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Synergistic effect on co-pyrolysis of capsicum stalks and coal

Yanqing Niu, Houzhang Tan*, Xuebin Wang and Tongmo Xu

State Key Laboratory of Multiphase Flow in Power Engineering,Xi'an Jiaotong University, Shaanxi 710049, China.

With the depletion of fossil fuel and the concern about environmental issues, the utilization of biomass resources has attracted increasing worldwide interest. The pyrolysis behavior of capsicum stalks and Baoji coal mixtures was investigated by TG-DSC. Results show that the thermal degradation temperature range of capsicum stalks was 290 to 387°C, while that of Baoji coal was 416 to 586°C. According to the comparison of experimental values and calculation results based on the algebraic sum of the fraction of individual mixture samples, the synergistic effect was significant at temperature ranges of 314 to 369 and 431 to 578°C. The synergistic effect could also be seen from the kinetic studies performed according to the Fried man Method. The rate of mass loss and k in the experiment is higher than the calculated values in the range of 314 to 368°C and that in the experiment is lower than the calculated values in the range of 431 to 578°C. Meanwhile, it was indicated that the pyrolysis process of capsicum stalks, Baoji coal and their mixtures could be described by one, two and four first order reactions, respectively.

Key word: Pyrolysis, capsicum stalks, mixing rate, kinetics, synergistic effect.

INTRODUCTION

With the depletion of fossil fuel and the concern about environmental issues, the utilization of biomass fuel has attracted increasing worldwide interest. Capsicum is an important cash crop and value-added processing product. The world production of red pepper has reached 14 to 15 million tons a year. India has 0.915 million hectares of cultivated area with 1.018 million tons of yield (Kulkarni and Phalke, 2009). Spain, where there is over one million tons annual output, is the most important pepper producer in Europe (Gonzalez-Diaz et al., 2009). According to the statistics of UN Food and Agriculture Organization, the capsicum production in China, which has ranked first with an annual output of 2.8×10^7 tons, accounting for about 46% of the world's total output, still grows at a rate of 9%

each year (Hou et al., 2006). Thus, the yield of capsicum stalks (CS) is huge in China. How to utilize the plant stalks to produce energy in an efficient and environmentally friendly way is of great importance.

Biomass can be converted to higher quality fuels by gasification (Brown et al., 2000; Moilanen et al., 2009), integrated gasification combined cycle (IGCC) (Uson and Valero, 2006), combustion (Youssef et al., 2009) and so on, but pyrolysis, as one of the promising thermochemical conversion means, plays a vital role in the conversion. So far, numerous studies based on pyrolysis and co-pyrolysis has been carried out. The products of pyrolysis are influenced by the content of hemicelluloses, cellulose and lignin in biomass. Hemicelluloses have a higher CO_2 yield, cellulose has a higher CO and lignin has a higher H_2 and CH_4 (Yang et al., 2007). Pyrolysis is also affected by heating rate and particle size (Biagini et al., 2008; Bridgeman et al., 2007; Haykiri-Acma et al., 2006). Meanwhile, the effect of additives on the pyrolysis has been performed (Brown et al., 2000; Muller-Hagedorn et al., 2002). Sodium and potassium chloride have a remarkable effect on the product distribution.

*Corresponding author. E-mail: tanhouzhang@yahoo.cn.

Abbreviations: CS, Capsicum stalks; **IGCC,** integrated gasification combined cycle; **BC,** Baoji coal; **DSC,** differential scanning calorimetry; **TG,** thermogravimetry.

Table 1. The proximate and ultimate analysis of BC and CS.

Sample	Composition	BC	CS
Proximate analysis	M_{ad}	7.38	4.44
	A_{ad}	19.10	5.17
	V_{ad}	37.66	71.79
	FC_{ad}	35.86	18.60
Ultimate analysis	C_{ad}	57.89	44.04
	H_{ad}	3.34	3.94
	O_{ad}	10.98	41.19
	N_{ad}	0.60	0.91
	$S_{t,ad}$	0.71	0.31

At present, whether there exists interaction between the mixtures still fails to have a unified point of view. The synergistic effect during co-pyrolysis of plastic blends occurs mainly in the high temperature region (higher than 530°C), the thermal degradation of plastics is with one first-order reaction, low volatile coal is described by three first-order reactions (Zhou et al., 2009). Aboulkas and Harfi (2008) reported that a significant interaction is observed at 443 to 656 K for olive residue and poly blends. Sharypov et al. (2002) examined the combination of biomass with synthetic polymer mixtures and reported that biomass is thermally degraded at a lower temperature than the polyolefin, and independent thermal behaviors are observed for each component of biomass/plastic mixtures. Garcia-Perez et al. (2001) and Vuthaluru (2004) reported that there is no significant interaction between blends.

