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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_2, CO_2 and N_2/CO_2 atmospheres. In all atmospheres, only one degradation peak temperature was observed between 250-510 °C. The replacement of N_2 by CO_2 showed different effects on the activation energy. Mixtures of N_2/CO_2 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_2 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_2O_3[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_2. Dry (CO_2) reforming reaction, which has been studies 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_2. 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/γ-Al_2O_3 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_2 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_2 or CO_2 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_2 to CO_2 ratios on the thermal degradation of the waste plastics. 100% N_2 and 70%/30% of N_2/CO_2 mixtures were investigated which represented the N_2/CO_2 ratio of 1:0 and 7:3. Mixed plastics from household packaging, building construction and agricultural waste treatment plant (MP_{HP}, MP_{BC}, and MP_{AGR}) 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_{HP}) was collected and recycled from Fost Plus in Belgium. The 5.0 mm sized flakes of MP_{HP} were obtained from a low density fraction through the air separation process. In addition, mixed plastics from building construction waste (MP_{BC}) and mixed plastics from agriculture waste (MP_{AGR}) 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_{BC}, MP_{HP} and MP_{AGR}) 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_{BC}, MP_{HP} and MP_{AGR}).

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_{HP}	0.16	82.90	13.37	3.57	0.23	1.74	99.15	0.90	0
MP_{BC}	0.14	80.91	12.22	6.74	0.22	0.81	99.02	0.49	0
MP_{AGR}	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^{-1} from room temperature and kept at 500 °C for 30 min. The N_2 or CO_2 flow rate used was 50 ml min^{-1}. The second study was carried out to investigate the influence of N_2 and CO_2 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^{-1}. Three different flow gases were used with different ratios for HDPE pyrolysis, including 100% of N_2, 100% of CO_2, N_2/CO_2 of 70/30%, N_2/CO_2 of 50/50% and N_2/CO_2 of 30/70% (N_2/CO_2 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_2 and 70/30% N_2/CO_2 (N_2/CO_2 ratio of 1:0 and 7:3). The total flow rate of gas for each analysis was consistently at 100 ml min^{-1}.

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 α for the thermal degradation under a N_2 or CO_2 atmosphere and are presented as the following:

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

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

α is defined as the following:

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

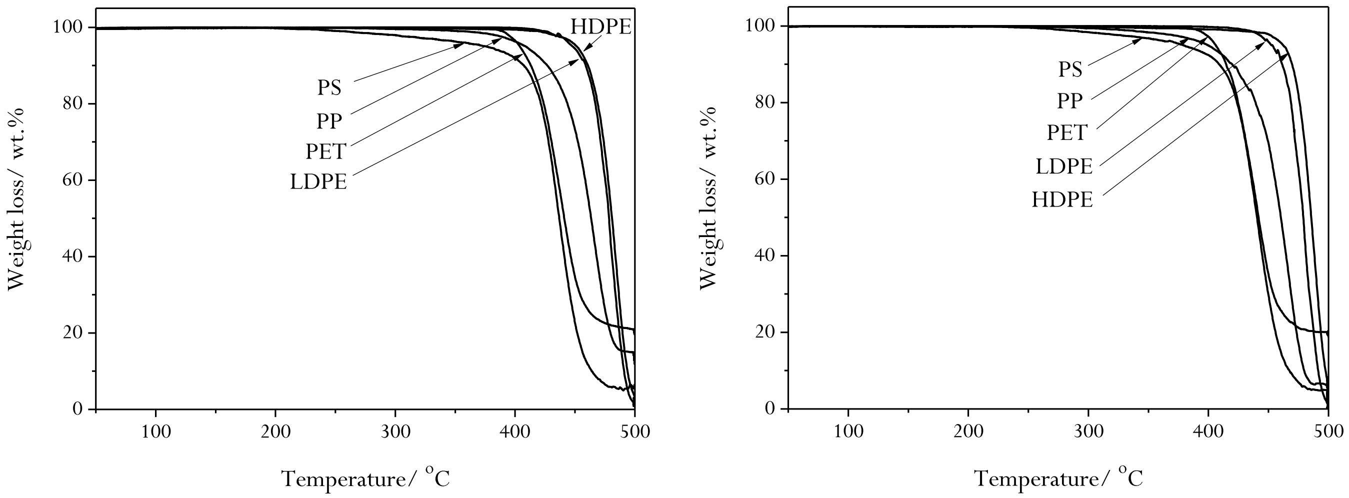
where m_o is the initial sample weight; m is the sample weight at time t, and m_f is the final sample weight. The slope of the resultant straight line from the plotted data represents the activation energy (-E/R) of the thermal degradation of the waste plastics. In this work, a reaction order of n=1.0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

