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ScienceDirect
Energy Procedia 66 (2015) 297 – 300
Energy Procedia

*The 12th International Conference on Combustion & Energy Utilisation – 12ICCEU

Thermal Behaviour of Corn/Cotton Stalk Blends during Co-pyrolysis

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Abstract

The pyrolysis behaviors and pyrolysis kinetics of corn straw（YM）, cotton stalk(MG) and blends at different proportion were studied by TG-DSC technique. The results indicate that two kinds of biomass straw can be mixed fully. The pyrolysis process with its blend ratio is not a linear relationship and solid product reduced compared with single-stalk. In addition, the major pyrolysis process of mixture within the main range can be well described by a two-dimensional diffusion model with Malek method. Among the tested samples, the 40:60 MG/ YM blend shows the lowest activation energy of 51.7 KJ/mol. Besides corn straw plays a dominant role on the course of the thermal conversion. The experimental results may provide useful data to promote the application of biomass thermochemical conversion technology of biomass mixture.

Peer-review under responsibility of the Engineering Department, Lancaster University

Keywords: Pyrolysis，Mixture proportion，Cotton stalk，Corn straw

1. Introduction

As a renewable source, biomass has become increasingly important for the production of energy. Over the last two decades, current energy consumption of biomass accounts for about 14% of total word energy consumption, second only to oil, coal, and nature gas [1]. The mixing techniques study of the biomass pyrolysis is relevant as it is the initial step of biomass combustion, pyrolysis, briquetting technology and other major routes of biomass utilization technology. As an important step of gasification, liquefaction, carbonization and combustion, the pyrolysis behavior and characteristics play an extremely important role in the design, behavior prediction and operation parameters specification of the reactor [2]. However, the mutual influence study of typical biomass has been a controversial issue. Presently, there are no systematical researches reported about pyrolysis of mixture of corn straw and cotton stalk. In this paper, some pyrolysis experiments of blends were conducted by simultaneous thermal analyzer. The study described in this paper was focused on interaction, thermal properties and reaction kinetics of biomass straw blends.

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Peer-review under responsibility of the Engineering Department, Lancaster University
doi:10.1016/j.egypro.2015.02.062

2. Experimental

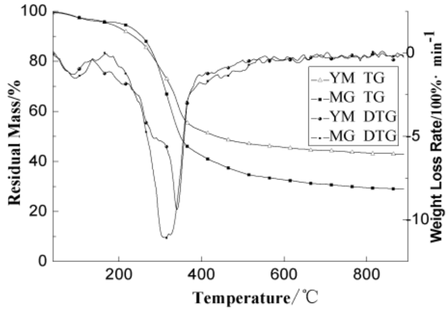
Typical agricultural straw in the Anhui China, corn straw and cotton stalk were chosen for investigation. The materials were milled twice for more tiny particles (more than 90% were particles below 80 mesh) in a laboratory mill after being mixed with their different mixture ratios. After being sieved on a vibration sieve for 15 min, the milled powder between the screen of 80 mesh and 120 mesh was collected. All analyses were performed three times. Ultimate and proximate analyses of the samples are shown in Table 1.The experiments were performed from ambient temperature up to the maximum temperature of 1173 K at the constant heating rate of 20 K/min. The sweeping gas was 70ml/min nitrogen (99.999%).

Table 1. Analysis data of corn stalk and cotton stalk

Proximate analysis					Chemical composition analysis			Ultimate analysis			
	M	V	A	FC	Cellulose	Hemicellulose	Lignin	N	C	H	S
MG	8.37	62.9	13.6	21.9	42.0	24.0	15.0	1.09	41.8	5.7	0.11
YM	8.31	80.9	11.99	13	41.7	27.2	20.3	0.69	43.0	5.9	0.06

