Co-pyrolysis of *Miscanthus Sacchariflorus* and coals: a systematic study on the synergies in thermal decomposition, kinetics and vapour phase products

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ABSTRACT

In this work, co-pyrolysis of *Miscanthus Sacchariflorus* (MS) and three ranks of coal, namely lignite (LC), bituminous coal (BC), and anthracite (AC), was performed at the analytical scale. The co-pyrolysis kinetic and products were analysed and compared theoretically and experimentally. The results revealed the synergistic effects of the coal rank and biomass blend ratio (BBR) on the thermal decomposition and the products in gaseous phase.

The co-pyrolysis of MS-LC and MS-BC samples was characterised by three distinct stages, which were sequentially dominated by moisture removal, decomposition of MS, and decomposition of coal. The activation energies of the co-pyrolysis process were different from the activation energies of the pyrolysis of individual MS and coal samples. The kinetics analysis showed that increasing the BBR increased the activation energies of the MS-coal blends up to 25% at the temperatures below 350 °C. However, at the higher temperature range, this decreased the activation energies of MS-LC and MS-BC blends but increased those of MS-AC blends. Both of the coal rank and BBR had noticeable impacts on the thermal behaviour during co-pyrolysis. The optimum positive synergistic effects were obtained on MS-LC blend with a BBR of 1:1. The FTIR analysis results showed the evolution profiles of CH_4, CO, CO_2, water, formic acid, phenol and xylene. All the products analysed showed L-peaks (250-400 °C) corresponding to MS decomposition. Increasing the BBR promoted the release of all the analysed products from MS-LC and MS-BC, indicating the synergistic effect of the co-pyrolysis.

Keywords: *Miscanthus Sacchariflorus*; biomass-coal blend; co-pyrolysis; synergistic effect

1. Introduction

Coal is the most widely used and distributed energy source worldwide. According to the BP Statistical Review of World Energy, there was over 3700 million tonnes of oil equivalent (mtoe) of coal consumed globally in 2017 [1]. Coal, as an essential fossil fuel, will continue to play a significant role in worldwide energy demands in the next a few decades. However, considering the excessive carbon emission from conventional coal combustion, seeking alternative solid fuel to replace the role of coal in the future energy matrix has become increasingly important [2, 3]. Biomass is considered a carbon-neutral and reliable energy resource. Large-scale utilisation of biomass for energy production reduces net carbon emission and the dependence on fossil source [4].

As a second generation bioenergy feedstock, energy crops have attracted wide attention and become broadly cultivated across Europe, due to its rapid growth, low mineral content, high availability and favourable carbon balance [5,6,7]. Miscanthus, *Miscanthus sacchariflorus* (MS) and asparagus are regarded as the most promising energy crops [8]. MS has strong adaptability, high growth rate and no competition with food production [9]. However, as a biogenic feedstock, MS shares the same utilisation challenges as other biomass feedstock have, including 1) property limitation due to the fact biomass contains a high levels of oxygen with high moisture and has low bulk density and low energy density; 2) seasonal availability, which result in complications in transport, storage and supply.

In the recent years, thermochemical conversion of biomass has been seen as an effective method to produce bioenergy and biofuels. Blending coal into biomass can enhance the feedstock quality in terms of reducing moisture content, improving the grindability and enhance the overall thermal reactivities. During the thermal conversion process, the hydrogen donor mechanism from lignocellulosic biomass is an important factor that impacts the synergistic effect. Meanwhile, the alkali and alkaline earth metals in biomass have a catalytic effect on the primary devolatilisation and secondary cracking, which can reduce the activation energy and increase the liquid and gas product yields. From a practical point of view, co-processing biomass with coal can mitigate also the biomass feedstock supply issues mentioned above. It is therefore a promising way to progress the transition from fossil heavy generation to low carbon and renewable generation, particularly in the largest coal consumers, such as China and India.

Considering co-processing, it is then important to research the interaction between different types of material. The synergistic effect is the result of two or more processes interacting to produce an effect that is greater than the cumulative effect that is produced individually [10, 11]. Synergistic effect, in the case of co-pyrolysis a combination of feedstocks, is essentially characterised by the reducing the activation energy of decomposition, the promoting the rate of devolatilisation and improving the product yield and quality. Synergistic effect can lead to the increase of productivity and process economic viability. A number of previous research works have identified synergies in co-pyrolysis of different types of coal and biomass. Haykiri-Acma et al. [12] studied co-pyrolysis of Hazelnut shell (HS) and different rank coals by TGA method. It was found that the addition of reactive HS led to some increases in the volatilisation rates of coals especially at temperatures below 500°C, showing synergistic effects between pyrolysis of HS and coals. The presence of HS led to increase of char yield for peat, but decrease of char yield for lignite. The HS addition did not affect the char yields of bituminous coal and anthracite significantly. It was concluded that the structure of biomass had some similarities with those of low rank coals in comparison to the higher rank coals, and the availability of the interactions between the constituents of biomass and low rank coals were more evident. Meng et al. [13] studied the co-pyrolysis characteristics of wood and different rank coals under five biomass blend ratios (BBRs). It was reported that the co-pyrolysis of coal with platanus wood (PW) could noticeably promote the devolatilisation by the existence of alkali and alkaline-earth metal (AAEM) in the biomass and large amounts of H and OH radicals generated during pyrolysis reactions of PW. However, it was argued that PW could also become soften and generate a large amount of soft residue during pyrolysis process. This residue could form coke and congest the pores of coal particles, and as a result inhibit the coal pyrolysis. Since the cohesiveness of bituminous was stronger than that of lignite, the inhibiting effects on lignite pyrolysis caused by soft residues adhesion were weaker than that on bituminous. Concerning the promotion of coal devitalisation, it was reported that the remarkable positive synergistic effects were obtained when the coal blend ratios were 30% for lignite and 50% for bituminous coal. These were demonstrated by the increase of devolatilisation rates by 6.4% and 11.1% for 30% lignite and 50% bituminous coal, respectively. The authors argued the main reason for the differences in the increase of devolatilisation rates were due to the difference in the structure of coal samples. Lignite had a weaker internal cohesive structure that bituminous coal and hence had a better interaction with biomass during the co-pyrolysis. Jeong et al. [14] studied co-pyrolysis of wood and bituminous coal under five blend ratios by TG method with real-time gas analysis. The synergy on the reactivity of co-pyrolysis was observed only at specific temperatures. The TG results showed promoted overall gas productionat temperatures between 450 and 500°C, and strong H_2 promotion at between 350 and 650°C. The synergy was strongly related to the evolution of H_2 during the pyrolysis. While there was no synergy in the char yield by co-pyrolysis, the liquid and total gas exhibited synergy for all blend ratios. He et al. [15] investigated the pyrolysis behaviour of rice straw and bituminous coal blends. The results showed that co-pyrolysis had little effect on char yields but the reaction rate was increased below 380°C. During co-pyrolysis, the secondary reaction of coal was inhibited at around 700°C. The graphitisation degree of biomass char increased, but the crystalline structure of coal char was deteriorated. The activation energy of the blends also changed at different pyrolysis stages. Guo et al. [16] studied the co-pyrolysis characteristics of lignite and pine sawdust in a TGA. This study found that the obtained activation energies were generally lower than the calculated values. Particularly in the conversion range of 0.2-0.6, most of the relative deviation values was lower than 10% for the blends, indicating positive synergistic effect between lignite and pine sawdust in volatiles release during non-isothermal pyrolysis. This attributed to that the reactivity of cellulose and lignin components in biomass were different from that of coal in the two stages. Qiu et al. [17] reported that the presence of poplar wood enhanced the thermal decomposition of lignite coal at a temperature range of 240-650°C during co-pyrolysis. The interaction between coal and biomass reduced their apparent activation energy and frequency factor. According to the author, this was mainly attributed to the release of hydrogen and hydroxyl radical from biomass along with the catalytic effects of alkali and alkaline earth metals on the cracking of volatiles. The added poplar had a positive effect on decomposition of the organic functional groups. Interactions would indirectly lead to higher hydrocarbon-generating potential and thermal maturity, and reduced aliphatic chains length and aromaticity. Lu et al. [18] reported that the synergistic effect of co-pyrolysis of Cryptomeria japonica and an anthracite coal was little. At high BBR, the activation energy of the blends was increased in the devitalisation stage, but decreased in the carbonization stage. This was attributed to that the reactivity of cellulose and lignin in biomass were different from that of coal in the two stages.