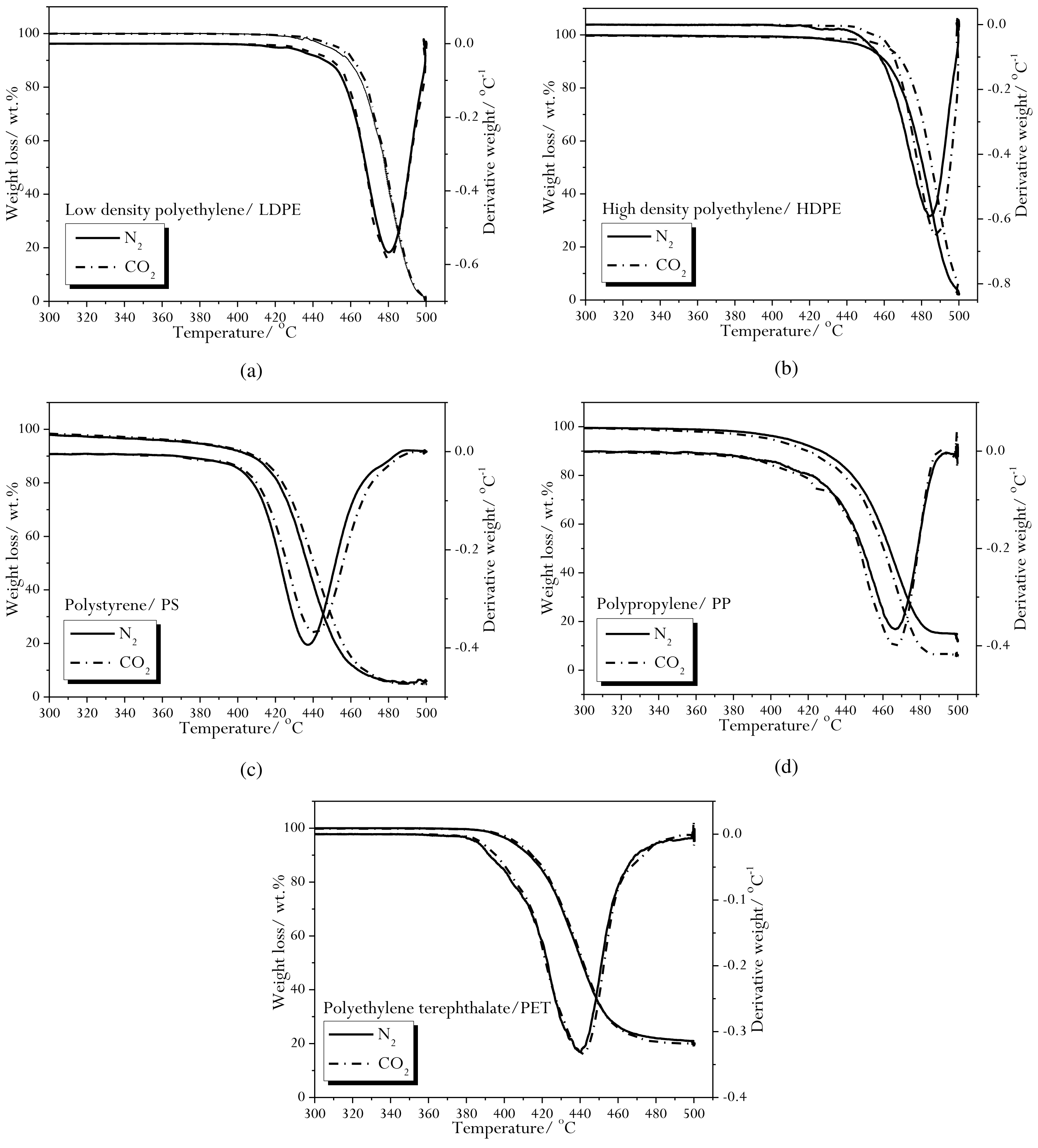
3.1.1. Thermogravimetric characteristics

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_2 or CO_2. 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_2 or CO_2 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_2 atmosphere with a heating rate lower than 10 °C min^{-1}, 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.



