions compared to other samples, 317.5 kJ mol<sup>-1</sup> at N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 320.4 kJ mol<sup>-1</sup> at N<sub>2</sub>/CO<sub>2</sub> ratio of 7:3. In contrast, PS showed the lowest activation energy at N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 with 203.1 kJ mol<sup>-1</sup> while at N<sub>2</sub>/CO<sub>2</sub> ratio of 7:3, the lowest activation energy was observed in PP. It should also be noted that the activation energy of mixed plastics, MP<sub>HP</sub>, MP<sub>AGR</sub> and MP<sub>BC</sub> are in between the range of the individual plastics. The variation of mixed plastics composition and characteristic was due to the different thermal stability of each individual plastic in the mixture sample [33]. Silvarrey and Phan [42] also suggested that E<sub>a</sub> and A value of mixed plastics varied depending on the nature of the feedstock, indicating the complexity of mixed plastics pyrolysis.

#### 4. Conclusions

It is important to understand the influence of pyrolysis atmosphere on the thermal degradation of waste plastics. In this study, the decomposition of waste plastics; high and low density polyethylene (HDPE and LDPE), polypropylene (PP), polystyrene (PS), and polyethylene terephthalate (PET) were investigated from ambient temperature to 500 °C within nitrogen or carbon dioxide atmospheres. Only one peak of thermal degradation was observed for all plastics in both atmospheres, but it was shifted to a higher temperature in the carbon dioxide atmosphere for almost all plastics. It was found that the residual mass of each plastic was higher in a nitrogen atmosphere than in carbon dioxide. The activation energy of each individual waste plastic decreased in the following order; LDPE > HDPE > PS > PP > PET in a nitrogen atmosphere. The order with a carbon dioxide atmosphere was; HDPE > LDPE > PET > PP > PS. In addition to individual plastic sample, real-world mixed plastic waste was also investigated. The N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3 were investigated based on the low amount of residual mass left after pyrolysis reaction and the low activation energy observed in the pyrolysis of HDPE. No further plastic decomposition was observed for any of the plastics after 500 °C with only one degradation peak observed below 500 °C. LDPE showed the highest degradation peak temperature at around 480 °C in both N<sub>2</sub>/CO<sub>2</sub> ratios, while PS showed the lowest at 426 °C and 429 °C in N<sub>2</sub>/CO<sub>2</sub> ratio of 1:0 and 7:3 respectively. Low activation energies were observed in almost all plastics in N<sub>2</sub>/CO<sub>2</sub> ratio of 7:3 except for individual HDPE, PS and PET, suggesting low energy required to proceed with the reactions.

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**Data availability.** The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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