Other factors such as use of catalyst [13, 16, 19], pre-treatment [18, 20] and reactor configuration [16, 19, 21] can also affect the synergistic effect on the co-pyrolysis of biomass and coal. Some studies have been focused on the thermal behaviour and kinetic analysis of coal blended with different biomass, such as forestry residues[13,14,16,17], agricultural residue[15,19], microalgae [22, 23], switchgrass [21], sugarcane residues [24], shell [12, 20] etc.

Typical coal is rich in aromatic C=C bonds, but biomass is rich in O-H group and C-O group with highly variable content depending on species and culturing environment and conditions. Previous work has indicated that there was no general correlation on the thermal behaviour of different biomass and coal combination in co-pyrolysis process. Currently, there has been no comprehensive research reported the thermal behaviour of co-pyrolysis of the MS with coal. Hence there is still a knowledge gap in the fundamental study in this area. Considering the wide distribution and availability of MS and its strong potential as an important bioenergy feedstock to replace fossil resources, it is important to investigate the co-processing of MS with coal, in order to assess the potential of application and develop dataset that could be used in the process design and reactor development.

In this work, the co-pyrolysis of MS and three different ranks of coal (i.e. lignite, bituminous coal and anthracite) were studied using the thermogravimetric analysis method. The important kinetic parameters of the co-pyrolysis process were calculated and compared. The synergistic effect of the co-pyrolysis was evaluated and quantified by comparing TG characteristics between the experimental and calculated theoretical values. The characteristics and composition of the pyrolysis gas were evaluated using the infrared spectroscopy during the co-pyrolysis experiment.

2. Materials and methods

2.1. Biomass and coal materials

MS sample was obtained from a farm in Changsha City, Hunan Province, China. Lignite (LC), Bituminous coal (BC) and anthracite (AC) were received from different local coal mines in Hunan Province. The MS and coal samples were firstly milled, then sieved to fine particles of less than 74 μm. The tested blends were prepared with three different Biomass Blend Ratios (BBRs) i.e. 1:2, 1:1 and 2:1, in a mixer at a constant speed of 300 rpm for more than 12 hours. The proximate analysis, ultimate analysis, ash analysis and higher heating values (HHV) measurement of the received samples were performed in accordance to Chinese Standard Methods GB/T 212-2008, GB/T 31391-2015 and GB/T 1574-2007, respectively. Ash composition was analysed with an XRF (X-rayfluorescence) instrument (EAGLE III, EDAX Inc., USA). Three scanning points were analysed to obtain an average value, in order to minimize error. These parameters are presented in Table 1.

Table 1 Proximate, ultimate analysis and ash analysis of MS and coal samples

		MS	**LC**	**BC**	**AC**
Ultimate Analysis ^{a} (wt, %)	C	50.73	75.38	78.92	87.20
	H	7.08	4.41	5.75	2.09
	O*	41.95	18.20	12.46	7.65
	N	0.14	1.08	1.51	0.53
	S	0.10	0.93	1.36	2.54
Proximate Analysis ^{b}	Volatile	65.65	34.59	34.12	6.99

(wt, %)	Ash	5.34	19.21	16.31	13.39
	Moisture	10.67	3.71	5.03	3.20
	Fixed carbon	18.34	42.49	44.54	76.42
Heating Value ^{b} (MJ/kg)	HHV	17.00	18.74	23.23	28.40
Ash Analysis ^{b} (wt, %)	SiO_2	56.41	41.34	47.01	46
	Fe_2O_3	1.71	35.66	10.23	18.79
	Al_2O_3	0.65	16.67	21.48	14.81
	CaO	12.84	1.73	7.36	7.92
	SO_3	0.63	1.67	2.91	6.09
	K_2O	21.24	0.92	1.67	0.56
	TiO_2	0.51	0.90	1.68	0.60
	MgO	4.19	0.60	2.32	1.69
	Na_2O	1.23	0.37	2.28	1.80

^{a} Dry-ash free basis. ^{b} Air dried basis. * by difference.

2.2. TGA-FTIR method

Non-isothermal pyrolysis experiments were carried out using an Netzsch STA 449 TGA coupled to a Nicolet iS10 FTIR spectrometer. Approximately 10 mg sample was tested in each run. The sample was heated at a heating rate of 20 $°C\cdot min^{-1}$ from room temperature to 900 °C. Nitrogen with a purity of 99.999% was used to maintain an inert atmosphere. The volatiles produced were analysed by an online FTIR spectrometer with a capillary heated to 200 °C. The FTIR analysis was carried out at a resolution of 4 cm^{-1}, and the IR spectra was recorded from 4000 to 400 cm^{-1}. The test data was processed using the OMNIC software. To minimize the background noise in the TG and IR results, blank experiments were carried out before the samples. TGA runs were performed at least three times for each sample to assure the repeatability of the results. The average results were taken.

2.3 Analytical and calculation methods

2.3.1 *Pyrolysis kinetics*

During pyrolysis process, a great number of reactions take place simultaneously or consecutively. It is assumed that those reactions occur simultaneously and independently [25]. Applying Arrhenius equation, the pyrolysis reaction rate of a solid samples can be expressed as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\exp(-\frac{E}{\mathrm{R}T})\mathrm{f}\left(\alpha\right)\tag{1}$$

where α isthe conversion degree; A and E are the Arrhenius parameters-pre-exponential factor and activation energy, respectively; f(α) is the reaction kinetics which depends on the reaction mechanism; T and β arethe temperature of reaction and heating rate, respectively; R is the universal gas constant , which equals to 8. 314J/ (K·mol). The conversion degree α is derived from the equation $\alpha=(m_0-m_t)/(m_0-m_f)$ where m_0 is initial mass, m_t is instantaneous mass and m_f is final mass of the sample.

The function f(α) can be expressed as

$$\mathrm{f}(\alpha)=(1-\alpha)^n \tag{2}$$

where n isreaction order.