(a) Under N_2 atmosphere (b) Under CO_2 atmosphere

Figure 1 Weight loss profile of individual plastic (HDPE, LDPE, PS, PP and PET) over N_2 *(a) or* CO_2 *(b) atmosphere.*



(a)

(b)

(c)

(d)

(e)

Figure 2 TGA and DTG plots of LDPE (a), HDPE (b), PP (c), PS (d) and PET (e) over N_2 *or* 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	T_i (°C)		T_f (°C)		T_m (°C)		Residue (wt. %)	
samples	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 stared 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_2 [35]. The degradation of individual plastics reach their maximum slightly higher in CO_2 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_2 atmosphere compared to N_2 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_2 and CO_2 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_2 atmosphere, while in a CO_2 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_2 than in the CO_2. As discussed by Irfan [37] for coal pyrolysis-gasification in $N_2/O_2/CO_2$ atmospheres, these differences may be due to the density difference and transport properties of these two gases in which the mass of the CO_2 molecule is different from that of N_2. 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_2 and CO_2 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_2 and CO_2 atmospheres. It was found that slightly higher activation energy was required for thermal decomposition of the plastics in a CO_2 atmosphere than in the N_2 atmosphere for HEPE, LDPE, and PET. In contrast, PS and PP showed marginally higher activation energy in the experiments in N_2 atmosphere compared to CO_2 atmosphere. Chen et al. [36] also observed a slight decrease in the activation energy of PS under CO_2 atmosphere compared to N_2 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_2 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^{-1}) to initiate the reaction than PP (274 kJ mol^{-1}). The relationship between activation energy and initial degradation temperature between N_2 and CO_2 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_2 atmosphere and HDPE>LDPE >PET>PP>PS in CO_2 atmosphere.

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

Sample	Condition	Temperature (°C)	E (kJ mol^{-1})	A (min^{-1})	R^2
HDPE	N_2	467-494	445.9	$5.27x10^{30}$	0.99
	CO_2	468-497	472.1	$2.40x10^{33}$	0.99
PP	N_2	444-480	274.2	$1.47x10^{19}$	0.99
	CO_2	438-478	264.8	$3.44x10^{18}$	0.99
PS	N_2	423-449	283.4	$3.47x10^{20}$	0.99
	CO_2	420-459	260.3	$5.03x10^{18}$	0.99
PET	N_2	417-453	273.2	$5.84x10^{19}$	0.99
	CO_2	421-450	281.2	$2.20x10^{20}$	0.99
LDPE	N_2	460-492	446.7	$7.61x10^{30}$	0.99
	CO_2	465-494	467.0	$1.83x10^{32}$	0.99

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

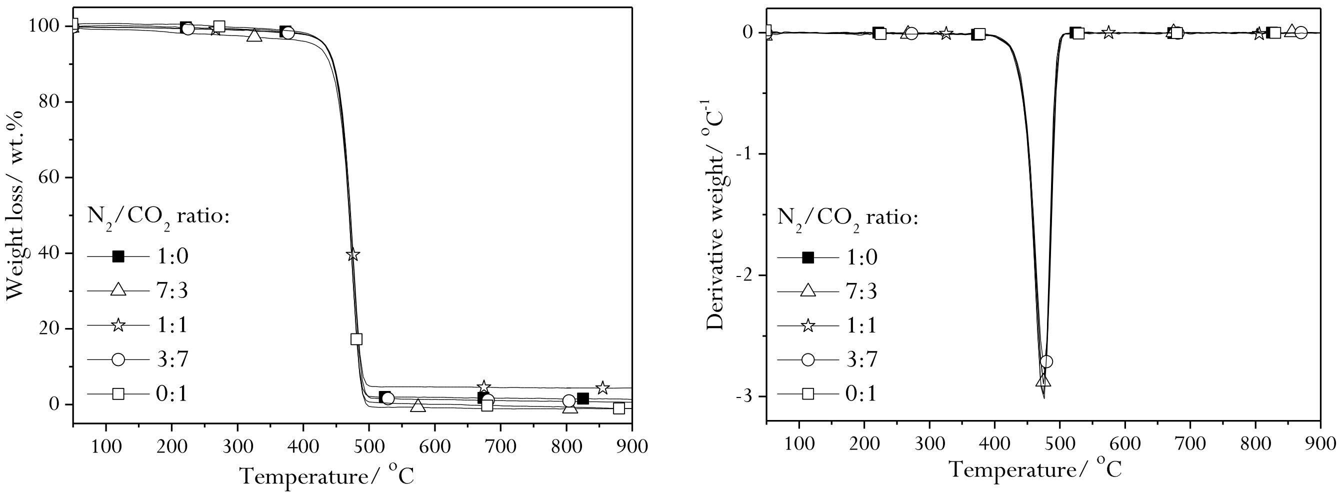
3.2.1. Thermogravimetric characteristics