Therefore, the aim of this work is to understand the characteristics of co-pyrolysis of CS/coal blends with different mixing rates (γ). Experiments in a DSC-TGA were performed. The pyrolysis was carried out by continuously weighing only a micro sample of fuel at a constant heating rate. Synergistic effects were also deduced from the comparison of the mass loss, rate of mass loss and kinetic parameters of CS and Baoji coal (BC) blends. Additionally, kinetic studies were performed with the Fried man method (Antal et al., 1998; Biagini et al., 2008; Garcia-Perez et al., 2001; Zhou et al., 2009).

MATERIALS AND METHODS

Materials

The feedstock materials used in this work included CS, BC obtained from Baoji, Shaanxi province and corresponding mechanically synthesized mixtures (CS10BC90, CS20BC80 and CS40BC60). Here, CS10BC90 means that CS takes up 10% and BC 90% weight, respectively, and the latter two have the same implication. The capsicum stalks were crashed with a micro crasher, and then dried at 105°C for 12 h. Finally, the particles were further ground by the coal pulverizer and sieved with size ranges of 198 ~ 450 μm for the experimental purpose. The particle mass of BC, which is less

than 100 μm, takes up 80.01% of the total mass. The mixtures were kept homogeneous as much as possible by mixing in a certain proportion and subsequent rolling (Zhou et al., 2009) for 12 h. Some characteristic parameters of the used BC and CS are given in Table 1.

Experiment techniques and instruments

A thermal balance (NETZSCH-490PC, GERMANY) was applied in the experiment. Differential scanning calorimetry (DSC) analysis was performed along with thermogravimetry (TG), the mass of sample was approximately 6 mg and the temperature range was from room temperature to 1300 at 30°C/min. Purified nitrogen (99.999%) at a flow rate of 100 ml/min was used as carrier gas to provide an inert atmosphere for pyrolysis and to remove the gaseous and condensable products. An Electronic Balance (AEL-200, Shimadzu in Japan) with an accuracy of one ten thousandth was used to weigh the mixtures in different proportions. In addition, a microgram balance (Sartorius Company, Germany) with an accuracy of one millionth in tolerance was used to weigh the sample. The reproducibility of the experiments is acceptable and the experiment was carried out two times.

RESULTS AND DISCUSSION

Effect of mixing rate on pyrolysis

To investigate whether there is interaction between CS and BC, a theoretical thermogravimetr/derivative thermo-gravimetry (TG/DTG) curve is calculated by the following equation:

$$w_{\text{blend}} = x_1 \times w_{\text{CS}} + x_2 \times w_{\text{BC}} \qquad (1)$$

Where, w_{blend} represents the algebraic sum of individual components in the mixture; w_{CS} and w_{BC} represent the mass loss of each material under the same operational condition; x_1, and x_2 are the mass fraction of CS and BC in the mixtures. The calculated and experimental curves for CS/BC mixtures at different mixing rates (10, 20 and 40%) are illustrated in Figure 1. The corresponding characteristic parameters are given in Table 2.

