THE INFLUENCE OF ALKALI COMPOUNDS ON BIOMASS PYROLYSIS

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Abstract: This paper aims the influence of alkali matters on the pyrolysis property of biomass. Firstly, typical biomass sample — peanut shell, was washed with 5 wt% acid (H_2SO_4, HCl) and distilled water, respectively. The concentrations of inorganic compounds in original and washed biomass were characterized with ICP-AES. The pyrolysis characteristics was investigated using thermal balance at heating rate of 10 ℃ min^{-1} and N_2 flow rate of 100ml min^{-1}. It can be observed that the DTG curves of deashed peanut shell obviously were shifted to higher temperature and the char yield increased greatly. Then, K_2CO_3 and dolomite were added into acid washed and original biomass samples with the concentration of 1 wt% and 10 wt%. With inorganic addition, the DTG curves of original peanut shell was shifted to low temperature, while that of acid-washed biomass was moved to even higher temperature. In comparison with dolomite, K_2CO_3 displayed much higher effect on biomass pyrolysis behavior. The kinetic analysis showed that $n = 1$ as the reaction order is fit for biomass pyrolysis. The activation energy increased greatly with demineralization. It is great for the understanding of the influence of mineral matters on biomass pyrolysis; it is favorable for the development of biomass pyrolysis technology.

Keywords: pyrolysis, alkaline cation, demineralization, catalyst addition.

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1. Introduction

Biomass is one of the most promising renewable energy in the world. Pyrolysis is an important way for biomass utilization efficiently. In the past 25 years, people have made many researches on biomass pyrolysis, and those researches are mainly divided into two categories. The first part is focused on the pyrolysis parameters, such as temperature, pressure, heating rate and so on. The other part is focused on the influence of biomass characteristics on pyrolysis, such the particle size, biomass ash, water content and so on. Some alkaline cations exist in biomass and the amount varies according to various biomass types. Those alkaline cations are mainly Ca, K, Na, Mg and a small amount of Fe, Mn and Al (Zevenhoven et al., 2001).

Many researches (Williams and Horne, 1994; Raveendran et al., 1995; Agblevor and Besler, 1996; Szabo et al., 1996; Blasi et al., 2000) were carried out to study the catalytic effect of mineral matters on biomass pyrolysis through various technologies, such as: demineralization (water washing or acid washing) and minerals addition, and found that some minerals (such as Ca, K, Na, Mg and Fe) exert significantly catalytic effect, even a small amount of them is sufficient to alter the pyrolysis behavior to a large extent. Nevertheless, most of the previous studies focused on the influence of mineral matters on the product yields from biomass pyrolysis, few were carried out to understand the nature of catalytic behavior of minerals in pyrolysis involving a natural biomass. In this paper, different demineralization pretreatments technologies including acid washing (HCl and H_2SO_4) and DI (distill water) water washing were applied to peanut shell. Then, typical inorganic matters (K_2CO_3 and dolomite) were added to original biomass and acid-washed biomass sample. Pyrolysis characteristics of those untreated and pretreated biomass were investigated with thermal balance, and their kinetics properties were determined. It is great for the understanding of biomass pyrolysis.

2. Materials and Experimental Methods

2.1 Materials

Peanut shell of less than 100 mesh was chosen for Demineralization and salt-added pretreatment. The result of proximate and ultimate analysis is shown in Table 1.

Table 1 proximate and ultimate analyses of biomass material

	Proximate analyses (wt.%)				Ultimate analyses (wt.%)				
	M_{ad}	V_{ad}	A_{ad}	FC_{ad}	C	H	N	S	O*
Peanut shell	8.84	68.48	4.69	17.99	46.15	3.07	1.27	0.07	49.44

* The O content was determined by difference;

ad: on air dried basis; M, moisture content; V, volatile matters; A, ash; FC, fixed carbon.

2.2 Experimental Setup

2.2.1 Pretreatment Methods

Demineralization 20 grams of peanut shell was washed in 500 ml distilled water (DI water) or 500ml acid (5wt% HCl, 5% H_2SO_4). The beaker containing biomass solution was put in the water bath of 80℃ to accelerate the solution of minerals in biomass. The biomass solution was stirred for 2h and then filtered. The pH value of filter water was tested and the result was much more less than 7.0. The solid remainder of filtered solution was washed by distilled water repeatedly until the result of acidimeter for filtered water was ~ 7.0. At last the solid remainder of filtered solution was collected and dried in the oven of 105±5℃ for 24h.