The weight loss and rate of degradation curves of HDPE over five different N_2/CO_2 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_2/CO_2 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_2/CO_2 ratio of 3:7. This indicates the ratio N_2 to CO_2 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.



(a)

(b)

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_{11}^{+} hydrocarbons are the primary products derived from raw polymer cracking; (ii) gaseous products, C_1-C_4 are the primary or secondary products depending on the reaction; (iii) non-aromatic C_5-C_9 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^{-1} for waxes (> C_{11}), char, liquids (non-aromatics C_5-C_{10}), rich gases (C_1-C_4), and aromatics (single ring structures), respectively. Based on the residual mass observation, the addition of more than 30% of CO_2 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_2/CO_2 ratios; 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). The results show that the values of activation energy increased with the increase of N_2/CO_2 ratio, from 317.5 kJ mol^{-1} under 100% N_2 to 345.9 kJ mol^{-1} under 100% CO_2. It should be noted that the addition of CO_2 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_2/CO_2 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_2/CO_2 ratios from Arrhenius model; activation energy (E), pre-exponential factor (A) and correlation coefficients (R2).

N_2/CO_2	Temperature (°C)	E (kJ mol^{-1})	A (min^{-1})	R^2
1:0	429 – 490	317.5	1.03×10^{22}	0.99
7:3	434 – 495	320.4	1.66×10^{22}	0.99
1:1	433 – 491	331.5	9.48×10^{22}	0.99
3:7	435 – 494	345.2	8.53×10^{23}	0.99
0:1	433 – 491	345.9	1.06×10^{24}	0.99

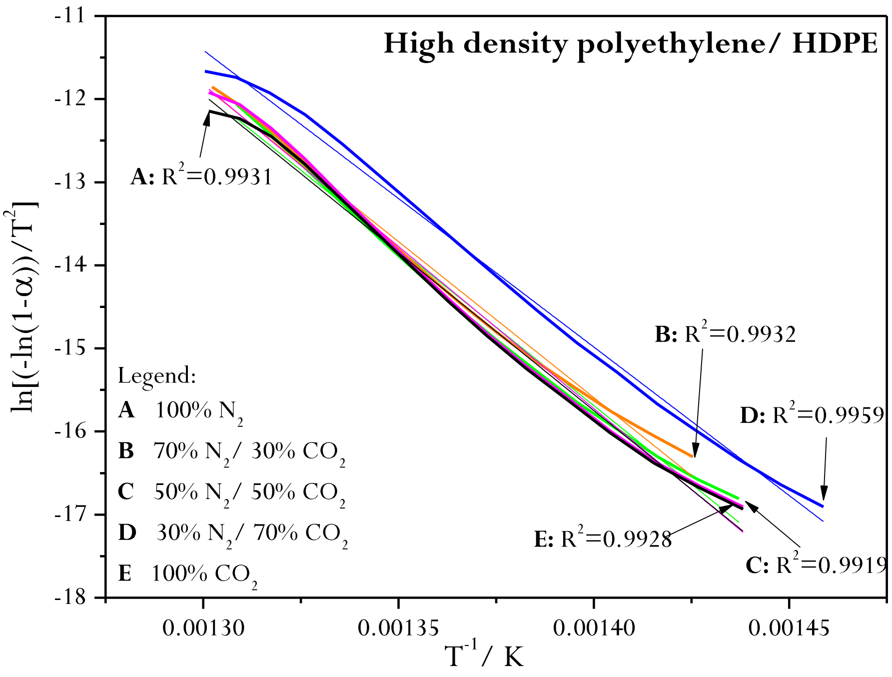


Figure 4 Plot of ln[(-ln(1-α))/T2] versus 1/T of HDPE in different N_2/CO_2 ratio; 100% N_2 (1:0), 70% N_2/30% CO_2 (7:3), 50% N_2/50% CO2 (1:1), 30%N_2/70% CO_2 (3:7) and 100% CO_2 (0:1).