In Figure 1a and b, it is apparent that there are three mass loss peaks and the later two are overlapped, the first one denotes the loss of water. In comparison with the isolated raw material, it could be deduced that the second peak (305 - 371°C corresponding to 304 to 387°C of the isolated CS pyrolysis) is chiefly the CS pyrolysis and the third peak (430 to 588°C corresponding to 416 to 586°C of the isolated BC pyrolysis) corresponds to the BC pyrolysis. Similar observations are reported by Vuthaluru (2004). And it can be noted that the initial temperature (T_{i2}) increased from 1 to 10°C, terminal temperature (T_{f2}) decreased from 16 to 19°C, the initial temperature (T_{i3}) increases by about 15°C and the fluctuant terminal temperature (T_{f3}) wass also affected by γ. Overall, the peak intervals, ΔG_1 and ΔG_2, increase linearly at the mixing
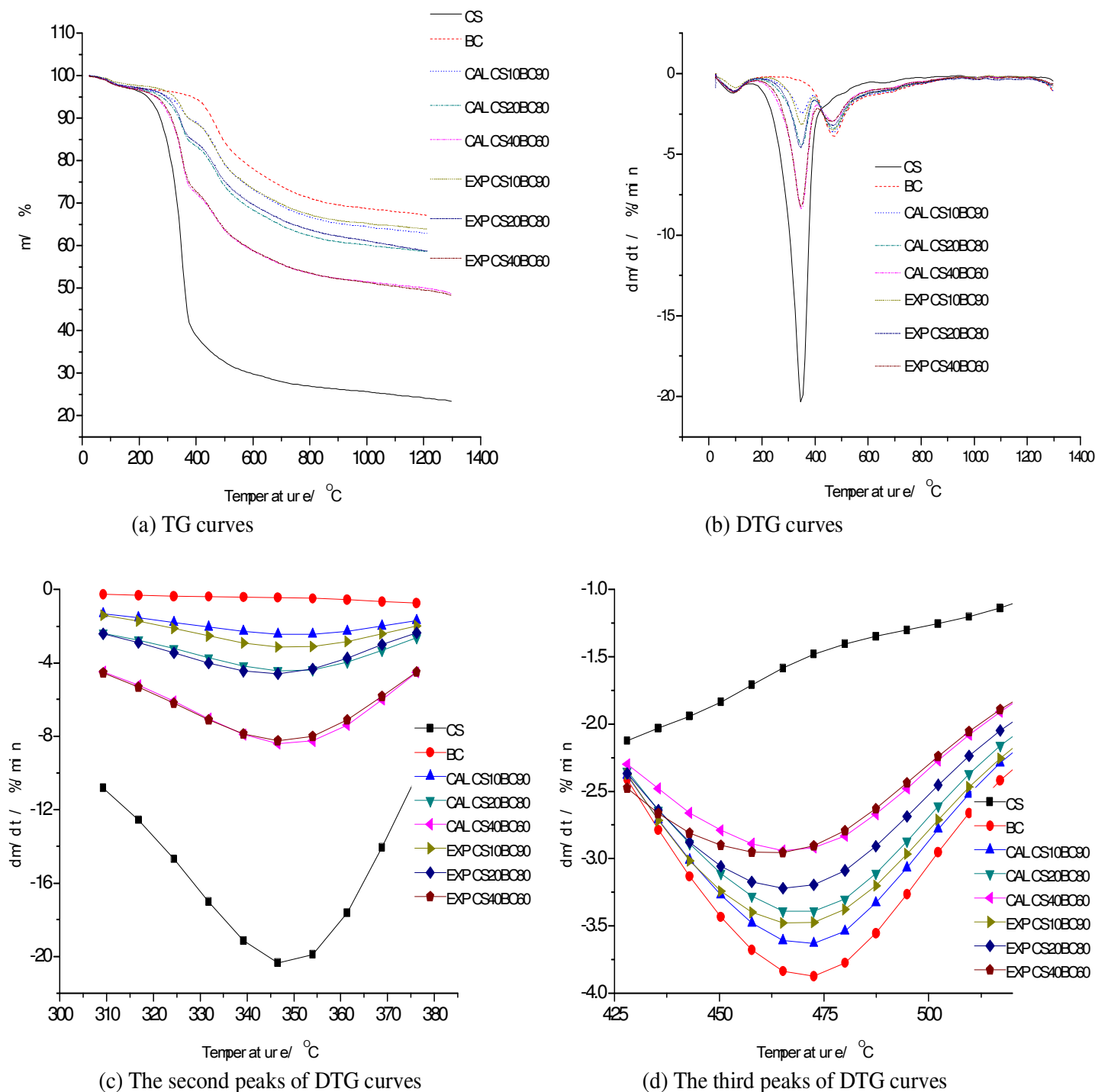
Figure 1. TG-DTG curves vs. temperatures of blends; γ = 10, 20 and 40%; β = 30°C/min; Size: 198 to 450µm; N_2 = 100 ml/min. a, TG curve; b, DTG curves; c, the second peaks of DTG curves; d, the third peaks of DTG curves.

rate and corresponding residues decrease linearly due to the linear increase in CS. This can be explained by the fact that BC contains more fixed carbon and more stable dense polycyclic aromatic hydrocarbons (Vuthaluru, 2004). Furthermore, there is a higher mass loss rate of the

experimental data than that of the calculation values in the range of 314 to 368°C (Figure 1c) and an opposite trend in the range of 431 to 578°C (Figure 1d). All this indicates that the interaction had significant impact on the degradation of CS/BC blends when compared with the

Table 2. Characteristic parameters of CS and BC determined by DSC-TGA in different γ.