The integration function of Coats-Redfern at different reaction order is shown as below:

$$\ln\left[\frac{\mathrm{G}(\alpha)}{T^2}\right]=\ln\left[\frac{A\mathrm{R}}{\beta E}\right]-\frac{E}{\mathrm{R}T} \tag{3}$$

where G(α) is integral form of f(α), and it can be approximated by

$$\mathrm{G}\left(\alpha\right)=\frac{1-\left(1-\alpha\right)^{1-n}}{1-n} \qquad \text{if} \qquad n\neq1; \tag{4}$$

$$\mathrm{G}\left(\alpha\right)=-\ln(1-\alpha) \qquad \text{if} \qquad n=1. \tag{5}$$

For each reaction order n, the plot of $\ln[\mathrm{G}(\alpha)/T^2]$ versus $1/T$ becomes a straight line with slope E/R and the intercept $\ln[AR/\beta E]$. The reaction order is determined by comparing the correlativity of $\ln[\mathrm{G}(\alpha)/T^2]$ and $1/T$ which is analysed using the unitary linear regression equation.

2.3.2 *Evaluation of synergistic effects during co-pyrolysis*

In order to investigate the synergistic effects during the co-pyrolysis, a series of theoretical TG curves of MS-coal blends at different BBRs were calculated based on the experimental results of each individual coal and MS sample. Then the calculated values were compared with their experimental TG curves. The calculation of theoretical

TG curves at any given temperature are expressed as:

$$TG_{\mathrm{blend}} = x \cdot TG_{\mathrm{biomass}} + (1-x) \cdot TG_{\mathrm{coal}} \qquad (6)$$

where x and 1-x are the weight percentage of biomass and coal in the blends, respectively; TG_{blend}, TG_{biomass} and TG_{coal} are the weight loss for blend, biomass and coal, respectively.

The difference between the calculated and experimental TG curves are defined as:

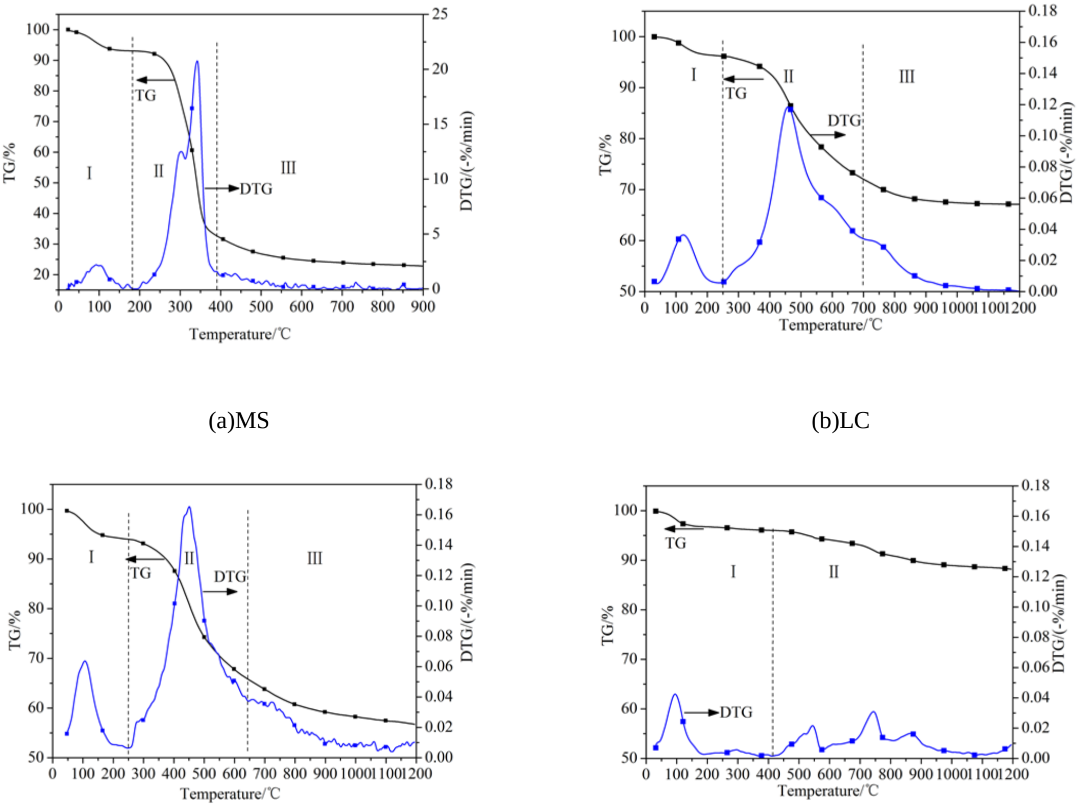
$$\Delta TG = TG_{\mathrm{exp.}} - TG_{cal.} \qquad (7)$$

Where ΔTG is the difference between the calculated and experimental values, which can be taken as an indicator of interaction; TG_{exp} and TG_{cal} are the calculated and experimental weight losses, respectively.

3. Results and discussion

3. 1 Characteristics of the TGA curves

Fig. 1 shows the TG mass loss curves for MS, LC, BC and AC samples with associated mass loss derivatives. In general, except AC, the pyrolysis processes of the other three types of samples were characterised by a three-stage thermal degradation, i.e. moisture removal, devolatilisation and carbonisation, but pyrolysis of AC only was consisted of two stages: moisture removal and carbonisation. The main decomposition of MS, LC, BC and AC took place in the second stage, with heating temperatures at 190-390, 250-700, 250-640 and 400-1000°C, respectively. The maximum peak intensity in the derivative thermogravimetry (DTG) of MS is 0.94 %/min at 345 °C, which is much greater than the maximum peak intensities for the coals (0.043-0.17 %/min). There are two peaks in the DTG of the LC and BC samples. The first peak is seen at 120 °C representing moisture removal and the second one at 450 °C representing devolatilisation. For the DTG of the AC sample, only one noticeable peak is shown in the first stage. At the end point of the non-isothermal TG analysis, the total percentages of the volatile released from MS, LC, BC and AC were 78.0, 32.9, 43.26 and 11.8 %, respectively.