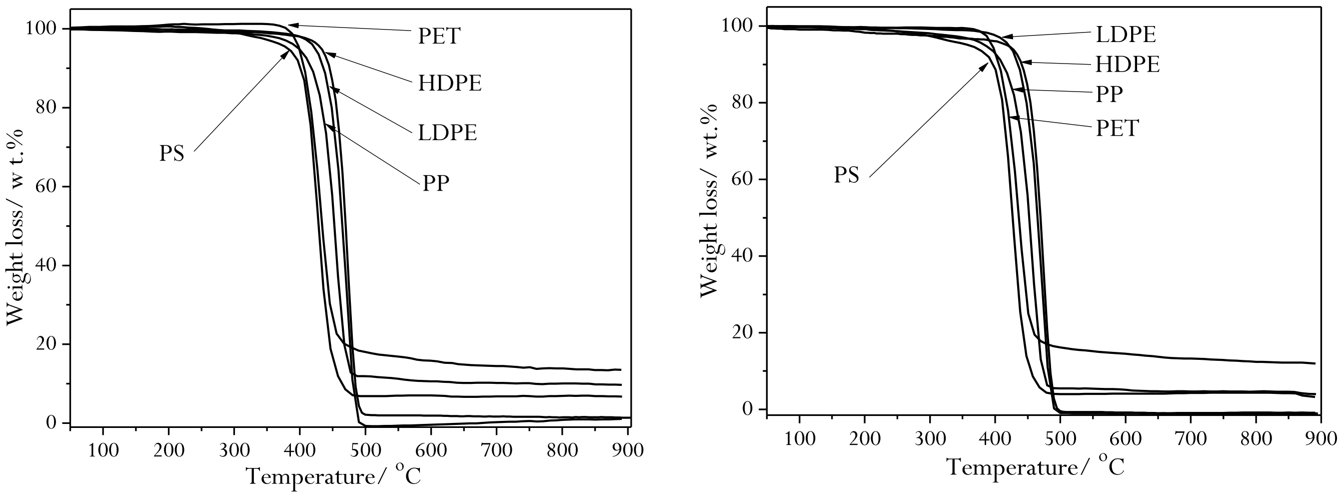
3.3. Thermogravimetric characteristic and kinetic analysis for individual plastics and mixed plastics at N_2/CO_2 ratio of 1:0 and 7:3

The TGA and DTG thermographs of each plastic in N_2/CO_2 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_2 and CO_2 compared to only N_2. The highest increment of degradation peak temperature from the experiment with only N_2 compared to a mixture of N_2 and CO_2 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_2/CO_2 ratio of 1:0 and 7:3.

