Effect of the addition of different waste carbonaceous materials on coal gasification in CO_2 atmosphere

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Abstract

In order to assess the utilisation of waste carbonaceous materials and the feasibility of using CO_2 as a gasifying agent, the gasification characteristics of coal, a suite of waste carbonaceous materials, and their blends were investigated by using a thermogravimetric analyser (TGA). The results showed that the CO_2 gasification process of polystyrene completed at 470 °C which was lower than other carbonaceous materials. This behaviour was attributed due to the high content of volatile coupled with its unique thermal degradation properties. It is found that the initial decomposition temperature decreased with the increasing amount of waste carbonaceous materials in the blends. Overall, CO_2 co-gasification process was enhanced as a direct consequence of interactions whose intensity and temperature of occurrence were influenced by the chemical and compositional properties of carbonaceous materials. The strongest interactions were noticed in coal/polystyrene blend at the devolatilisation stage as indicated by its highest value of Root Mean Square Interaction Index (RMSII), caused by highly reactive characteristic of polystyrene. On the other hand, coal/oat straw blend revealed the highest interactions at char gasification stage. The catalytic effect of alkali metals content in oat straw, particularly CaO and K_2O, was believed to be the reasons

for these strong interactions. Furthermore, co-pyrolysis was compared with CO_2 gasification through RMSII value, while the effect of CO_2 as a gasifying agent on interactions during co-gasification was also evaluated. It is clear from this study that CO_2 gasification of coal can be enhanced significantly via the addition of polystyrene and oat straw.

Keywords: CO_2 gasification; Carbonaceous materials; Interactions; Catalytic effect

1 Introduction

In order to minimise CO_2 emissions, different waste carbonaceous materials are used as energy source because of their carbon neutral nature. In recent years, co-utilisation of waste carbonaceous materials has become increasingly popular to replace a portion of coal in existing coal-fired boilers for power generation [1, 2].

Over the years, many techniques have been developed to utilise coal with biomass and other carbonaceous materials. Co-gasification is one of the promising methods because it has the potential to improve the gas yield and corresponding heating value of the product when low quality coal is gasified [3, 4]. Moreover, improved overall carbon conversion and cold gas efficiency can also be achieved by increasing the proportion of biomass in the feed.

For gasification process, CO_2 is a potential gasification medium [5-7]. It is less corrosive than steam and can be used to adjust syngas composition for different applications [8]. In the past decades, a lot of research has been carried out on biomass gasification using CO_2 as a

gasifying agent [5, 7, 9-12]. These researches were mainly focused on the kinetics [5, 9, 11, 12], gasification reactivity [7, 10, 13, 14] and gasification characteristics [14-16] in general. In spite of huge potential of CO_2 in coal and biomass gasification, limited effort have been made to understand gasification behaviours, particularly on interactions during co-gasification. Apart from these, limited study has been conducted understanding how to enhance co-gasification via choosing suitable waste carbonaceous materials for the co-gasification of certain coal. In addition, information on waste carbonaceous materials such as non-metallic part of printed circuit boards, tyre scraps and polystyrene are very limited compared with the conventional fuel and biomass. Moreover, not much work has been performed to understand the effects of CO_2 on the gasification process of these carbonaceous materials. Thus, there are still needs to achieve in depth understanding of gasification characteristics of coal, waste carbonaceous materials and their blends.

In this paper, gasification characteristics of coal, a suite of waste carbonaceous materials and their blends were investigated in a TGA using CO_2 as the only gasifying agent. In addition, the influence of mass fractions of carbonaceous materials on gasification characteristics of the blends was analysed. The interactions during co-gasification were also studied and the reasons for these interactions were explored.

2 Experimental

2.1 Samples preparation

In this study, an Australian bituminous coal was selected as the coal sample. Oat straw (OS), Non-metallic part of printed circuit boards (NMPCBs), tyre scraps (tyre) and polystyrene (PS) were chosen as the waste carbonaceous materials samples. All samples were air-dried at ambient temperature prior to further processing. Size reduction was carried out by using an industrial hammer crusher (CSF570, Fengli Pulverization Ltd., China) and ball mill (SM2000, MM400, Retsch, Germany), respectively. All samples were ground to a size smaller than 106 microns (Endecott 106 microns aperture sieve) following the standard milling procedure (CEN/TS 15443:2006). Before characterization and testing, all samples were treated following international accepted standard procedure to ensure representativeness of the samples [17].The blend samples were prepared from these materials by mixing manually at (coal to waste carbonaceous material) mass ratios of 90:10 and 70:30 (with a maximum deviation of ± 0.1 mg), which is denoted as high and low bending ratios, respectively. These ratios are representative of typical co-gasification parameters, corresponding to 5%-35% on thermal basis.

2.2 Sample characterisation

Proximate analysis of the samples was conducted based on the standard practice for Proximate Analysis using a TGA following procedures described elsewhere [18] . All the

77 experiments were repeated three times and average value was used for the study. Carbon (C),
78 hydrogen (H), nitrogen (N) and sulphur (S) contents were determined using a CHNS/O
79 Element Analyser (PE2400, PerkinElmer, USA) following the standard testing procedure
80 described in the manual. The standard sample was firstly applied to calibrate the Elemental
81 Analyser. Approximately 1.5 mg of dried fine powder was used for each test, which was
82 repeated at least three times. Oxygen content was calculated by difference on dry and ash free
83 basis. The tests were carried out in helium carrier gas with an accuracy of ≤0.3% and a
84 precision of ≤0.2%. Calorific value of all the samples was determined using a calorimeter
85 (IKA C 200, Germany), which was calibrated prior to testing using benzoic acid to achieve a
86 relative standard deviation less than 0.2%. As for ash composition, each sample was analysed
87 twice using an X-Ray Diffraction (XRD) (Bruker D8 Advance, Germany) to minimize
88 experimental error to be within ±1.5%.