3. Results and discussion

3.1 Experimental results



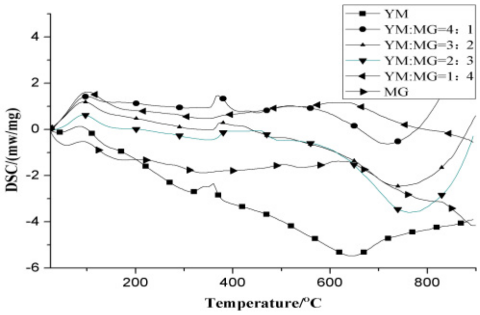


Fig 1. TG-DTG curves of cotton stalk and corn straw **Fig 2.** DSC curves of blends under different proportion

Fig 1 shows TG and DTG curves drawn using recorded experimental data of corn straw, cotton stalk. Comparison of TG and DTG curve shows that the whole process can be divided into the well-known four stages: Drying of biomass, Heating of biomass, Degradation of biomass, Heating and aggregation of char.

Table 2. Characteristic parameters of pyrolysis of blends under different proportion

Samples	$(dx/dt)_{max}$	T_{max}	Ts	M
MG	11.2	307	260	28.80%
20%MG+80%YM	10.6	332	245	29.70%
40%MG+60%YM	11.8	337	250	29.30%
60%MG+40%YM	9.2	340	243	38.10%
80%MG+20%YM	11.4	338	237	30.90%
YM	9.3	341	232	43.50%

$(dx/dt)_{max}$ (wt.%/°C) :The maximum weight loss rate , T_{max} (°C) Corresponding temperature of the maximum weight loss rate, Ts(°C) Initial pyrolysis temperature , M(100%): Residual mass.

From Fig 1 and Table 2, great differences are found among the pyrolysis behaviors of the samples. Corn straw starts its decomposition easily, with the weight loss mainly happen at 220-315°C. It gets the maximum mass loss rate 9.3% at 307°C, and there is still 55.6% solid residue left even at 900°C. Cotton stalk pyrolysis is focused at a higher temperature range with the maximum weight loss rate 11.2% at

332°C. When comparing the two kinds of biomass stalk, cotton stalk is the more difficult to decompose. DSC curve of corn straw is significantly lower than the rest of several sets of mixture. Corresponding temperature of the endothermic peak is increased with corn straw/cotton stalk blend ratio increase. Wang et al. [3] in corn straw pyrolysis experiments also reaches the similar conclusion.

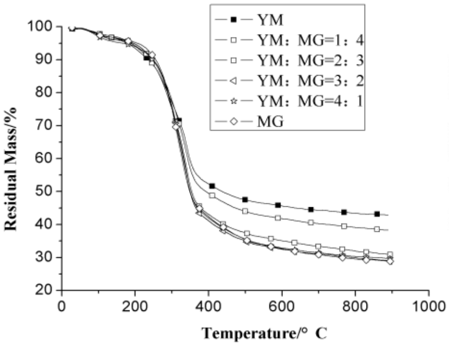


Fig 3. TG curves of corn stalk, cotton stalk mixtures under different proportion

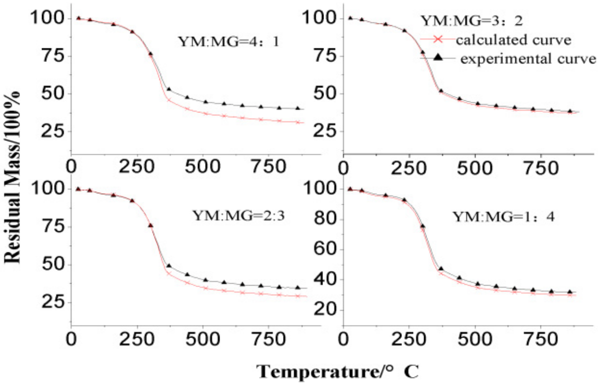


Fig 4. TG curves of corn straw-cotton stalk mixtures and calculated data

Fig 3 show that within the main range, the TG curves of the samples pyrolysis show a similar tendency, pyrolysis parameters vary from blend ratio. Corresponding temperature of the maximum weight loss rate: cotton stalk is 307°C, while corn straw and mixture under different proportions' maximum mass loss happen in a wide temperature range from 332°C to 341°C. The main reason was that corn straw had relatively high cellulose content and low lignin content which was consistent well with the industrial component analysis of the samples. Comparisons of TG curves under different proportion are showed curves of blends are smoothly. It is also shown that the cotton stalk and corn straw can be fully mixed, and they are prone to copolymerization and co-eutectic effect.