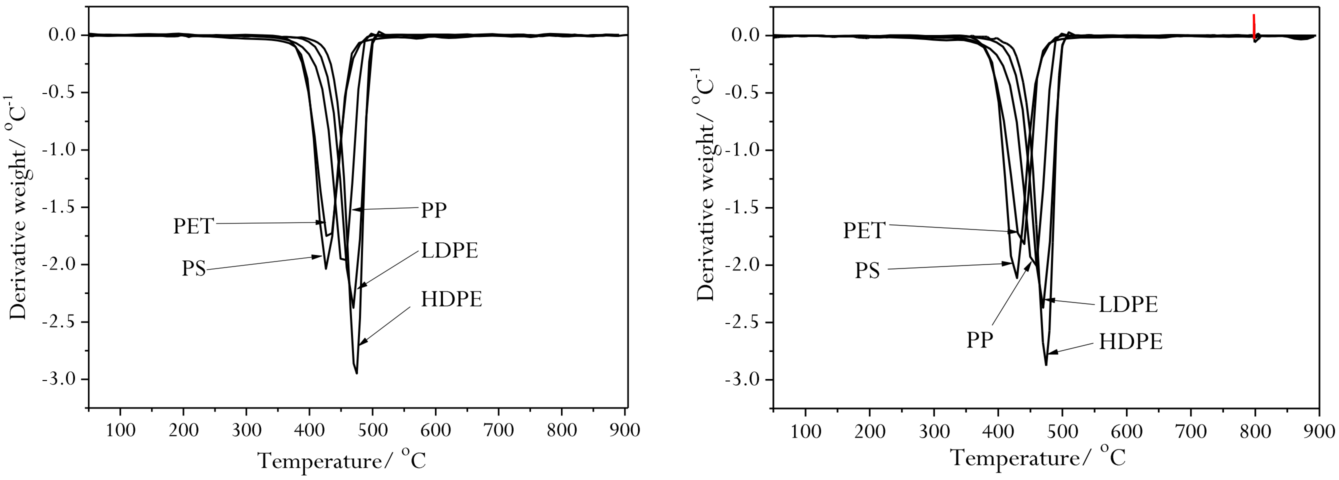
Plastic samples	T_i (°C)		T_f (°C)		T_m (°C)		Residue at 900 °C (wt.%)		Weight loss (wt.%)	
	1:0	7:3	1:0	7:3	1:0	7:3	1:0	7:3	1:0	7:3
HDPE	397	393	500	500	475	475	4.4	4.2	95.6	95.8
PP	349	340	488	480	458	460	9.7	6.9	90.3	93.1
PS	273	275	492	479	426	429	7.9	7.3	92.1	92.7
PET	369	367	579	509	436	441	14.7	15.9	85.3	84.1
LDPE	359	378	500	500	480	480	2.2	3.2	97.8	96.8
MP_{HP}	274	263	497	509	479	479	4.8	5.0	95.2	95.0
MP_{BC}	340	330	489	499	469	470	7.3	7.2	92.7	92.8
MP_{AGR}	298	286	499	501	480	481	5.0	3.8	95.0	96.2