89 ## 2.3 CO_2 gasification

90 CO_2 gasification of the coal, waste carbonaceous materials and their blends was carried out
91 using a STA 449/F3 Jupiter thermal analyser (NETZSCH Geraetebau GmbH, Germany) with
92 a weighing precision of ± 0.01% and TGA resolution of 0.1 μg. In each test, the sample was
93 heated to 50 °C in N_2 (30 ml/min) from room temperature and kept isothermal for 10 min. It
94 was then heated from 50 to 1200 °C at a constant heating rate of 20 K/min in the presence of
95 pure CO_2 (40 ml/min). Prior to each test, the sample was further manually grounded to

smaller than 90 microns to minimize diffusion effects. About 5 mg of sample (accuracy up to 0.01 mg via PerkinElmer AD 6 autobalance) was loaded into a ceramic crucible for each test. This slow heating rate and small amount of sample used would minimise mass transfer effects and eliminate the heat transfer limitations in the CO_2 gasification process. Each test was repeated three times to minimize the experimental error.

2.4 Interactions indexes

Thermal characteristics of coal, waste carbonaceous materials and their blends in CO_2 atmosphere were extracted from the TG/DTG profiles. The theoretical TG/DTG curves of the blends were calculated by Eq. (1) based on the mass loss rates of each individual sample assuming additive property applies. The deviation between experimental and calculated curves was used to show the degree of interactions between samples [19, 20]:

$$\frac{dm}{dt} = x_{SP1}\left(\frac{dm}{dt}\right)_{SP1} + x_{SP2}\left(\frac{dm}{dt}\right)_{SP2} \quad (1)$$

where $\left(\frac{dm}{dt}\right)_{SP1}$ and $\left(\frac{dm}{dt}\right)_{SP2}$ are the mass loss rates (%/min) of individual samples while x_{SP1} and x_{SP2} are the corresponding mass fractions in the blends, respectively. The Root Mean Square Interactions Index (RMSII) was applied to quantify the interactions between components in the blend which compares the deviation of calculated value with experimental value. Normally, a higher value of RMSII indicates a larger interaction taking place in the process. The RMSII can be calculated using the Eq. (2) [21].

$$RMSII = \sqrt{\frac{\sum_{i=1}^{N}\left(\frac{(dm/dt)^{i}_{EXP} - (dm/dt)^{i}_{CAL}}{(dm/dt)^{i}_{CAL}}\right)^{2}}{N}} \quad (2)$$

where $(dm/dt)_{EXP}$ and $(dm/dt)_{CAL}$ denote experimental and calculated mass loss rates values, respectively. N represents the number of points undertaken.

3 Results and discussion

3.1 Properties of the samples

Table 1 shows proximate, ultimate and ash analysis results of the samples studied in present work. For the proximate analysis, the relative standard deviation was ± 3 wt%, while for ultimate analysis, it was ± 2 wt%. As can be seen, volatile content and oxygen content varied significantly. Among all the tested samples, NMPCBs had the highest percentage of ash, which is mainly due to the presence of glass fiber. Hence, it would have some influence on gasification process. It is clear that tyre showed very similar properties in term of proximate and ultimate analysis data as coal. Its heating value is also very close to that of coal. Therefore, it is expected that the co-gasification of tyre with coal would have very little influence on the overall gasification process. On the other hand, negligible amount of ash was detected in polystyrene, which was completely decomposed, resulting in no fixed carbon formed after pyrolysis. Besides, polystyrene contained no sulphur and low percentage of nitrogen compared with the other samples.

Higher heating value (HHV) of individual samples were also included in Table 1 with relative standard deviation controlled within ±4.5%. It is clear that polystyrene (41.7 MJ/kg, daf) exhibited the highest heating value, greater than that of coal (35.5 MJ/kg, daf). Meanwhile, the heating values of tyre (33.2 MJ/kg, daf) and NMPCBs (31.5 MJ/kg, daf) were all slightly lower than coal. Hence, blend with polystyrene, tyre or NMPCBs might not have a negative impact on co-gasification process. In contrast, oat straw (19.5 MJ/kg, daf) had the lowest heating value, which subsequently would result in a lower gasification temperature. As moderate low gasification temperature is one of the desired properties of the fuel, thus, it would enhance gasification performance in co-gasification process.

Table 1: Proximate, ultimate analyses and calorific values of the samples.

	AC	**OS**	**NMPCBs**	**Tyre**	**PS**
HHV (MJ/kg dry ash free)	35.5	19.5	31.5	33.2	41.7
Proximate analysis (wt %)					
Moisture	0.7	4.2	0.8	0.4	0.9
Volatile matter	34.6	70.7	25.1	62.9	99.1
Fixed carbon	48.2	18.2	6.9	19.6	-
Ash	16.5	6.9	67.2	17.1	-
Ultimate analysis [a,b] (wt %)					
C	81.3	37.4	39.8	80.9	92.1
H	4.9	5.3	3.6	6.4	7.7
O[C]	9.7	47.9	55.7	10.7	-
N	1.9	2.3	0.6	0.5	0.2
S	2.2	0.2	0.3	1.5	-
Ash composition (wt %, standard deviation ±5%)					

SiO_2	42.6	43.3	29.7	38.5	-
SO_3	1.4	3.4	-	6.2	-
CaO	4.2	10.6	5.3	3.5	-
Na_2O	2.3	2.6	1.4	2.7	-
Fe_2O_3	7.4	0.9	4.6	45.1	-
MgO	2.2	4.2	-	0.7	-
Al_2O_3	39.1	2.2	5.3	2.4	-
K_2O	0.8	32.8	-	0.9	-
CuO	-	-	38.4	-	-
ZnO	-	-	5.7	-	-
Ni_2O_3	-	-	9.6	-	-

[a]Dry basis. [b]Ash free basis. [c]By difference.