Sample	CS10BC90	CS20BC80	CS40BC60	CS	BC
T_{i1}/°C	94.7	-	71.4	65	76.9
T_{p1}/°C	98.6	95.6	95.6	90.1	96.2
T_{f1}/°C	122.2	-	120.3	109.5	131.9
ΔG_1/%	2.36	2.62	3.18	2.93	3.25
T_{i2}/°C	314.6	308.5	305.8	304.5	416.5
T_{p2}/°C	348.7	345.6	347.6	348.7	471
T_{f2}/°C	367.6	366.3	371	386.8	586.1
ΔG_2/%	8.58	12.85	24.61	73.74	31.18
T_{i3}/°C	431.1	431.1	430.1	-	-
T_{p3}/°C	467.7	466.2	462.2	-	-
T_{f3}/°C	588.3	577.9	582	-	-
ΔG_3/%	26.44	27.35	23.93	-	-
Residues/%	62.62	57.18	48.22	23.33	65.57

isolated raw materials at temperature ranges of 314 to 368 and 431 to 578°C. Other authors also reported the interaction between different mixtures. Zhou et al. (2009) reported that the synergistic effect during co-pyrolysis occurs mainly in the high temperature region (higher than 530°C), the margin calculated and experimental values are stable at 2.0 to 2.7%. But Aboulkas and Harfi (2008) reported that a significant interaction is observed at 443 to 656K. On the contrary, Garcia-Perez et al. (2001) and Vuthaluru (2004) reported that there is no significant interaction between mixtures.

Kinetic analysis

TGA provides general information on the overall reaction kinetics; it could be used as a tool to provide comparison of the kinetic data of various reaction parameters only with a single micro sample. Presently, we have employed the first order reaction and kinetic parameters obtained from the following expression (Antal et al., 1998; Biagini et al., 2008; Garcia-Perez et al., 2001; Zhou et al., 2009)

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \qquad (2)$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = -\frac{E}{R} \cdot \frac{1}{T} + \ln\frac{AR}{\beta E} \qquad (3)$$

Where, m_0, m_∞ and m are initial mass (sample mass), terminal mass (residues mass) and actual mass; α(%) is the pyrolysis rate corresponding to m; T(K) is the thermodynamic temperature; E (kJ/mol) is the activation energy; R (J/mol/K) is the universal gas constant (8.314); A (min^{-1}) is the frequency factor; $β$ is the heating rate

(°C/min). The data of mass loss measured from the TGA and the temperature for the tested samples are used to determine the two-side parameters of Equation 3. The calculated plot ln [-ln (1-α)/T^2] versus 1/T is able to provide a straight line with an intercept of ln($AR/\beta E$) and a slope of $-E/R$, thus enabling it to obtain kinetic parameters E and A. According to Equations 2 and 3, the calculated kinetic parameters, such as E and A, are given in Table 3. On the basis of the Arrhenius expression, we have calculated the chemical reaction constant (k) as shown in Table 3, which shows the combined effect of E and A. And corresponding fitting curves are plotted in Figure 2. As shown in Figure 2, the pyrolysis process of CS, BC and their mixtures can be described by one, two and four first order reactions, respectively.

It can be seen from Table 3 that k was the highest with 40% γ. It was also found that there was a higher experimental k than the calculated value in the range of 314 to 368°C and a lower experimental k than the calculated value in the range of 431 to 578°C, which shows that there are higher mass loss rate of the experimental data than that of the calculated values in the range of 314 to 368°C and an opposite trend in the range of 431 to 578°C (Figure 1). This demonstrates therefore, that there is synergistic effect on co-pyrolysis of CS/BC mixtures.

Conclusions

The thermal degradation temperature range of CS is 290 to 387°C and that for BC is 416 to 586°C. Three thermal peaks are observed during the co-pyrolysis of CS/BC blends, the first one denotes the loss of water, the second indicates the result of dominant CS pyrolysis and the third corresponds to the BC pyrolysis. The chemical reaction constant k is the highest with 40% γ. By kinetics analysis and comparing experimental and calculated data,

Table 3. Kinetic parameters for full testing[a].