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



(a) N_2/CO_2 ratio of 1:0

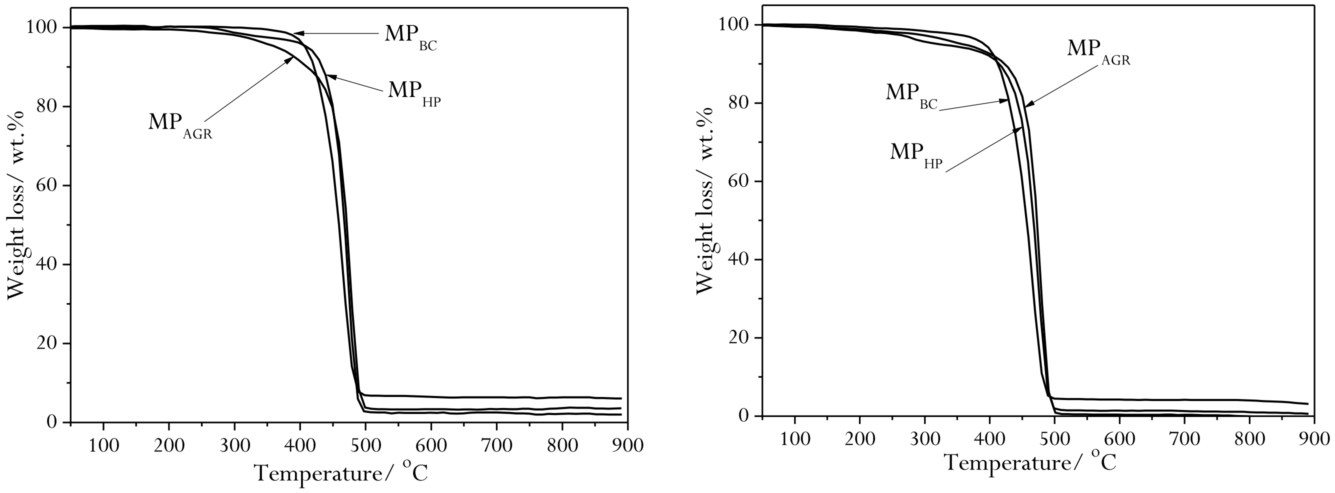
(c) N_2/CO_2 ratio of 7:3



(b) N_2/CO_2 ratio of 1:0

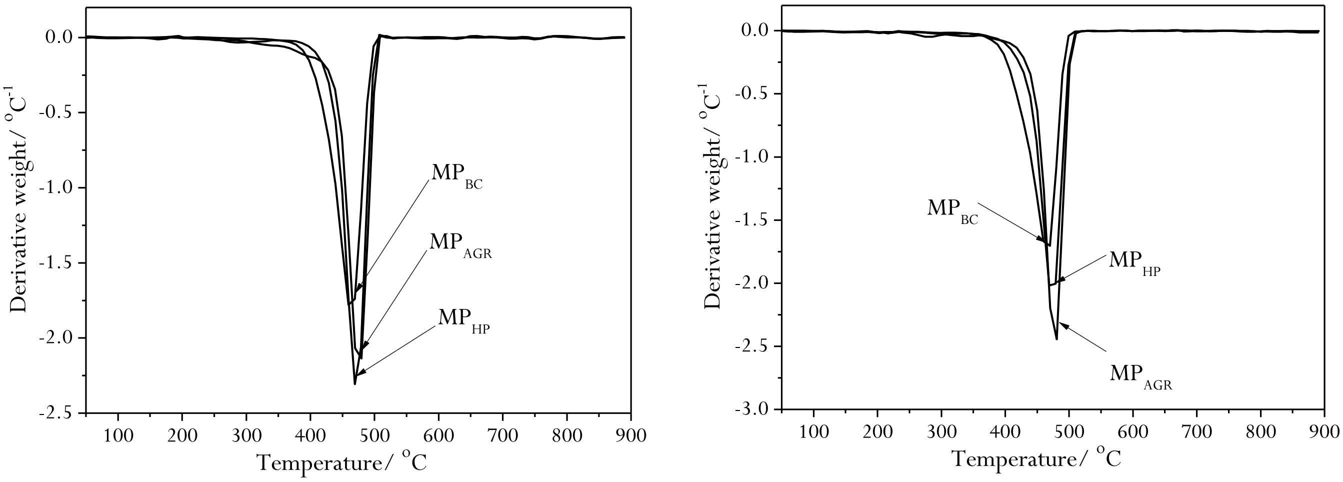
(d) N_2/CO_2 ratio of 7:3

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).



(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 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_2/30% CO_2 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_{HP} and MP_{AGR} 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_2/CO_2 ratio of 1:0 and 7:3 from Arrhenius model; activation energy (E), pre-exponential factor (A) and correlation coefficients (R2).

Sample	N_2/CO_2 ratio	Temperature (°C)	E (kJ mol^{-1})	A (min^{-1})	R^2
HDPE	1:0	429 – 490	317.5	1.03×10^{22}	0.99
	7:3	434 – 495	320.4	1.66×10^{22}	0.99
PP	1:0	410 – 468	228.3	1.17×10^{16}	0.98
	7:3	408 – 470	155.7	5.38×10^{10}	0.94
PS	1:0	397 – 469	203.1	3.99×10^{14}	0.97
	7:3	401 – 468	207.1	8.28×10^{14}	0.96
PET	1:0	398 – 467	210.2	1.13×10^{16}	0.96
	7:3	398 – 460	234.3	7.25×10^{16}	0.99
LDPE	1:0	429 – 490	293.4	2.88×10^{20}	0.99
	7:3	428 – 490	287.9	1.05×10^{20}	0.99
MP_{HP}	1:0	429 – 488	248.4	1.37×10^{17}	0.98
	7:3	418 – 499	200.1	4.43×10^{13}	0.97
MP_{AGR}	1:0	438 – 499	236.6	1.75×10^{16}	0.97
	7:3	429 – 491	224.4	1.88×10^{15}	0.95
MP_{BC}	1:0	408 – 479	207.4	2.28×10^{14}	0.99
	7:3	408 – 480	189.3	1.13×10^{13}	0.99