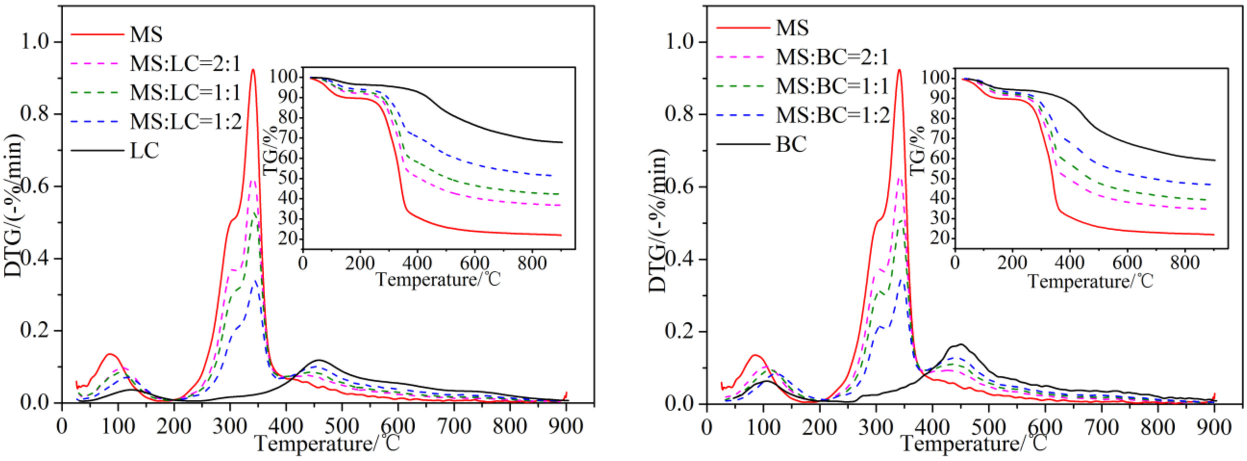


(a)MS (b)LC

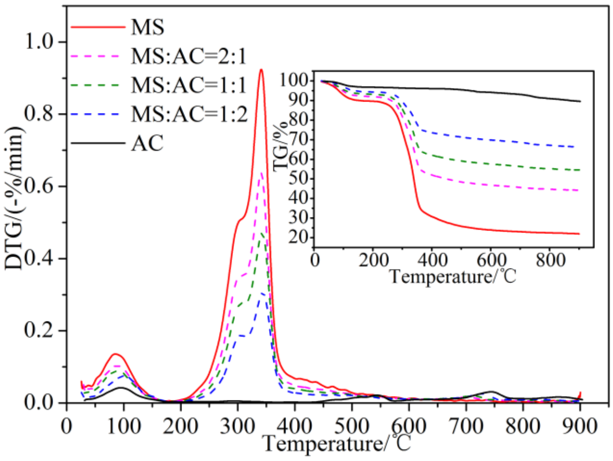
(c)BC (d)AC

Fig. 1. TG and DTG curves for pyrolysis of MS and coal samples

The noticeable differences in the quantity of volatile release are owing to the significant structural differences between biomass and coal. MS is consisted of mainly hemicellulose, cellulose and lignin macro-molecules, which are linked together by relatively weak R-O-R bonds. These three kinds of macro-molecule can be decomposed to smaller molecules under 500 °C [26]. It is well understood that pyrolysis of biomass starting with decomposition of hemicellulose (in the temperature range of 225-325 °C and then cellulose at 325-375 °C [27, 28]. The decomposition of lignin is in a wider temperature range between 250 and 500 °C. All of these contribute to the volatile production during pyrolysis. However, typical coals are composed of highly cross-linked aromatics, held together by significantly strong C-C bonds [26]. Compare to biomass, coal require higher energy to break the links. Hence, the more C-C bond is contained in the coal samples, the less volatile it can be produced under the same heating temperature.



(a)MS-LC (b)MS-BC



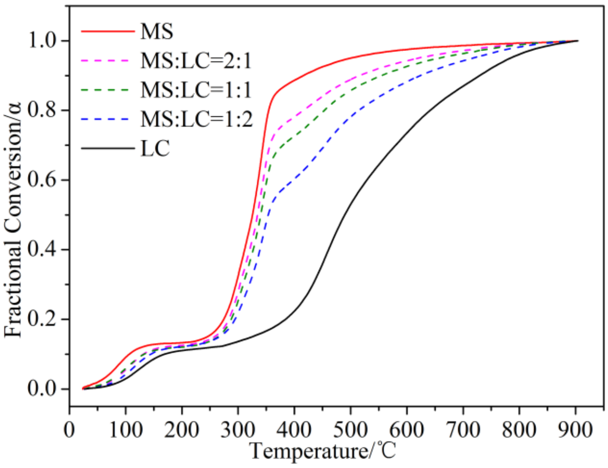
(c)MS-AC

Fig. 2 TG and DTG curves for pyrolysis of MS-coal blends

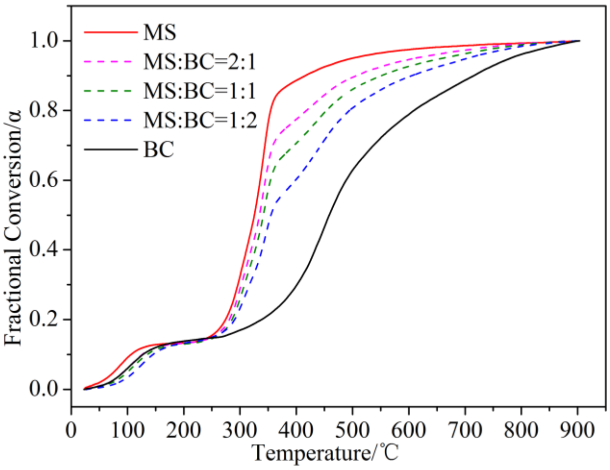
Fig.2 shows the TG and DTG curves of biomass and coal blends in different BBRs. Again, the co-pyrolysis of MS-coal blends also present a three stage decomposition characteristic. Similar to biomass pyrolysis, the first stage (around 100 °C) was for dehydration; the second stage (190-390 °C) represented the decomposition of MS and the third stage (about 450 °C) of MS-LC and MS-BC blends was due to coal decomposition. Most of the volatile release was seen in the last two stages and their DTG peak intensities were depended on the coal rank and BBR. It can be observed that increasing the BBR promoted the peak related to MS, but inhibited in the peak corresponding to coals. The TG curves shown in Fig. 2 also indicated that higher BBR resulted in lower solid residue left at the end point of the reaction (i.e. 900 °C). The solid residue of MS-LC at the BBRs of 1:2, 1:1, and 2:1 were 51.3, 42.3, and 36.8 wt.%, respectively.

3. 2 Kinetic analysis

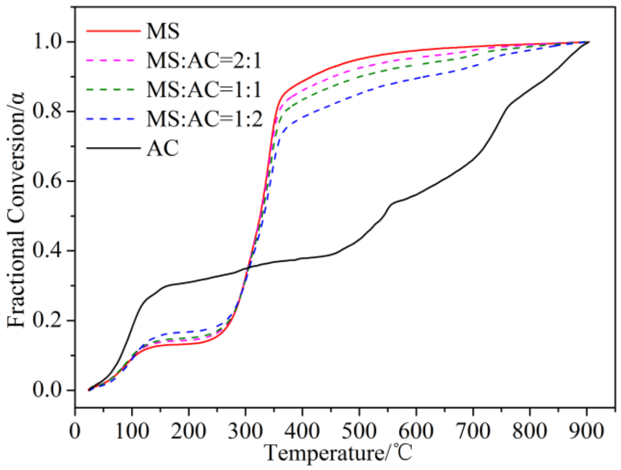
The results of fractional conversion degree *α* (calculated based on the experimental data from TG analysis) under different blend combination and BBRs are shown in Fig. 3. From the curves, it can be observed that, for a same BBR, the higher the coal rank, the higher temperature would be required to achieve a same thermal conversion degree (taking 0.95 char conversion as the reference point). This is evidenced by the fact that AC blends required a temperature of 880 °C to achieve the reference conversion degree, comparing to LC and BC which required 790 °C and 840 °C respectively. By contrast, the temperatures of MS-coal blends under the same BBR were significantly different, showing strong coal rank dependence. Specifically, to reach the reference conversion degree at BBR of 1:2, the temperatures required by the MS-LC, MS-BC, and MS-AC blends were approximately 745, 725, and 752°C, respectively. At all BBRs, the variation of fractional conversion degree with temperature of MS-coal blends was in a similar tendency. Considering the effect of BBR variation on a certain blend, the higher the BBR ratio, the less heat it would require to achieve a same conversion degree.