Inorganic matters addition The most three alkaline cations in peanut shell are Mg, Ca and K. Taking account of the influence of different anions, K_2CO_3 and $CaCO_3 \cdot MgCO_3$ (dolomite) were added into both original biomass and acid washed biomass (including sulfuric acid washing and hydrochloric acid washing). The salt concentration in original biomass was 10wt% and the concentration in acid washed biomass were 1wt% and 10wt%, respectively.

2.2.2 Concentrations of Alkaline Cations in Biomass

The biomass ash was firstly prepared to measure the concentrations of alkaline cations in biomass. After the crucible was burnt at 550±20℃ in muffle furnace to constant weight, 2-5 grams of biomass was put into the cooled crucible carefully, and it was burnt at 550±20℃ in muffle furnace to constant weight. The remainder of the burned biomass was regarded as biomass ash. The second step was to digest the biomass ash. About 0.1 gram of ash was dissolved with 2ml nitric acid and 2ml hydrofluoric acid. The mixture was digested by microwave for 22 min and then cooled for 30min. 25ml boric acid was added into the digested solution and went on microwave digestion for 3min. The final digested solution was diluted to 250ml. At last, the alkaline cations, such as Fe, Mg, K, Na, Ca and Al were measured by the inductively coupled plasma atomic emission spectrometry (ICP-AES).

2.2.3 Pyrolysis Procedure

Biomass pyrolysis was carried out using a thermogravimetric analyzer (TGA). Sample size was maintained at ~20 mg for every trial and the flow rate of carrier gas (N_2) was set at 100ml/min. the temperature program is as follows. The sample was heated up at 10°C /min, first from ambient to 150℃ and keeping it for 10 min to remove moisture. Then, it was heated to 800℃ and kept isothermal for 3 min.

3. Results and Discussion

3.1 Influence of Demineralization on Biomass Pyrolysis

The metals compounds of biomass samples are shown in Table 2. It can be observed from the measurement results of ICP-AES that the order of alkaline cation concentration is Mg>Ca>K>Na>Al>Fe. The K in peanut shell is easy to dissolve in water and HCl. Mg and Ca compounds were difficult to dissolve in water. The K, Mg and Ca were easily dissolved by acid. Neither water nor acid solution had much influence on the content of Al or Fe.

Table 2 Alkaline cation of washed biomass particles (ppm wt/dry biomass)

Sample	Fe	Mg	K	Na	Ca	Al
Original biomass	2309.8	47884.2	6616.7	5348.9	13036.2	4684.5
Washed with DI water	3235.1	35481.5	1163.3	3446.4	13686.0	6601.8
Washed with H_2SO_4	3849.5	20386.2	1405.8	4203.4	4859.1	8328.8
Washed with HCl	1810.3	7818.2	815.1	1448.0	2446.6	6377.2

The pyrolysis curves of washed biomass samples are plotted in Fig. 1 with that of original biomass sample. It can be observed that demineralization increased the biomass pyrolysis char content, which was attributed to the high content of lignin in peanut shell(Raveendran et al., 1995), and part of cellulose or hemicellulose in biomass sample might be digested with acid or distilled water. The pyrolysis curves of three washed biomass were similar. Compared to that of original biomass, the DTG curves of washed biomass were shifted to high temperature zone. It might be attributed to the catalysis of mineral compounds, which is decreased with washing. From Table 2, it was known that only concentrations of K decreased a lot in both distilled water Demineralization biomass and acid Demineralization biomass. Hence, it can be deduced that K was the main catalyst in peanut shell pyrolysis.