Sample	TR/℃	Fitting equation	r	E/kJ·mol^{-1}	A/min^{-1}	ET/℃	k/ min^{-1}
BC	413-516	y=-5646.9x-6.5074	-0.99659	46.96	5.27E-02	450	2.14E-05
	516-591	y=-1587.7-11.694	-0.99288	13.19	9.64E-08	550	1.40E-08
CS	301-391	y=-7480.7x-1.1389	-0.99071	62.16	1.63E+04	350	9.97E-02
EXP CS10BC90	308-368	y=-4853.8x-6.5638	-0.99288	40.34	3.98E-02	350	1.65E-05
	368-427	y=-1037.4x-12.507	-0.98884	8.62	9.68E-09	400	2.07E-09
	427-516	y=-3447.1x-9.0556	-0.99735	28.65	9.10E-05	450	7.74E-07
	516-590	y=-1039.9x-12.125	-0.99222	8.64	2.34E-08	550	6.62E-09
EXP CS20BC80	301-369	y=-5121.0x-5.8582	-0.99494	42.56	2.13E-01	350	5.75E-05
	369-428	y=-692.06x-12.77	-0.97719	5.75	3.53E-09	400	1.26E-09
	428-510	y=-2376.4x-10.367	-0.9978	19.75	3.06E-06	450	1.14E-07
	510-584	y=-667.48x-12.557	-0.98722	5.55	5.55E-09	550	2.47E-09
EXP CS40BC60	301-369	y=-6099.0x-3.8846	-0.99735	50.68	2.39E+01	350	1.34E-03
	369-428	y=-636.46x-12.377	-0.93557	5.29	8.01E-09	400	3.13E-09
	428-517	y=-1252.8x-11.506	-0.99539	10.41	1.17E-07	500	2.07E-08
	517-584	y=-165.5x-12.89	-0.86105	1.38	6.40E-10	550	5.23E-10
CAL CS10BC90	308-368	y=-2985.2x-9.543	-0.9904	24.81	2.57E-05	350	2.13E-07
	368-427	y=938.37x-12.711	-0.97524	7.8	5.48E-09	400	1.36E-09
	427-516	y=-3533.5x-8.9973	-0.99695	29.36	1.07E-04	450	8.05E-07
	516-590	y=-1025.9x-12.192	-0.99045	8.53	1.98E-08	550	5.69E-09
CAL CS20BC80	301-369	y=-4383x-6.9774	-0.99373	36.43	1.39E-02	350	1.22E-05
	369-428	y=-596.56x-12.848	-0.96161	4.96	2.54E-09	400	1.05E-09
	428-510	y=-2486x-10.159	-0.99795	20.66	5.17E-06	450	1.66E-07
	510-584	y=-731.5-12.401	-0.98351	6.08	8.72E-09	550	3.58E-09
CAL CS40BC60	301-369	y=-5927.8x-4.1167	-0.99514	49.26	1.36E+01	350	1.00E-03
	369-428	y=-417.7-12.658	-0.84504	3.47	2.75E-09	400	1.48E-09
	428-517	y=-1260.9x-11.467	-0.99634	10.48	1.29E-07	450	2.26E-08
	517-584	y=-165.55-12.857	-0.87755	1.38	6.90E-10	550	5.65E-10

[a]CAL, EXP and TR are the abbreviation of calculated, experimental and temperature range, respectively; r is correlation coefficient; ET represents the selected temperature used to calculate chemical reaction constant k.
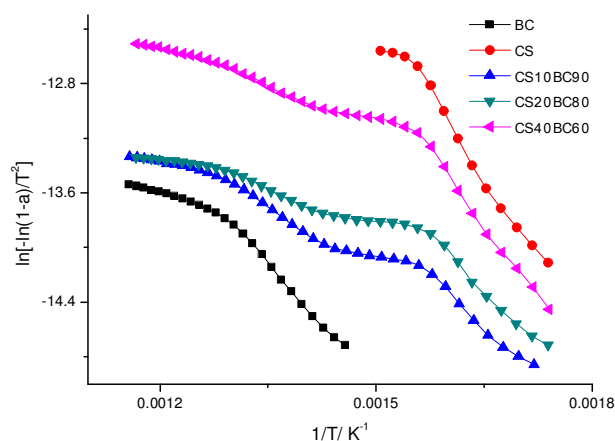

Figure 2. The fitting curves of all testing samples; β = 30℃/min; size = 198 to 450 μm.

it was found that the rate of mass loss and *k* in the experiment is higher than that in the calculated values in the range of 314 to 368°C and that in the experiment is lower in the range of 431 to 578°C. The synergistic effect is significant in the temperature ranges of 314 to 369 and 431 to 578°C. It was also found that the pyrolysis process of CS, BC and their mixtures can be described by one, two and four first order reactions, respectively.

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