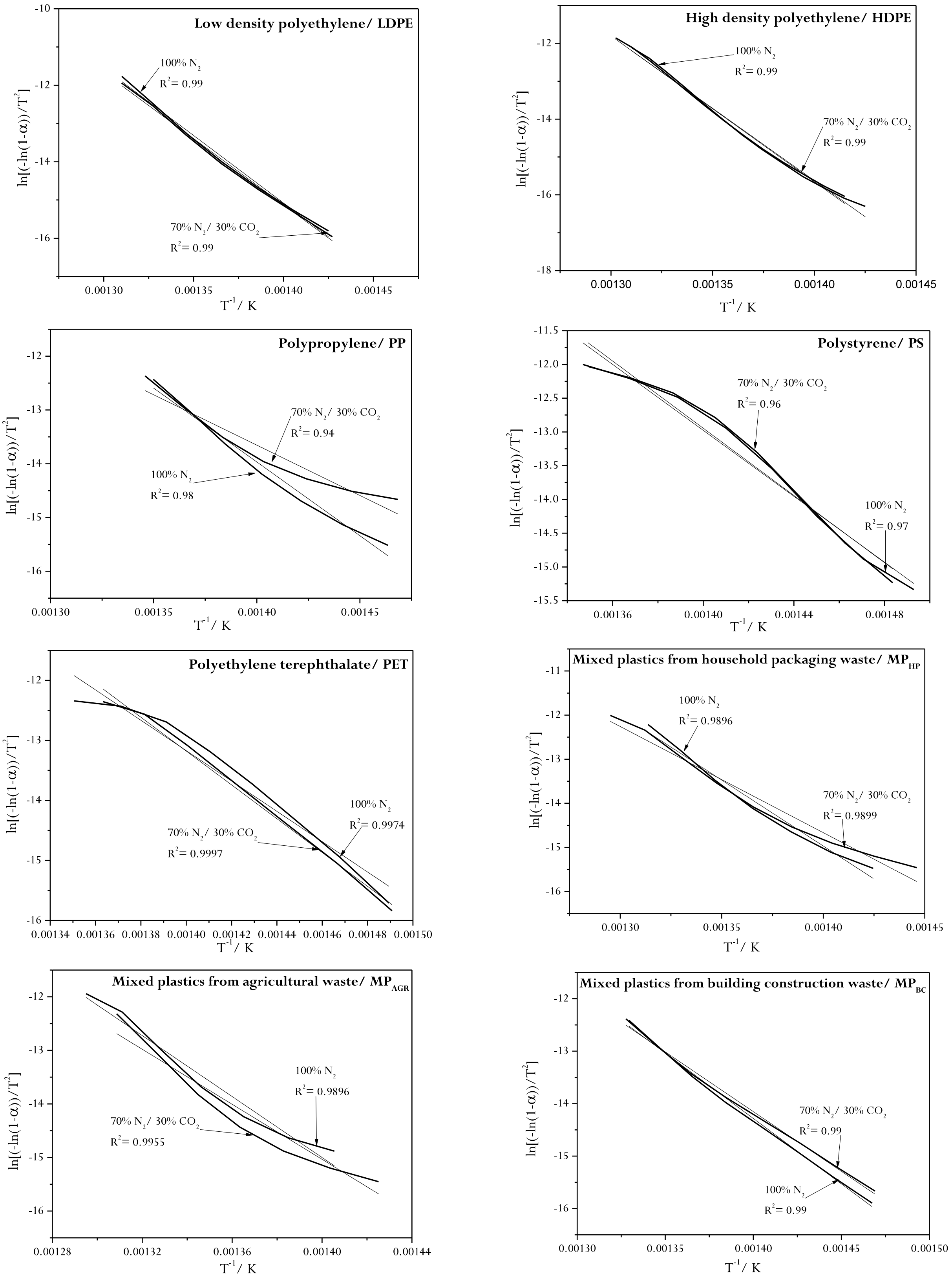


Figure 7 Plot of ln[(-ln(1-α))/T2] versus 1/T of individual plastics and mixed plastics at N2/CO2 ratio of 1:0 and 7:3.

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_2/CO_2 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^{-1} at N_2/CO_2 ratio of 1:0 and 320.4 kJ mol^{-1} at N_2/CO_2 ratio of 7:3. In contrast, PS showed the lowest activation energy at N_2/CO_2 ratio of 1:0 with 203.1 kJ mol^{-1} while at N_2/CO_2 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_{HP}, MP_{AGR} and MP_{BC} 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 Ea 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_2/CO_2 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_2/CO_2 ratios, while PS showed the lowest at 426 °C and 429 °C in N_2/CO_2 ratio of 1:0 and 7:3 respectively. Low activation energies were observed in almost all plastics in N_2/CO_2 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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