(a)MS-LC



(b)MS-BC



(c)MS-AC

Fig. 3 Pyrolysis of MS-coal blends- variation of fractional conversion degree with temperature

Considering the pyrolysis of MS-coal blends was a combination of the pyrolysis of individual biomass and coal samples, the reaction kinetics of blends in the second and third stages can be calculated based onthe kinetics of MS and coal samples in their corresponding stages. By applying the Arrhenius equation and the second order reaction, the pre-exponential factors and activation energies of MS, coals and their blends at three BBRs were calculated. The results are shown in Table 2. All the derived R^2values were greater than 0.9808, proving that the pyrolysis processes in these two stages were well correlated. The activation energy of MS was the highest being 98.66 KJ/mol, which was more than twice higher than those of LC, BC and AC. Increasing the BBR lead to an increase of the activation energy in the second stage. Specifically, when the BBR increased from 1:2 to 2:1, the activation energies of MS-coal blends at the temperatures under 350 °C increased from 84.54 to 105.71 kJ·mol^{-1} for MS-LC blends, from 81.65 to 99.24 kJ·mol^{-1} for MS-BC blends and from 101.9 to 111.35 kJ·mol^{-1} for MS-AC blends. As shown in Table 1, the volatile of MS was 65.65%, which was much larger than the volatiles of coals (6.99-34.59%). The volatiles from MS formed carbonaceous deposits which may cover the surface of the coal particles, resulting in reduction in the reaction rate of the blends and increased activation energies [13,16].A similar correlation was reported by Li et al when performing co-pyrolysis of coal and rice straw [29].

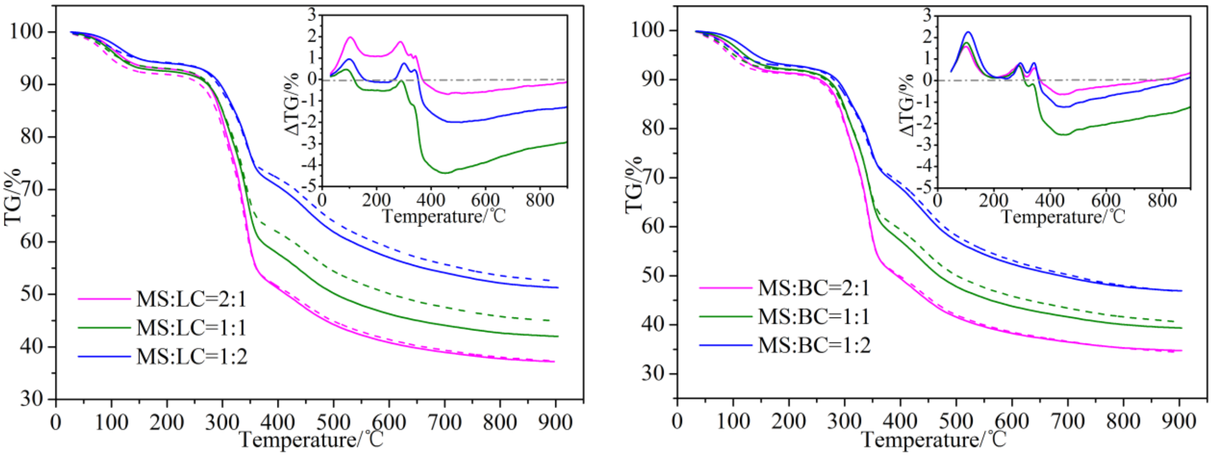
Table 2. Kinetic parameters of individual MS and coal samples and MS-coal blends at three BBRs

	Stages	Temperature/°C	E_a/kJ·mol^{-1}	A/min^{-1}	R^2
MS	Second stage	190-390	98.66	2.30×10^{8}	0.9889
LC	Second stage	373-690	48.85	329.14	0.9923
BC	Second stage	290-640	45.26	70.34	0.9864
AC	Second stage	450-580	44.65	45.11	0.9808
MS:LC= 1:2	Second stage	250-373	84.54	4.08×10^{6}	0.9961
	Third stage	373-600	27.44	23.86	0.9898
MS:LC=1:1	Second stage	250-373	99.44	1.42×10^{8}	0.9971
	Third stage	373-600	25.43	27.82	0.9912
MS:LC=2:1	Second stage	250-373	105.71	6.59×10^{8}	0.9969
	Third stage	373-600	24.63	31.76	0.9929
MS:BC= 1:2	Second stage	250-373	81.65	2.15×10^{6}	0.9946
	Third stage	373-600	32.07	64.26	0.9948
MS:BC= 1:1	Second stage	250-373	96.82	7.59×10^{7}	0.9951
	Third stage	373-600	28.90	53.54	0.9961
MS:BC=2:1	Second stage	250-373	99.24	1.70×10^{8}	0.9966
	Third stage	373-600	27.76	61.01	0.9971
MS:AC=1:2	Second stage	250-373	101.90	2.92×10^{8}	0.9976
	Third stage	373-600	9.37	0.75	0.9958
MS:AC=1:1	Second stage	250-373	106.92	1.05×10^{9}	0.9974
	Third stage	373-600	13.57	3.34	0.9991
MS:AC=2:1	Second stage	250-373	111.35	3.05×10^{9}	0.9963
	Third stage	373-600	18.09	12.50	0.9995

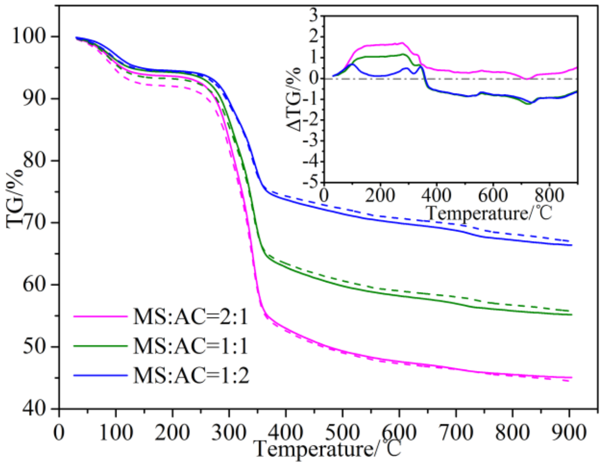
At the third stage shown in the TG curve, coal played an important role in determining the activation energy. Increasing BBRs caused a decrease in the activation energy of the MS-LC and MS-BC blends, but an increase in that of the MS-AC blend. As discussed above, high BBR ratio means more chances of biomass volatiles to form carbonaceous deposits on the samples surface to inhibit further reaction. As for AC which had little volatile, the obstruction of the volatiles deposit was dominant. A similar correlation has been reported by Guo et al [16] and Qiu et al [17], who also the reported lower actual activation energies than the calculated values during co-pyrolysis of lignite and biomass. Meng et al [13] further pointed out that the increase of BBR can reduce the activation energy of biomass and bituminous coalblends. In addition, adding biomass into coal also reduced the thermal conductivity of the samples which can also cause reduced reaction rate. When comparing the activation energies of MS-coal blends, the MS-AC blend at a given BBR generally had the highest activation energy in the second stage but the lowest value in the third stage. This was in an agreement with the results from Lu et al [19], when they performed co-pyrolysis of Cryptomeria japonica and anthracite coal.

3.3 Synergetic effects during co-pyrolysis

Fig. 4 shows the plots of the ΔTG curves developed from the experimental and calculated TG of the blends under three BBRs. There were three noticeable differences between the experimental curves and the calculated curves, which revealed the synergistic effects between the MS and coals during the co-pyrolysis of the blends.