3.2 Thermal behaviours of the individual samples

Fig. 1 shows the TGA and DTG curves of coal and different waste carbonaceous materials under CO_2 gasification. In this study, the instrument was calibrated to ensure that the precision of ≤0.2% in TGA analysis was achieved. In Fig. 1, it is apparent that the gasification processes involved a multi-stage thermal degradation where the number of stages and the unique features of individual stage varied. The main mass losses in coal gasification took place at 400-570 °C and 935-1190 °C, respectively (Fig. 1a). The first mass loss was due to the release of volatiles while char gasification and thermal decomposition of minerals contributed to the second mass loss. As expected in CO_2 gasification, the heterogeneous reaction between coal char and CO_2 was much slower compared with combustion process. This is because CO_2 is a weak oxidizing agent and the CO_2 gasification via Boudouard reaction ($C\ (S) + CO_2 \rightarrow 2CO$) is slow [22, 23]. Normally, at atmospheric pressure, the

153 Boudouard reaction is thermodynamically favourable at temperatures above 900 °C (initiated
154 at 800 °C) while the combustion of char can occur at significantly lower temperatures (below
155 630 °C). Two stages of mass losses were observed in oat straw as seen in Fig. 1b. The first
156 loss (240-375 °C) was attributed to the complete decomposition of hemi-cellulose and
157 cellulose and the partial decomposition of lignin [20, 24, 25]. The decomposition of
158 remaining lignin, char gasification and minerals decomposition contributed to the second
159 mass loss (820-950 °C). Unlike coal, CO_2 gasification of char derived from oat straw took
160 place at a lower temperature range. In general, biomass has a higher amount of volatiles
161 which generate a highly porous char compared with char derived from coal [26]. The porous
162 structure of char facilitates CO_2 diffusion, which leads to a better gasification performance.
163 The gasification of oat straw therefore completed at lower temperatures. It was reported that
164 the reactivity of biomass char is usually higher than the chars produced from coal [27, 28].
165 This implies that compared with coal char, biomass char can be gasified at much lower
166 temperature which is the case for oat straw.

167 Fig. 1c shows the main mass loss experienced by NMPCBs in the second stage which is
168 illustrated at temperature from 295 to 410 °C. In spite of NMPCBs having the lowest
169 volatiles, its maximum mass loss was occurred at low temperature region.

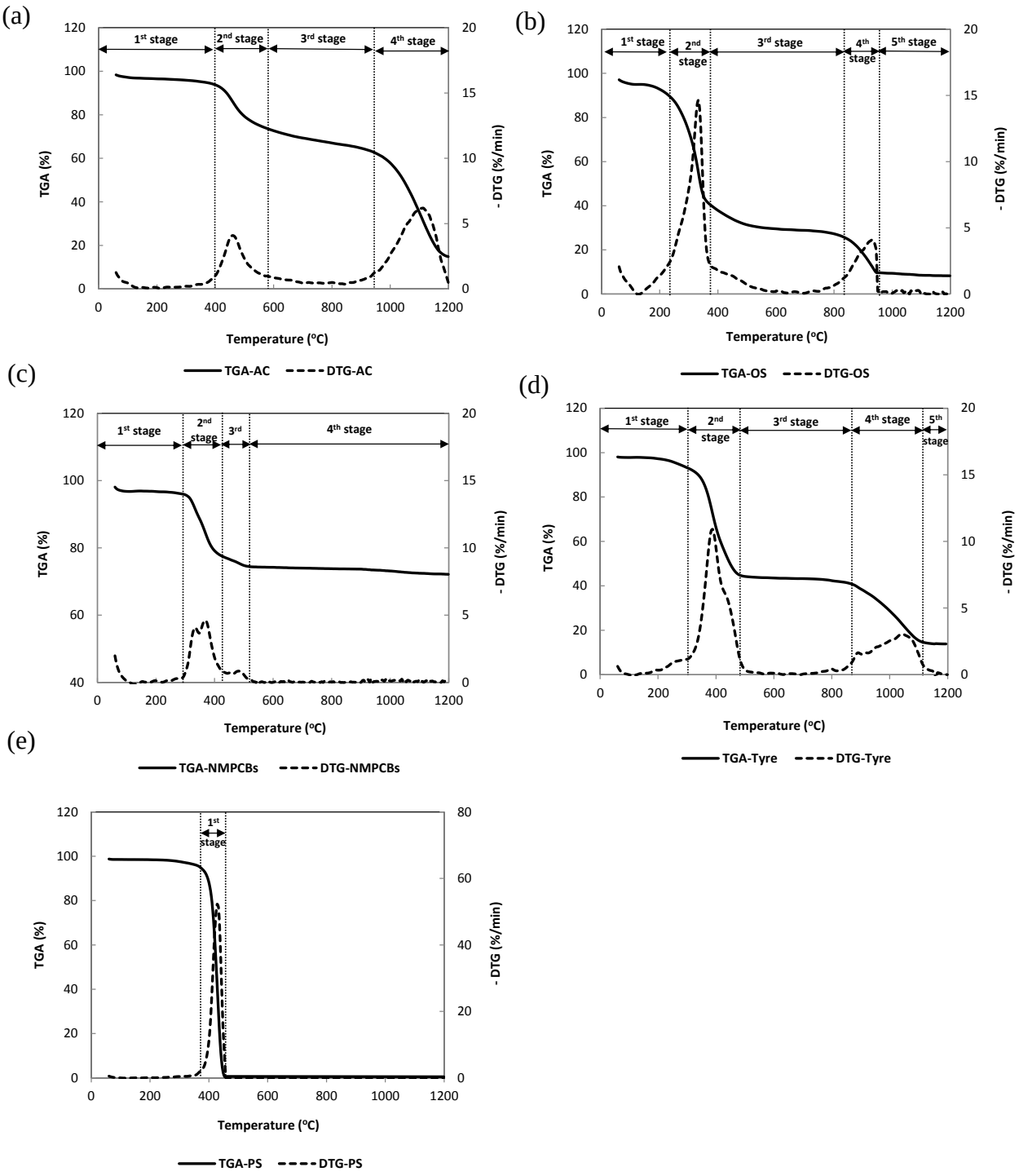

Figure 1: CO_2 gasification distribution of the TGA and DTG curves of (a) coal, (b) oat straw, (c) NMPCBs, (d) tyre and (e) polystyrene.