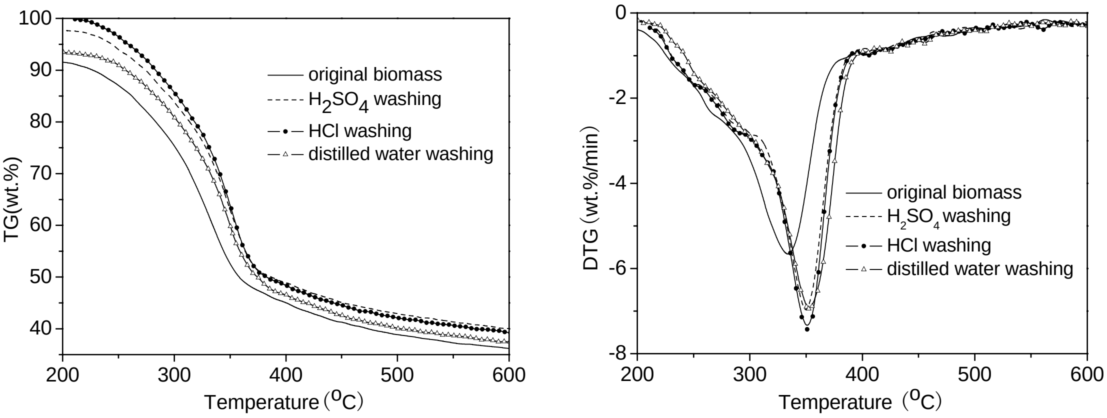

Fig.1　TG and DTG curves of original and washed peanut shell

It can be seen that the maximum pyrolysis rate of deashed peanut shell increased a lot, as mineral matters was removed. Demineralization not only removed alkali cations, but also removed many impurities, which made more pathways for the liberation of volatile.

The kinetics parameters (Yang et al., 2004) of pretreated biomass pyrolysis are listed in Table 3. It can be observed that the activation energy of washed sample was larger than that of original biomass. The order of Em of 4 samples is original < DI water < H_2SO_4 < HCl. It is contrary to the tendency of K, Mg and Ca of biomass particles with different washing methods. The existence of K, Mg and Ca in original biomass samples displayed great catalysis. With water and acid washing, alkali matters diminished from biomass samples, and the pyrolysis was lowered down, and E increased greatly.

Table 3　Kinetic properties of original and Demineralization peanut shell

Sample	Temperature (℃)	CR*	n	E(KJ/mol)	A(s^{-1})	Weight loss(%)	Em (KJ/mol)
Original biomass	231-371	0.98863	1	37.16	1.77×10^2	--	--
Washed DW	245-330	0.99845	1	34.81	64	20.69	51.49
	330-385	0.99433	1	64.18	4.32×10^4	27.2	
Washed with H_2SO_4	232-327	0.99768	1	48.58	1.45×10^3	20.72	60.88
	327-377	0.99572	1	71.16	1.89×10^5	24.81	
Washed with HCL	236-331	0.98961	1	66.77	7.58×10^4	23.13	71.84
	331-376	0.99477	1	76.68	5.57×10^5	24.29	

CR: correlation coefficient

3.2 Influence of Alkali Compounds Addition on Biomass Pyrolysis

The profile of curve of washed biomass pyrolysis with K_2CO_3 addition is shown in Figs. 2 and 3. The variations of peanut shell pyrolysis curves are listed as follows: 1) the char content of acid-washed biomass containing 1% K_2CO_3 was less than that of acid-washed biomass, and almost the same as that of original biomass; 2) the char content of acid-washed biomass containing 10% K_2CO_3 was far more than that of acid-washed biomass and original biomass; 3) the maximum pyrolysis rate was decreasing while the concentration of K_2CO_3 was increasing; 4) K_2CO_3 made the DTG curves of original biomass shift to low temperature by ~15℃, but the DTG curves of acid-washed biomass shift to high temperature.

The profile of curve of washed biomass pyrolysis with dolomite addition is shown in Figs. 4 and 5. The variations of peanut shell pyrolysis curves after dolomite addition were list as follows: 1) the maximum pyrolysis rate was increased gently; 2) dolomite made the DTG curves of original biomass shift to lower temperature, but that of acid-washed biomass was shifted to higher temperature; 3) char yield of biomass pyrolysis increased greatly with dolomite addition (except the sulfuric acid washed biomass with 1wt% dolomite).