Figure 4 shows calculated and experimental weight loss curves of blends under different blend ratio. The calculated weight loss curves are calculated from corn straw and cotton stalk weight loss curves in proportion superposition, while the experimental curve is drawn by blends pyrolysis results. Comparing pyrolysis behaviors of biomass stalk with blends in different proportions, there are some differences between pyrolysis parameters and the final product. It can be seen that there is not linear relationship between the mass of solid product and blend ratio. It is indicated that cotton-corn stalk mixture pyrolysis characteristics is the result of the two joint action pyrolysis process. Synergistic effects also are deduced from the comparisons of mass loss versus temperature and char yield profiles of corn straw, cotton stalk and corn straw/cotton stalk blends. Overlap of the two individual behaviors, difference of absorption or liberation of heat range, scattered pyrolysis temperature difference may be the factors lead to this interaction.

3.2 Kinetic Analysis

Studies of the thermal degradation of biomass samples are a matter of major interest for determining the reaction mechanism and kinetic parameters [5]. It is evident that accurate kinetic models are needed in order to design the pyrolysis process. Several researchers have investigated pyrolysis of Cotton stalk, rice straw, plankton , et al [6,7]. Co- pyrolysis of biomass straw is a relatively new area. So in order to select the best reaction model, Malek method is applied and eight kinds of common solid pyrolysis reaction models are selected to fit the calculation in this paper. In general the results obtained in the present work clearly indicate that the two-dimensional diffusion model is the most probable reaction mechanism function.

Then the pre-exponential A and the activation energy E of the reaction are obtained. The results of the kinetic analysis were summarized in Table 3. Among the tested samples, corn straw shows the lowest activation energies of 54.5 KJ/mol. The activation energy values and pre-exponential values of cotton straw samples are higher than those of corn straw samples. Pyrolysis kinetics calculation results are consistent with thermal decomposition weight loss rule, and low activation energy of the reaction determines that initial temperature of the corn straw pyrolysis was relatively low. It can also be found that initial temperature of the corn straw is 232°C, lower than other samples based on the TG curves analysis. By blend technology in different proportions, the activation energy decreases significantly during the main pyrolysis stage, which is helpful for the successful reaction. The pre-exponential factors and activation energy of the blends approximate the value of corn straw, suggesting that corn straw play a leading role in the whole blends reactions.

Table 3. Kinetic results fitted by Malek of biomass

Biomass sample	Temperature range(°C)	E (KJ/mol)	Correlation coefficient	A(min^{-1})	Fitting equation
100%YM	248-423	54.5	0.987	3.50E+03	y=-6.555x+3.622
20%MG+80%YM	258-498	61.1	0.988	1.19E+03	y=-7.349x+2.517
40%MG+60%YM	226-423	51.7	0.955	1.44E+03	y=-6.219x+4.461
60%MG+40%YM	226-408	54.6	0.937	2.18E+03	y=-6.574x+4.100
80%MG+20%YM	264-423	66.41	0.959	3.98E+03	y=-7.987x+1.39
100%MG	279-418	83.45	0.979	1.69E+04	y=-10.037x+2.11

4. Conclusion

Comparisons of calculated and experimental weight loss curves show that there is not linear relationship between the mass of solid product and blend ratio , hence synergistic effects also are deduced. Cotton stalk and corn straw can be fully mixed. Dynamics calculation results show that: corn straw/cotton stalk blends pyrolysis behaviors can be well described by two-dimensional diffusion model. And 40:60 blend shows the lowest activation energy. The value of activation energy decrease with increasing corn straw content in the blend.

5. Acknowledgment

This work was supported by The National Key Technology R&D Program (contract no: 2012BAD30B00) and the Fundamental Research Funds for the Central Universities (contract no: 2013BHZX0034).

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