Typically, epoxy resin is the major component of the NMPCBs which is mixed with brominated compounds [29, 30]. The decomposition of epoxy resin, degradable part of NMPCBs, started at around 300 °C. Consequently, thermal decomposition of NMPCBs

consists of two stages, the decomposition of brominated compounds and decomposition of non-brominated compounds. The possible reason for the existence of small peak before the main peak was the partial overlapping of these two reactions [30]. As seen in Fig. 1c, a smaller DTG peak which was situated between the temperatures of 465 to 510 °C, denoted the second main mass loss due to the release of volatiles due to the decomposition of brominated compounds in NMPCBs. It is important to notice that the value of this mass loss rate was smaller (0.85 wt%/min) in comparison with mass loss rates noticed in other samples. As seen in Fig. 1d, tyre also exhibited the first mass loss at low temperature region (300-490 °C) similar to NMPCBs while the second mass loss happened at relatively high temperature region (875-1110 °C). Generally, tyre contains small portion of additives (less than 30 wt%) and the rest is rubber (natural and synthetic) [31, 32]. The first mass loss was caused by the decomposition of the additives and both types of rubber which occurred at lower temperature. Afterwards, the second mass loss depicted CO_2 char gasification. Higher percentage of carbon in tyre might be the reason for this slow gasification reaction. On the other hand, polystyrene experienced a single stage degradation at a higher temperature region (350-455 °C) compared with other waste carbonaceous materials. From Fig. 1e, it can be seen that polystyrene had a negligible mass loss up to 250 °C, whereas a slight mass loss was detected at temperature between 250 to 350 °C. This confirmed that polystyrene was thermally stable up to 350 °C. Degradation completed at 455 °C and during this stage the mass loss observed was 98.5 wt% due to the thermal cracking of light organics and other carbonaceous heavy organics to low

196 molecular weight compounds. The overall mechanism is believed to be dictated by the
197 combination of end-chain initiation, depolymerisation, intramolecular hydrogen transfer, and
198 bimolecular termination processes. The changes in mass loss are caused by inter-molecular
199 transfer reactions while devolatilisation is governed by intramolecular transfer reactions.
200 Above 455 °C, no residue was observed, which confirmed the complete degradation of
201 polystyrene in CO_2 gasification. In general, gasification characteristics such as initial
202 decomposition temperature and final mass loss temperature are the crucial parameters of the
203 fuel performance. As can be seen in Fig. 1, oat straw had the lowest initial decomposition
204 temperature (281 °C). In contrast, coal and polystyrene experienced the two highest initial
205 decomposition temperatures (415 and 407 °C). However, the final maximum mass loss
206 temperatures was in the order of polystyrene (428 °C), NMPCBs (479 °C) and oat straw (931
207 °C), respectively which suggested that polystyrene and NMPCBs were more reactive
208 compared with oat straw. Moreover, the highest maximum mass loss rate (49.7 wt%/min) and
209 the lowest gasification time (18.9 min) were observed for polystyrene. Therefore, the use of
210 polystyrene as a fuel for co-gasification application would be more beneficial.

211 ## 3.3 Co-gasification characteristics of coal and carbonaceous materials

212 Fig. 2 describes the co-gasification behaviours of coal and carbonaceous materials and the
213 characteristics of individual samples and blends are listed in Table 2.