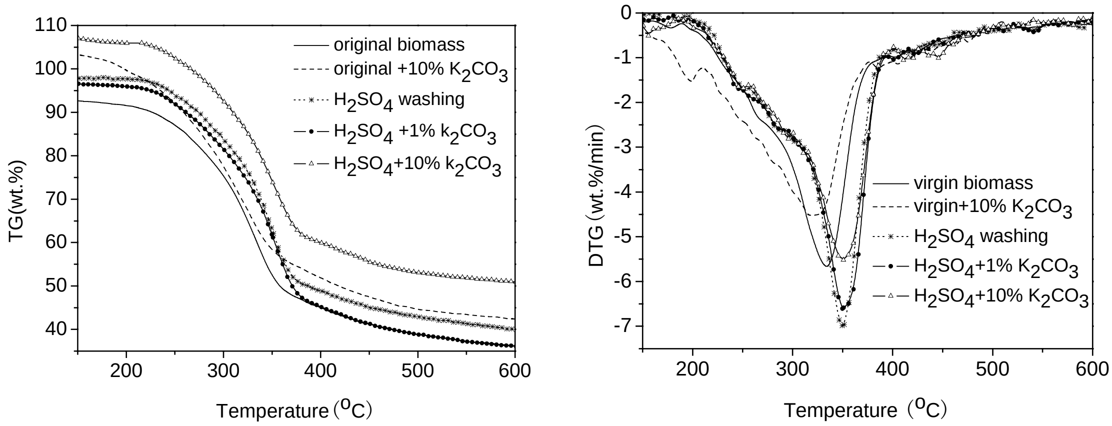

Fig.2 Pyrolysis curves of H2SO4 washed biomass with K_2CO_3 addition

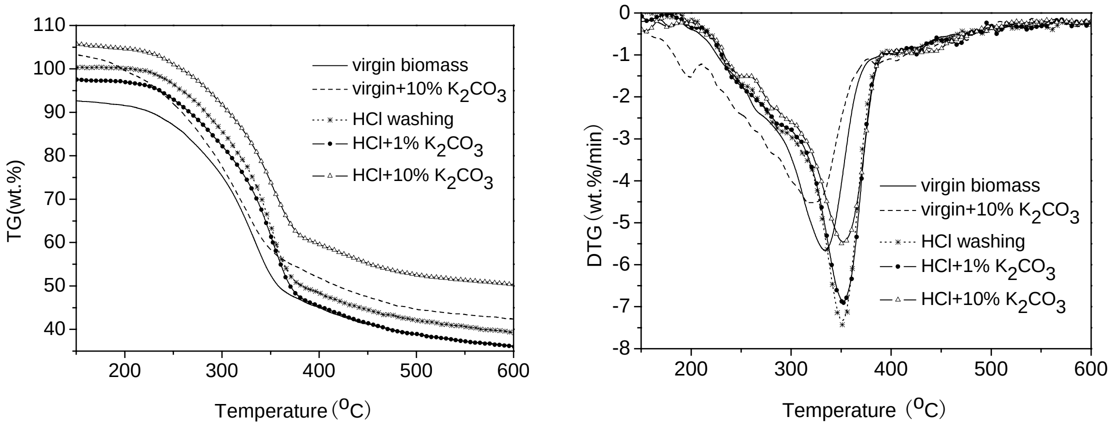

Fig.3 Pyrolysis curves of HCL washed biomass with K_2CO_3 addition

Kinetic calculations were also carried out based on the assumption of a first order reaction on main pyrolysis zone. The main pyrolysis section was separated according to the pyrolysis peaks on DTG curves. Calculation results are listed in Table 4. From the Table, it can be observed that K_2CO_3 increased the activation energy of original peanut shell but decreased that of acid-washed peanut shell. Dolomite had no effect on the activation energy of original peanut shell. Dolomite decreased the activation energy of sulfuric acid washed biomass but increased that of hydrochloric acid washed biomass. In comparison of dolomite addition, K_2CO_3 displayed much greater effect on activation energy.