(a) MS-LC (b) MS-BC



(c) MS-AC

Fig.4. Comparison of experimental and calculated TG curves for pyrolysis of MS-coal blends

As seen in Fig. 4, apart from the MS-LC blend at BBR of 1:1, nearly all ΔTG value between room temperature and 350°C were greater than zero. This meant that the experimental weight loss values were higher than those of calculated values for MS-coal blends. At the same temperature the higher the ΔTG value, the less weight loss the process had during co-pyrolysis. This proved the hypothesis of the coal devitalisation inhabitation by biomass discussed in the last section. MS started to devolatilise at around 190 °C and this generated a large amount of soft residues which could adhere to coal particle surface and reduce the thermal conductivity and congest the initial devolatilisation of coal which began from about 250 °C. Nevertheless, with the increase of heating temperature the inner pressure of particles increased because of the gas expansion and the MS residues may start to flow and be pyrolysed, which was beneficial to volatiles release [30,31]. Above 350 °C, all the ΔTG valueexpect MS-AC blend at BBR of 2:1were less than zero, which meant the value of experiment was lower than that of calculated for MS-coal blends. The actual experimental weight losses were higher than those of calculated values at the same temperature. This meant that positive synergistic effects on promoting the devitalisation existed between MS and coals during co-pyrolysis processes above 350 °C.

From Fig. 4, it can be observed that both coal rank and BBR have significant impacts on the thermal behaviour of the co-pyrolysis. Concerning the impact of BBR, the weight loss difference between the experimental value and calculated value was found the largest in the BBR of 1:1, followed by 1:2 and 2:1. For the coal rank, the largest weight difference was found in LC blends, followed by BC and AC. The reasons for this the synergistic effects were threefold. Firstly, the presence of high levels of hydrogen and oxygen elements in the form of free radicals [31]. As shown in the ultimate analysis, the molar ratios of H/C and O/C were 1.68 and 0.62 for MS, but only 0.70 and 0.18 for LC, 0.87and 0.12 for BC, 0.29 and 0.06 for AC respectively. During co-pyrolysis process of MS and coal, large amounts of free radicals were generated during MS devitalisation, which acted as hydrogen sources and may participate in the coal decomposition [31]. It was well understood that the H and OH radicals had significant influences on coal pyrolysis by preventing the secondary condensation, recombination and cross-linking reactions, resulting in decreased secondary char yields and promoted volatile production [32]. Secondly, the promotion of volatiles release from coal can also be attributed to the introduction of high level Fe_2O_3, CaO and K_2O from biomass, as shown in results of ash analysis in Table 1. Previous works have demonstrated the catalytic effects of Fe, Ca and K oxidises and chlorides which could be used to crack the long carbon chain and break the carbonyl groups of the coal structure, leading to the increase in the production volatiles yields [30, 33]. However, with the temperature increase, the MS could melt and generate large amounts of soft residues during pyrolysis process, which cohered to the surface of the coal prior to its initial decomposition [30]. Thirdly, since the cohesiveness of bituminous coal was stronger than that of lignite, the inhibiting effects on lignite pyrolysis caused by soft residues adhesion were weaker than that on bituminous. Thus, LC was more likely to get the remarkable positive synergistic effects than BC. At a low BBR (e.g. 1:2), these synergistic effects between MS and coal were not noticeable. When increasing the BBR, the synergistic effects between MS and coal promoted by the three mechanisms mentioned above were enhanced. The strength of the synergistic effects was determined by the competition among these three mechanisms. When BBR was high the synergistic effect was weakened probably because the negative effects of biomass was dominant. In addition, the cohesiveness of bituminous was stronger than that of LC [31], hence the inhibiting effects on LC pyrolysis caused by soft residues adhesion were weaker than that on BC. AC had the smallest specific surface area and the least catalytic effect of minerals on it. Thus, the optimum positive synergistic effects were obtained when BBR was 1:1 for MS-LC blends.

3.4 Vapour phase product analysis

The FTIR analysis can provide information of an organic compound by generating a specific absorption profile. During pyrolysis, CH_4 (at wavenumbers of 3100-2800 cm^{-1}), H_2O (3800-3500 cm^{-1}), CO (2240-2040 cm^{-1}) and CO_2 (2390-2250 cm^{-1}) were the major gaseous products. The evolution profiles of CH_4, H_2O, CO, CO_2, phenol, formic acid and xylene from pyrolysis of MS-coal blends are showed in Fig. 5-11. The product evolutions corresponded to the TG profiles of the feedstocks shown and discussed in Section 3.1. Specifically, the main product release from MS mainly occurred at the temperature range from 250 to 400 °C and that of coals mainly occurred at a higher temperature range from 400 to 900°C. The product evolution profiles of MS-coal blends were analysed and discussed in two stages, namely the low temperature peak (referred as L-peak) from 250 to 400 °C and the high temperature peak (referred as H-peak) above 400°C.

From Fig 5, no production of CH_4 was seen until the temperature was increased to 250 °C. All the three blends presented the first CH_4 release at L-peak, but only MS-LC and MS-BC blends presented H-peaks at about 550 °C. The CH_4 release at L-peak was mainly from MS, and the highest peak of CH_4 release corresponded to the maximum peak intensity in the DTG of MS at 345°C (Fig.1). Hemicellulose and lignin contributed to the releasing of CH_4 from biomass pyrolysis, likely because of the decomposition of methoxyl ($-O-CH_3$). At the BBR of 2:1, the L-peak of the CH_4 evolution profiles of MS-LC and MS-AC blends were 29.5% and 14.8% higher that of MS, respectively. The CH_4 release from MS-BC blends and MS were almost identical, with a difference less than 2%. This suggested that co-pyrolysis of MS and coal had a moderate synergistic effect, especially when the BBR was 2:1. For the CH_4 evolution profiles of MS-coal blends, the H-peaks of MS-LC and MS-BC blends were related to LC and BC, respectively. They corresponded to the peaks at 450 °C representing devolatilisation the DTG of the LC and BC samples (see Fig.1). But for the DTG of the AC sample (see Fig.1), there was no volatile matter released at high temperatures, so the MS-AC blends did not present an H-peak. Blending affected the H-peak of the CH_4 evolution profiles in the form that increasing BBR caused a decrease in the H-peak intensity representing LC or BC. The H-peaks of the CH_4 evolution profiles of MS-BC blends under three BBRs were noticeably higher than that of BC because of the synergistic effect. CH_4 was generally released from $-OCH_3-$ and $-CH_2-$ groups in coal and biomass 0.