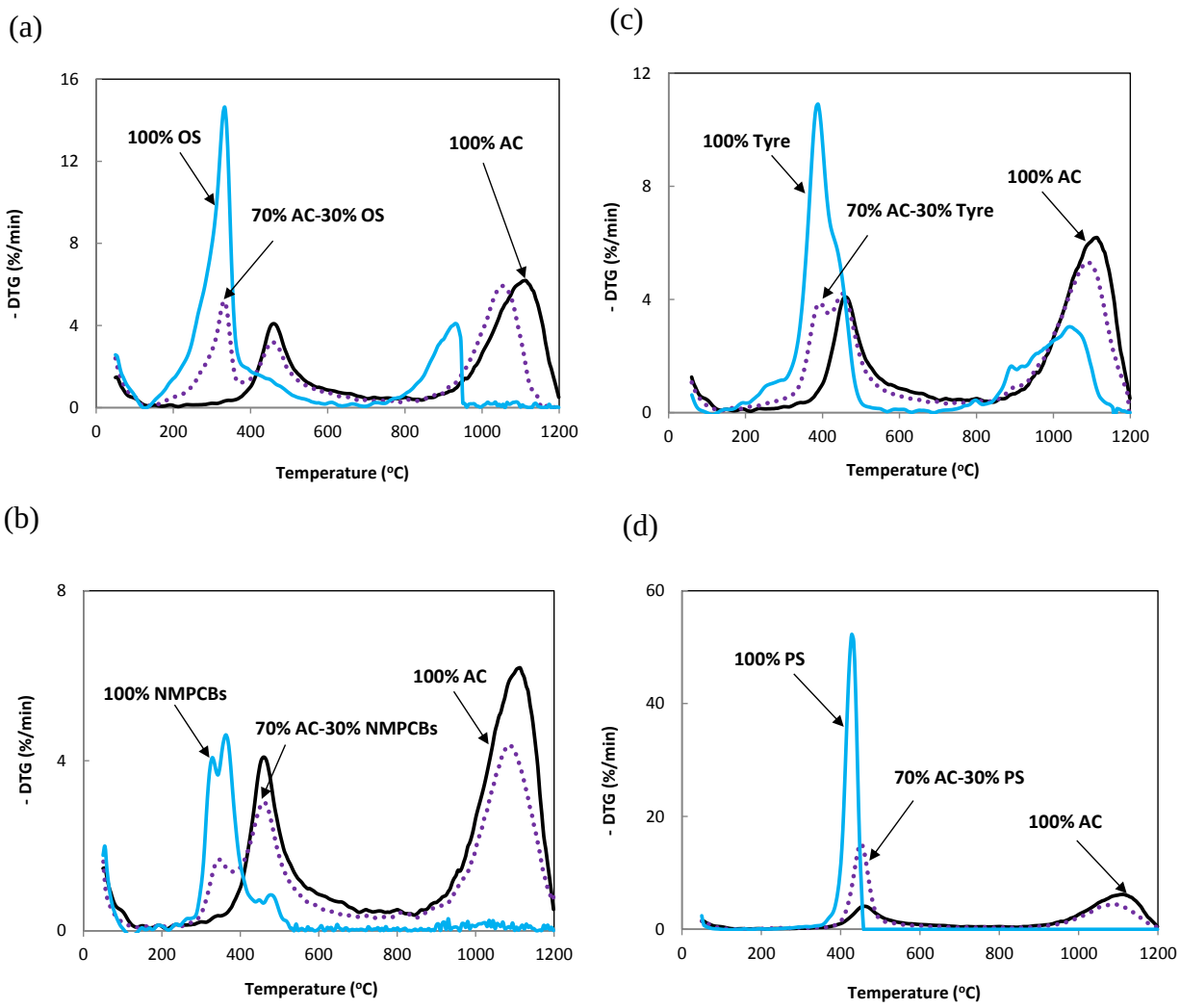

Figure 2: CO_2 gasification distributions of (a) coal/oat straw, (b) coal/NMPCBs, (c) coal/tyre and (d) coal/polystyrene blends (standard deviation ± 1.3%).

In general, curves of the blends were found in the location between those of the original samples. From Fig. 2a, it is clear that coal/oat straw blends had three-stage mass loss rather than the two-stage mass loss identified for the original oat straw sample. In the case of blends, the first mass loss was mainly due to the volatiles release from decomposition of hemicellulose and cellulose in oat straw whereas the third one was mostly caused by char gasification. Commonly, the initial devolatilisation temperature of coal is approximately the same as the terminal devolatilisation temperature of biomass. Therefore, the second mass loss

was attributed mainly to the devolatilisation of coal, while the gasification of chars derived from both oat straw and coal collectively resulted in the third mass loss. As shown in Table 2, the coal (415 °C) started to devolatilise at a higher temperature than that of the oat straw (281 °C). In addition, the maximum mass loss temperatures of coal and oat straw were 458/1108 °C and 332/931 °C, respectively. It is interesting to see that the first and the second mass loss temperatures of the blends did not vary significantly. However, the change of the third mass loss temperatures was noticed. This indicated that the blending of oat straw with coal did not have significant influence on the devolatilisation stage but affected the char gasification process. Besides, as oat straw percentage in blend increased, the reduction in the initial decomposition temperature (T_i) of the blends was also observed, which contributed to a lower devolatilisation temperature in co-gasification process. The experimental results also demonstrated that the addition of oat straw shifted the CO_2 gasification process to a low temperature region by reducing the overall maximum mass loss temperatures (T_{max}). The higher volatiles content in oat straw (shown in Table 1) was the reason for these phenomena as oat straw burns at a much lower temperature compared with coal. Besides, DTG value of the first mass loss increased (1.9 wt%/min to 5.2 wt%/min due to increment of blending proportion from 10% to 30%) due to higher volatiles content while it decreased (6 wt%/min to 5.9 wt%/min) in the third mass loss due to increasing amount of the char derived from coal.

Table 2: CO_2 gasification characteristic parameters of blends and individual samples.

Sample	T_i	T_{max} (°C)	t_{max} (min)	DTG_{max} (%/min)
Australian coal	415	458/1108	20.5/52.8	4.1/6.1
Blend 1 (10% oat straw)	301	335/460/1091	14.2/20.5/52.2	1.9/3.9/6
Blend 2 (30% oat straw)	294	333/456/1053	14.1/20.3/50.1	5.2/3.2/5.9
Oat straw	281	332/931	14.1/44.2	14.7/4.1
Blend 1 (10% NMPCBs)	407	456/1100	20.6/53.2	3.8/5.9
Blend 2 (30% NMPCBs)	353	344/453/1082	14.7/20.5/51.7	1.7/3.0/4.3
NMPCBs	305	364/479	15.7/21.5	4.5/0.9
Blend 1 (10% tyre)	400	457/1106	20.5/52.7	4.2/5.9
Blend 2 (30% tyre)	365	395/458/1088	17.3/20.3/51.8	3.9/4.2/5.3
Tyre	357	394/1046	17.2/50.1	10.4/3
Blend 1 (10% PS)	412	456/1104	20.2/52.5	7.3/5.6
Blend 2 (30% PS)	410	453/1082	20/51.8	15.1/4.5
Polystyrene (PS)	407	428	18.9	49.7

T_i=Initial decomposition temperature, T_{max}= Maximum mass loss temperature, t_{max}=maximum reaction time and DTG_{max}= Maximum mass loss rate.

Uncertainty of temperature: ±1°C. Uncertaintty of DTG_{max}: ±0.15 %/min.

When NMPCBs was gasified with coal at the high blending ratio, the gasification process featured three main mass loss stages as seen in Fig. 2b. The first mass loss stage occurred at temperature between 330 and 380 °C where the decomposition of NMPCBs took place. The second DTG_{max} (400-485 °C) indicated the release of volatiles from both coal and NMPCBs whereas the third DTG_{max} depicted the stage of CO_2 gasification of NMPCBs and coal derived chars. In contrast, at low blending ratios, such as 10 wt% NMPCBs, only two main mass loss stages were noticed at similar temperature ranges as coal in co-gasification. Here, the value of first DTG_{max} (Table 2) decreased because of the lower amount of volatiles in the

255 blend contributed by NMPCBs. Meanwhile, the decrement of the second DTG_{max} was as a
256 result of the lower amount of NMPCBs char. From Table 2, it is clear that the initial
257 devolatilisation temperature and the first DTG_{max} temperature of the blend were shifted to a
258 lower temperature region as the proportion of NMPCBs increased while the final DTG_{max}
259 temperature was also shifted to a lower temperature due to the reduced amount of coal derived
260 char. Therefore, it can be concluded that the co-gasification of coal and NMPCBs completed
261 at a relatively lower temperature despite of a slight reduction of the maximum mass loss rate.

262 For coal/tyre blends as presented in Fig. 2c, two-stage mass loss was noticed at the low
263 blending ratio. The results on gasification parameters listed in Table 2 demonstrated that coal
264 had a dominant effect on the blend of 10 wt% tyre since it showed similar behaviours with the
265 characteristics of coal. It's mainly because coal and tyre have similar physical and chemical
266 properties as shown in Table 1. These properties were assumed as a result of the narrow
267 difference of initial decomposition temperatures between coal (415 °C) and tyre (357 °C), and
268 also a very small amount of tyre being blended. In contrast, the blend of 30 wt% tyre
269 experienced three-stage mass loss. From Table 2, it can be found that the first and the second
270 mass loss of the blend occurred at the same temperature as the first mass loss of original tyre
271 and coal, respectively. This means that the decomposition of tyre and coal in the blend was
272 took place sequentially rather than simultaneously. However, it can be seen from Fig. 2c that
273 gasification was shifted toward lower temperature with the increase of tyre fraction in the

blends. The reason behind the shifting was because of the thermal properties of tyre which decomposes relatively lower temperature than coal. Besides, the third mass loss rate which represented the char gasification of both coal and tyre was reduced (about 10% because of increment of blending proportion from 10% to 30%) due to the low amount of char generated from coal in the blend.

Among all the blend samples investigated in this study, coal/polystyrene blends exhibited different behaviours as illustrated in Fig. 2d. As polystyrene decomposed through a single-stage mass loss without any solid residue and its initial decomposition took place at a slightly slower temperature than coal, a complete coincidence between whole polystyrene mass loss and first mass loss of coal was observed. Hence, devolatilisation stage of the blend samples was represented by a single peak in DTG profile. Compared with coal, polystyrene contained approximately three times higher amount of volatiles, which resulted in the substantial increment of the first mass loss rates in blends. Similar to other blends, a gradual decrement of the second mass loss rate was observed when polystyrene was blended with coal. At the same time, the temperature corresponding to the maximum mass loss was also reduced. This was affected by the combination of the decrease in the percentage of coal and the increment of volatiles from polystyrene in the blends.

3.4 Interactions between coal and carbonaceous materials

To further understand the interactions in blend, the experimental and calculated DTG curves of the blends under CO_2 atmosphere are compared in Fig. 3. Overall, the curves illustrate that the interactions existed as the experimental curves of blends deviated from the calculated curves for the same blends [19, 20]. However, the deviation was not consistent at different stages of the entire process and varied with the blending of different materials, blending ratio and temperature range. From Fig. 3a, deviations were observed for coal/oat straw blends at two different temperature regions. This indicated the existence of significant interactions in the range of 950 -1200 °C and weaker interactions between 390-700 °C for both high and low blending ratios. Similarly, as seen in Fig. 3d, coal/polystyrene blends also showed significant interactions at different temperature ranges of 400-500 °C and 1000-1200 °C. For coal/NMPCBs blends (Fig. 3b), analogous behaviours were noticed where stronger and weaker interactions occurred in the temperatures ranges of 1050-1200 °C and 600-900 °C, respectively. Correspondingly, Fig. 3c depicted that in temperature range of 1160-1200 °C, coal/tyre blends experienced noticeable interactions while insignificant interactions occurred from 400 to 600 °C.

In order to determine the intensity of the interactions in the whole process, the root mean square interactions index (RMSII) of the blends (as detailed in Eq. 2) were also evaluated and listed in Table 3, which is of an accumulated uncertainty of ±0.01. Overall, the presence of

310 interactions was evident in the blends as demonstrated by RMSII value. From Table 3, it is
311 apparent that the higher the amount of carbonaceous material was added into the blend, the
312 higher the value of RMSII was observed. Moreover, regardless of blending ratio, RMSII
313 values of char gasification stage were higher than those of devolatilisation stage, except for
314 polystyrene, which ratified the strong interactions during char gasification stage. However,
315 significant interactions were noticed in devolatilisation stage for coal/polystyrene blends as
316 demonstrated by high RMSII value. At both blending ratios, the highest RMSII values in
317 devolatilisation and char gasification stages were exhibited by coal/polystyrene blends and
318 coal/oat straw blends, respectively. It is important to point out that the interactions in char
319 gasification stage of coal/NMPCBs blend at high blending ratio were considerably lower than
320 those of other ash containing blends. As seen in Table 1, NMPCBs had the highest ash
321 content (67.2 wt%) among all the carbonaceous materials studied. Thus, the high ash content
322 of NMPCBs which subsequently result in ash inhibition effect contributing to its weakest
323 interactions [33].

324 Table 4 shows the comparison of RMSII values between co-pyrolysis and CO_2 co-gasification
325 processes which were conducted under the same temperature but different atmosphere. From
326 Table 4, it is apparent that coal/oat straw blend showed higher interactions during gasification
327 process as demonstrated by its RMSII value which was over two times higher than that of

328 pyrolysis process. The reasons behind the aforementioned characteristics can be well
329 explained as follows.

330 It was observed that DTG curves for the devolatilisation stage in pyrolysis were similar to
331 those in CO_2 gasification so that the main DTG_{max} was almost coincided each other at the
332 same temperature. With the increase of temperature (above 900 °C), considerable additional
333 weight loss was noticed in CO_2 gasification process. This was because of the reaction of CO_2
334 with the remaining char (mostly) (Eq. 3) as CO_2 has reaction activity at high temperature
335 condition [34, 35]. Thus, it is confirmed that char gasification process played a key role for
336 these interactions.