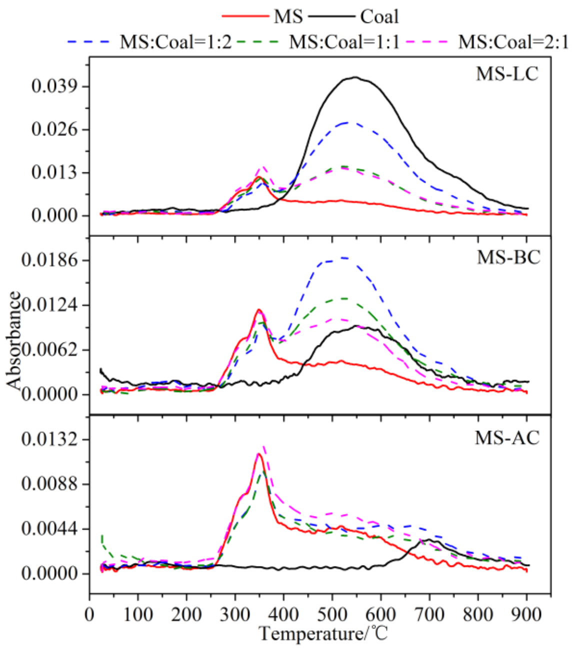


Fig.5. CH_4 evolution for pyrolysis of MS-coal blends

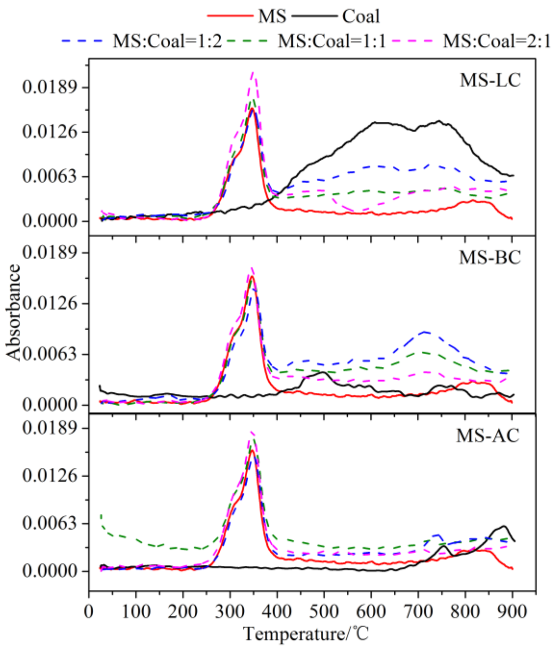


Fig.6. CO evolution for pyrolysis of MS-coal blends

As shown in Fig. 6, the CO evolution profile covered a temperature range from 250 to 900 °C with the highest peak shown at about 350 °C. For MS-coal blends, the L-peaks in the CO evolution profile were close to that of MS, and the H-peaks of MS-LC and MS-BC blends differed depending on the coal rank of the samples. Same to the case of CH_4 evolving, the highest peak of CO release corresponded to the maximum peak intensity in the DTG of MS at 345°C (Fig.1), which reflected the pyrolysis of hemicellulose and cellulose. BC released much more CO than LC, and consequently the MS-BC blends produced higher amount of CO than the MS-LC blends. The L-peaks in the CO evolution curves of the blends were higher than that of MS, especially at the BBR of 2:1. This indicated that the addition of coal could promote the CO release from MS. Concerning the H-peak, increasing the BBR led to a decrease in the H-peak intensity. It is worth noting that the H-peakof the blends were higher than that of the BC, particular at a BBR of 1:2. The H-peaks were shown from approximately 450 °C reaching to the highest at 750 °C for MS-LC blend and 700 °C for MS-BC blend, respectively. The precursors that produce CO is known to be related to alky aryl ethers at 400 °C, methylene bridges and aryl ethers at about 550 °C, and high condensed structures at 700 °C[35]. FTIR analysis showed that aryl ethers and aliphatic groups were degraded at about 550 °C, which provides a good agreement between the results reported here and in the literature [36].

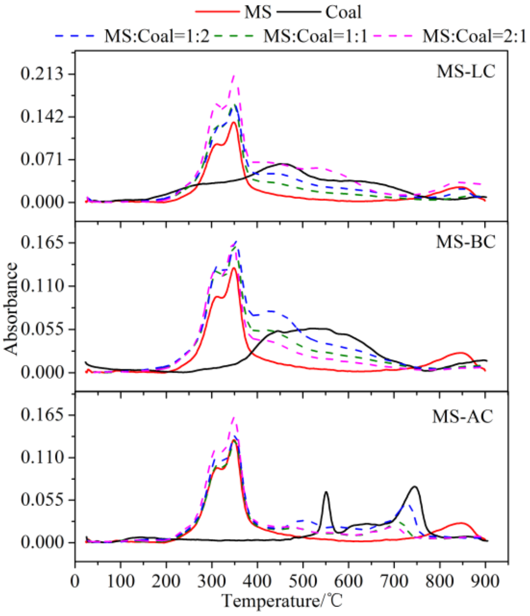


Fig.7. CO_2 evolution for pyrolysis of MS-coal blends

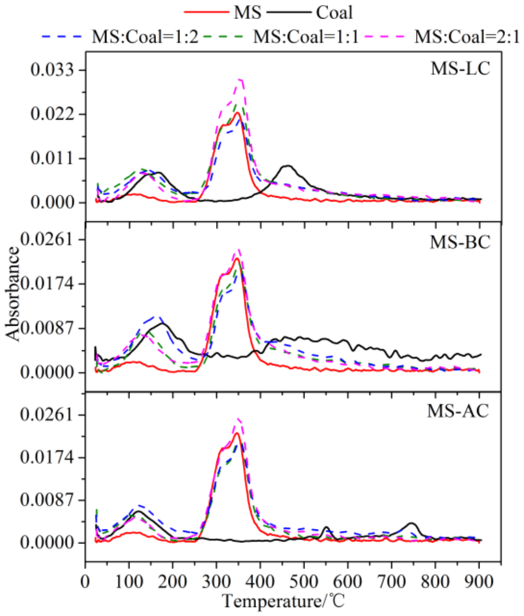


Fig.8. H_2Oevolution for pyrolysis of MS-coal blends

Fig. 7 shows the CO_2 evolution profile between 200 and 800°C. All the MS and blends samples showed the highest CO_2 intensity at above 350 °C. The CO_2 release from MS was highly intensive at the range of 200-400 °C. The CO_2 release was mainly from hemicellulose at low temperature, possibly attributed to the cracking and abscission of C-C and C-O bonds connected with the main branch of hemicellulose. Hemicellulose and lignin likely contributed to the releasing of CO_2 at high temperature. The L-peaks of the MS-coal blends were higher than that of MS, which was similar with the trend of CO evolution profile. This meant that the addition of coal could promote the CO_2 release from MS pyrolysis. The CO_2 production could mainly be correlated to the decomposition of carboxylic groups and esters[36]. It is know that alkyl aryl ethers could also be ascribed to CO_2 precursors because they were degraded at 380 °C. Increasing the BBR caused an increase in the L-peak intensity, but a decrease in the H-peak intensity. It is worth noting that most of H-peaks for CO_2 in the blend samples shown at temperatures about 50-100°C lower that the coal, indicating a synergistic effective in co-pyrolysis. At higher temperatures, CO_2 were derived from thermally stable ether structures (mainly aryl ethers), carboxylates, quinones, and oxygen-bearing heterocycles. Arenillas et al [37] reported that the formation of CO_2 from bituminous coals and lignite was due to the existence of intramolecular carboxylic acid anhydrides. Hence, the CO_2 release from LC and BC pyrolysis was relatively high. Consequently, this led to the difference in the CO_2 evolution profile in the co-pyrolysis. The CO_2 release from MS-LC and MS-BC was intensive at 400-700 °C, but that from MS-AC started from 500 °C and was relatively minor. It corresponded to the TG and DTG of coal samples (Fig.1), LC and BC had presented a high degree of mass loss between 400 and 700 °C, whilst AC had almost no mass loss above 500°C

Fig. 8 shows the evolution profile of H_2O during pyrolysis. The first sets of peaks (between 110 and 150 °C) were attributed to the moisture evaporation from the samples, and these corresponded to the TG and DTG of all samples. The water evolution of MS from 250 to 400°C was attributed to the decomposition of various oxygen-containing groups, mainly OH groups in the cellulose and hemicellulose, leading to the formation of pyrolysis water over a broad temperature range. Blending slightly affected the L-peak in the H_2O evolution profiles. Increasing BBR caused an increase in the L-peak intensity. At BBR of 2:1, the L-peak intensity of the H_2O evolution profiles was larger than that of MS. This was likely because the interaction of biomass and coal promoted the decomposition of various oxygen-containing groups in the blends. Comparing the profiles of other gases, the L-peaks in water profile of the blends were well matched to the L-peaks of CO, CO_2 and part of CH_4.