337 $$C + CO_2 \rightarrow 2CO \quad (3)$$

338 Similarly, enhanced interactions were noticed for the blends of coal with each NMPCB and
339 tyre in CO_2 co-gasification. However, the enhancements in these blends were considerably
340 lower than that of coal/oat straw blend. This was due to the fact that char derived from
341 biomass are normally more reactive compared with those derived from other carbonaceous
342 materials such as NMPCBs. Furthermore, this phenomenon might be originated from mineral
343 content in these samples which will be discussed in the following section. Exceptionally,
344 coal/polystyrene blend had a slightly lower RMSII value in CO_2 gasification process which
345 revealed weaker interactions than in its pyrolysis process. This indicated the influence of CO_2
346 in polystyrene devolatilisation process as the contribution of C + CO_2 reaction is extremely

small since char content was literally zero. It is reported that the devolatilisation of polystyrene mainly occurred because of the breaking of C-C and C-H bonds [36]. During CO_2 gasification, CO_2 reacts randomly with these bonds [34]. Hence, coal/polystyrene blend is likely to demonstrate less interaction in this process as also presented in Table 4. Thus, it can be summarised that char gasification process increased the interactions on blends of oat straw, NMPCBs and tyre with coal while the devolatilisation process had a significant role on coal/polystyrene blend. Nonetheless, it is interesting to note that coal/polystyrene blend revealed the highest interactions in both processes as shown by its highest RMSII values compared to the other blends. This was due to the high volatiles content in polystyrene sample which will be detailed in section 3.5.

The aforementioned discussion has suggested that the mechanism of interactions between coal and carbonaceous materials were highly influenced by the properties and percentage of carbonaceous materials being added into the blends. Furthermore, the effect of CO_2 as gasification agent on interactions was also noticed.

Table 3: RMSII value of experimental and calculated DTG curves.

Carbonaceous materials	**RMSII** (SD±0.01)			
	Devolatilisation		**Char gasification**	
	10%	**30%**	**10%**	**30%**
Oat straw	0.10	0.09	0.26	0.71
NMPCBs	0.13	0.25	0.20	0.24
Tyre	0.06	0.10	0.18	0.60
Polystyrene	0.32	0.92	0.13	0.17

Table 4: Comparison of RMSII values between co-gasification and co-pyrolysis processes (70:30 blends).

Blends	CO_2 co-gasification	Co-pyrolysis
AC/OS	0.43	0.20
AC/NMPCBs	0.25	0.22
AC/tyre	0.29	0.25
AC/PS	0.56	0.60

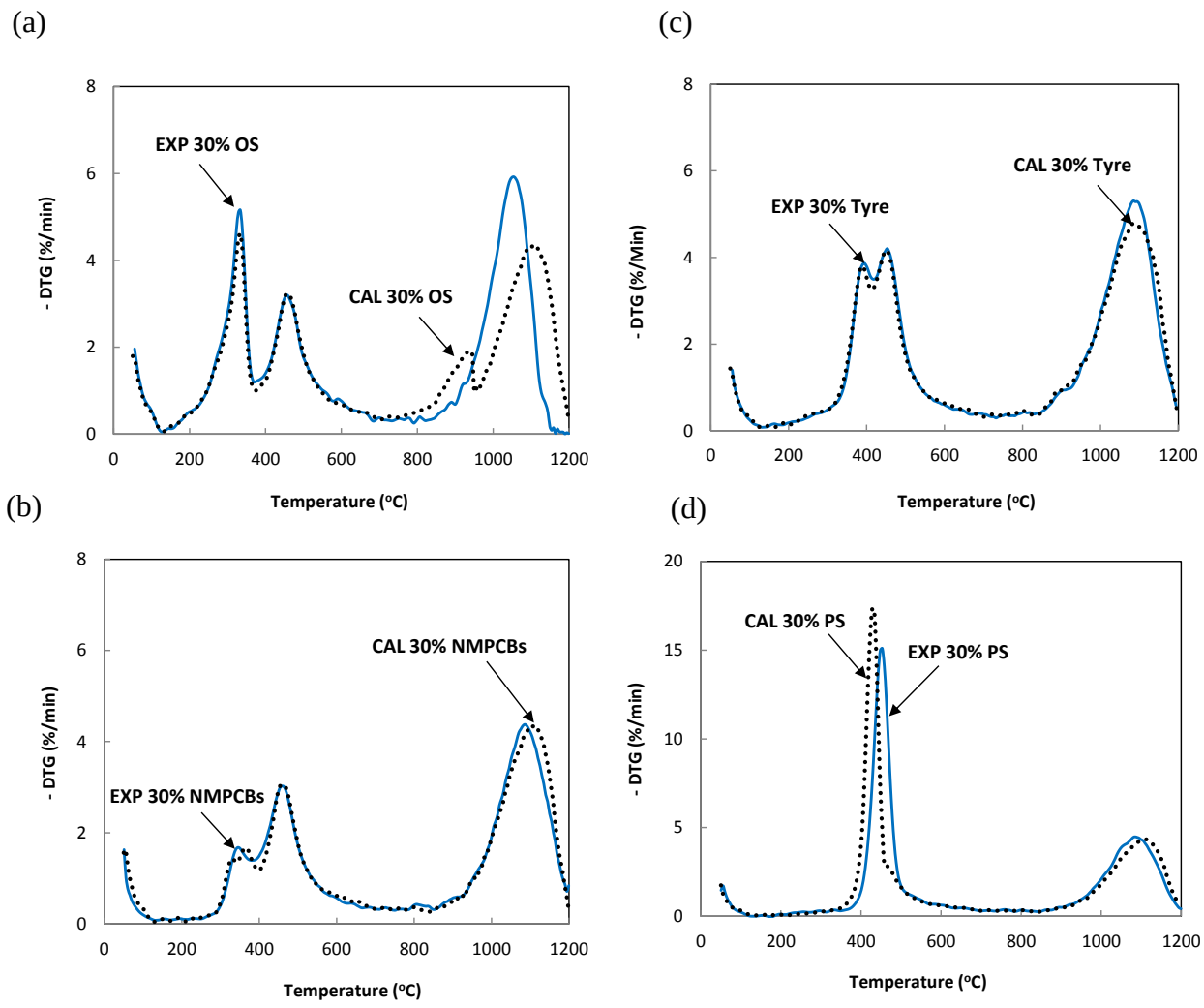

Figure 3: Comparison of experimental and calculated DTG curves of (a) coal/oat straw, (b) coal/NMPCBs, (c) coal/tyre and (d) coal/polystyrene blends.

3.5 Mechanism of interactions

In spite of blending equal proportions of different carbonaceous materials with coal, intensity and temperature at which interactions took place varied considerably. High level of volatile

content and high reactivity of carbonaceous materials were the reasons for the existence of interactions in the blends [19, 37]. As previously explained, at both low and high blending ratios, coal/polystyrene blends exhibited the highest interactions during devolatilisation stage. This was due to the generation of large amount of reactive free radicals from polystyrene cracking of as a result of containing a relatively higher amount of volatiles. The free radicals were released through thermal decomposition of polystyrene, which react with coal and enhance the devolatilisation and coal char gasification. In addition, the volatiles generated by coal can react with the gases resulted from the cracking of the heavy volatiles as well as light molecules (mostly hydrocarbon) derived from polystyrene. Therefore, a sluggish increment of the secondary char generation is observed because of the inhibition of reverse Boudouard reaction. Furthermore, the maximum weight loss rate also influences the generation of different kinds of radicals. The rate of radicals formation is increased by their stability; hence the conversion rate is greater when more stable radicals formed during devolatilisation process [38]. Applying this concept to carbonaceous materials, the maximum weight loss rate obtained by polystyrene is very high and this suggests the generation of stable radicals. This phenomenon also assisted to the significant interactions during devolatilisation stage. On the other side, even though NMPCBs had lower amount of volatiles, stronger interactions were observed at devolatilisation stage. This behaviour was due to epoxy resin, a main part of NMPCBs, which decomposed at relatively low temperature because of its high reactivity.

390 The interactions can also be caused by the catalytic effect of alkali and alkaline earth metals
391 (AAEM) contained in ash of the original samples [37, 39, 40]. It is reported that AAEM,
392 particularly, Ca and K species are active catalyst for gasification process [41, 42].
393 In the beginning of decomposition process, calcium, potassium and the other AAEM species
394 are combined with the carboxyl and phenolic groups, forming organic molecules in coal or
395 carbonaceous sample [43]. At the same time, the organic substances in the solid surface are
396 transformed to a micro-crystalline char, favouring the structure of char to become more
397 porous which enhances the reactivity in gasification [42].
398 Afterwards, this porous char adsorbs the AAEM onto its surface during the volatile-char
399 interactions stage [44]. Moreover, the presence of intermediate alkali-surface compounds
400 creates a bigger gap between AAEM and carbon which result in significant volume
401 expansion. These behaviours therefore contribute to the promotion of the gasification reaction
402 through weakening the carbon-carbon bonds present between layers [41].
403 As seen in Table 1, oat straw ash has demonstrated mostly the highest amount of these AAEM
404 among the others. In particular, CaO and K_2O in oat straw were found to be 10.6 wt% and
405 32.8 wt%, respectively, which were essential components for catalytic effect. Therefore, these
406 mainly contributed to the highest interactions in char gasification stage shown by coal/oat
407 straw blends compared with other blends. Meanwhile, the ash from NMPCBs, tyre and coal
408 samples contain a comparable percentage of AAEM, much lower than those of oat straw.

Moreover, ash compositional data showed that oat straw had high silica content which has been demonstrated to reduce the reactivity of char [45]. However, the proportion of silica in the other samples were relatively similar to each other, thus, the overall effect from silica was assumed to be similar regardless of types of samples. Similarly, alumina also acts as a deactivator for the catalytic effect [46]. As the lowest percentage of Al_2O_3 (2.2 wt%) was observed in oat straw ash, so that oat straw had the least obstacle to undergo the catalytic activities. It is worth noting that coal/tyre blend exhibited higher interactions than NMPCBs at high blending ratio despite both had almost equal percentage of AAEM. The reason behind these characteristics can be explained by Fe_2O_3 in the ash. Previous study revealed that metal oxide such as Fe_2O_3 increased the gasification activity of coal due to the catalytic effect in CO_2 gasification [47]. As tyre ash contain higher percentage of Fe_2O_3 (45.1 wt%), hence, it could act as a catalyst for char-CO_2 reaction.

4 Conclusion

CO_2 co-gasification of coal with four different waste carbonaceous materials was investigated in a thermogravimetric analyser. The influence of waste origin on the mechanism of interactions was also discussed. The main findings are summarised as follows: (i) significant high volatiles content of carbonaceous materials could plays a vital role in enhancing the degree of interactions during devolatilisation stage; (ii) AAEM metals content such as CaO and K_2O had a key influence on strong interactions in char gasification stage due to their

catalytic effect; (iii) the improvement of coal gasification performance is noticed as demonstrated by its gasification characteristics such as initial decomposition temperature and final mass loss temperature with the addition of carbonaceous materials, irrespective of stage at which the interactions occurred. The best performances of gasification process in CO_2 atmosphere were achieved by using polystyrene and oat straw as carbonaceous materials to be blended with coal. These phenomena were as expected mainly due to polystyrene having the highest volatiles content whereas oat straw presented the catalytic effect from its AAEM metals. Furthermore, the comparison between co-pyrolysis and CO_2 gasification processes by using RMSII values confirmed the influence of CO_2 as a gasifying agent on the presence of interactions in the blends. Hence, these experimental findings have confirmed that CO_2 gasification of coal can be considerably improved by adding polystyrene and oat straw into the process.

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