The phenol and formic acid evolution profiles of MS-coal blends are shown in Fig. 9 and 10 respectively. It was observed that all the blend samples had similar L-peaks to MS, which corresponded to the decomposition of MS in the temperature range of 250-400 °C (see the TG and DTG of MS in Fig.1). It is known that formic acid was produced from the cleavage of oligosaccharides, and phenol was mainly produced by the degradation and cracking of biomass macromolecules, which were formed by the polycondensation of aromatic structures and hydrogenated aromatic structures in biomass. Coal rank and the BBR affected the L-peaks of the phenol and formic acid evolution profiles. Increasing BBR caused an increase in the peak intensity of the phenol and formic acid evolution profiles. At the MS-LC BBR of 2:1, the L-peaks intensity of the phenol and formic acid evolution profiles were higher than that of MS, which indicated that the addition of coal could promote the phenol and formic acid release from MS.

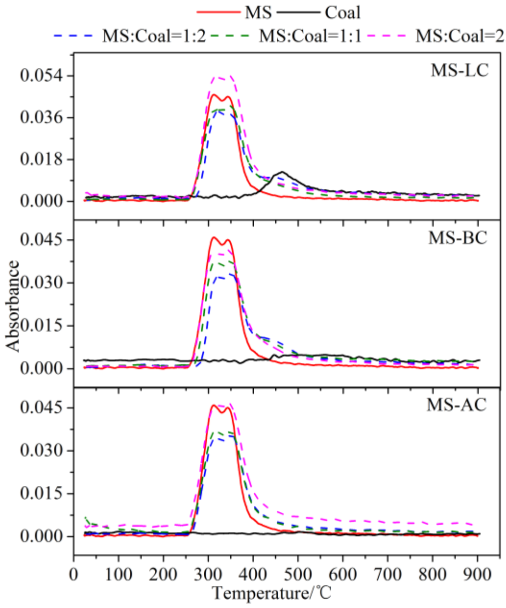


Fig.9. Phenol evolution for pyrolysis of MS-coal blends

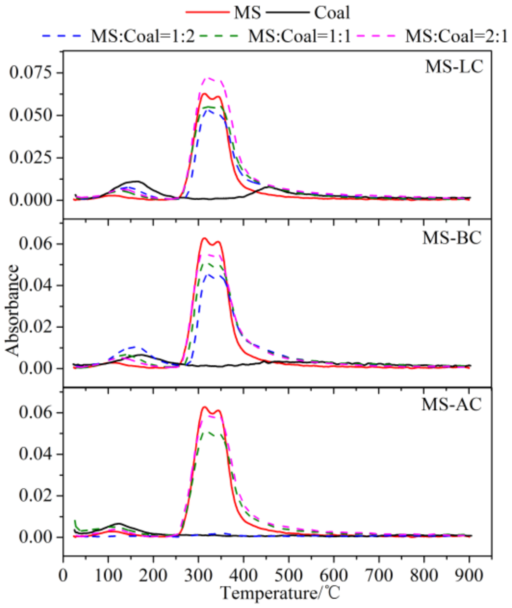


Fig.10. Formic acid evolution for pyrolysis of MS-coal blends

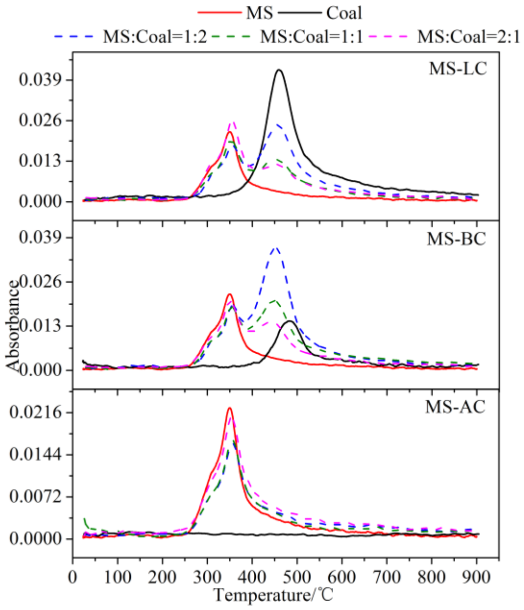


Fig.11. Xylene evolution for pyrolysis of MS-coal blends

The L-peak of xylene evolution profile of MS-coal blends was similarity that of MS, and the H-peak of MS-LC and MS-BC blends differed depending on the coal rank of the samples, as illustrated in Fig. 11. Blending affected the L-peak of the xylene evolution profiles. Increasing the BBR caused an increase in the L-peak intensity. Concerning the effect of BBR, increasing the coal fraction in MS-coal blends led to an increase in the H-peak intensity of the xylene evolution profiles of MS-LC and MS-BC blends. The H-peak of the xylene evolution profiles of MS-BC blend were higher than that of BC, while that of MS-LC blend were lower than that of LC. This was similar to the tendency of CH_4 and CO. It reported that CH_4 was conducive to produce more tar with lighter fraction due to the recombination of radical fragments originated from methyl and methylene groups [38].

4. Conclusion

The co-pyrolysis of miscanthus, three ranks of coal and their blends were studied in this work. TGA-FTIR method was used to characterise the thermal decomposition behaviour, kinetics and the synergy effect of the co-pyrolysis process.

The TGA resultsshowed that the pyrolysis of the MS-LC and MS-BC blends were characterizsd by a three-stage thermal degradation. The first stage was due to the dehydration of MS and coals, the second stage between 190 and 390 °C was from the thermal decomposition of MS; and the third stage from 450 °C was due to coal decomposition. Pyrolysis of the MS-AC only showed the dehydration and carbonisation stages. Increasing the BBR led to an increase in the intensity of the MS decomposition peak, but a decrease to the peak intensity corresponding to coals. The higher the BBR, the less the weight of solid residue at the end of pyrolysis. Concerning pyrolysis of coals, a high rank coal required a higher temperature to complete the pyrolysis reaction. Increasing BBR raised the activation energy in the second stage. Coal played a dominating role in determining the activation energy. Increasing the BBR led to a decrease the activation energy of MS-LC and MS-BC blends, but an increase in the activation energy of the MS-AC blends. The orders of magnitude of the weight loss difference between the experimental and calculated values were

1:1>1:2 >2:1 in terms of BBR and LC>BC>AC in terms of coal rank. The optimum positive synergistic effect was obtained on MS-LC blend with a BBR of 1:1.

The FTIR analysis results showed the product evolution profiles of CH_4, CO, CO_2, water, formic acid phenol and xylene. All the products analysed showed L-peaks (250-400 °C) that were corresponding to the decomposition of MS. Increasing the BBR promoted the release of all products from MS-LC and MS-BC, indicating the synergistic effect of the co-pyrolysis. There were also releases of CH_4, CO, CO_2 and xylene from coal decomposition at H-peak range (over 400 °C). Increasing the BBR slightly reduced the releases of CH_4, CO, CO_2 and xylene products.

In thefuture work, it can be considered to utilise the in-situ DRIFTs to investigate the catalytic effect of the inorganic components in terms of promoting the coal devolatilisation and vapour secondary cracking. This will be useful to provide information to develop the fundamental mechanism of the synergy from co-pyrolysis of MS and coal.

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