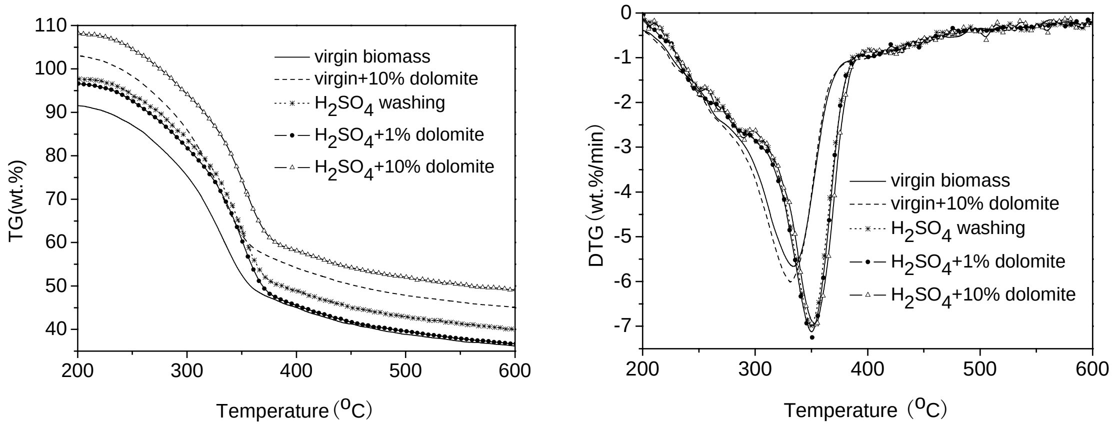

Fig.4 TG and DTG curves of H_2SO_4 washed biomass with dolomite addition

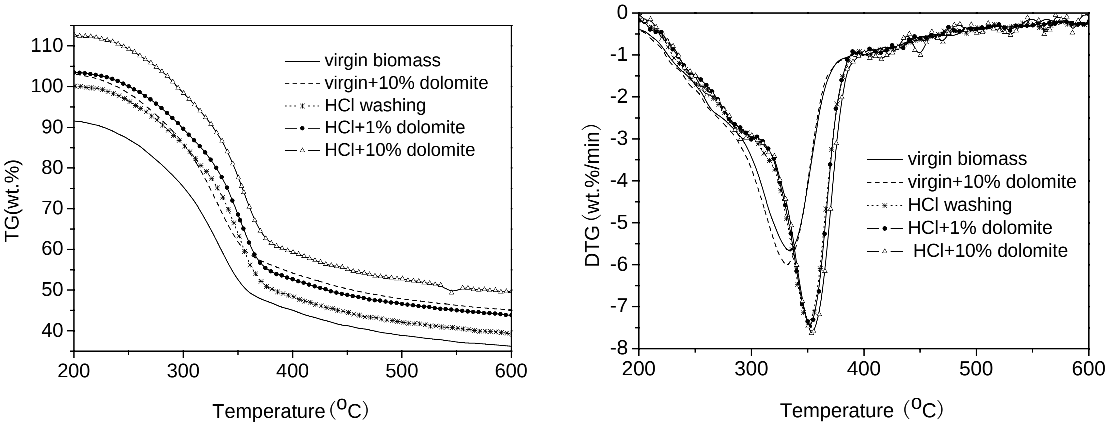

Fig.5 TG and DTG curves of HCl washed biomass with dolomite addition

Table 4 Kinetic properties of peanut shell before and after salts addition

Sample	Temperature (℃)	CR	n	E(KJ/mol)	$A(s^{-1})$	Weight loss (%)	Em (KJ/mol)
Origin +10% dolomite	230～360	0.9877	1	37.17	2.22×10^2	--	--
Origin +10%K_2CO_4	230～355	0.9979	1	50.56	3.56×10^3	--	--
H_2SO_4 +1% dolomite	231～331	0.9995	1	42.54	3.83×10^2	23.33	56.61
	331～376	0.9960	1	70.46	1.65×10^5	23.70	
H_2SO_4 +10%dolomite	235～335	0.9993	1	43.26	4.29×10^2	23.69	55.75
	335～380	0.9936	1	68.82	1.09×10^5	22.65	
H_2SO_4 +1% K_2CO_4	231～331	0.9998	1	37.95	1.35×10^2	22.78	52.12
	331～381	0.9962	1	65.28	5.41×10^4	24.51	
H_2SO_4 +10% K_2CO_4	236～331	0.9991	1	35.86	88	21.28	47.07
	331～381	0.9975	1	58.23	1.28×10^4	21.38	
HCl +1% dolomite	255～330	0.9850	1	81.80	1.71×10^6	19.29	83.08
	330～375	0.9965	1	84.09	2.38×10^6	24.61	
HCl +10%dolomite	245～330	0.9866	1	74.22	3.44×10^5	21.14	76.69
	330～380	0.9958	1	78.62	7.40×10^5	27.15	
HCl washing +1%K_2CO_4	231～331	0.9994	1	42.30	3.54×10^2	23.11	54.59
	331～381	0.9951	1	67.03	7.75×10^4	22.84	
HCl washing +10%K_2CO_4	236～331	0.9971	1	30.06	23	20.52	43.73
	331～381	0.9977	1	56.92	9.65×10^2	21.26	

4. Conclusion

(1) Demineralization increased the char production of peanut shell pyrolysis and made the DTG curves shift to high temperature. Different washing methods have similar pyrolysis curves.

(2) K_2CO_3 had much more effects on biomass pyrolysis than that of dolomite. Salts made the DTG curves of original peanut shell shift to low temperature but that of acid-washed biomass shift to even higher temperature. The pyrolysis char yield of acid-washed biomass containing 1% salts is similar to that of original biomass. However, the pyrolysis char production of acid-washed biomass containing 10% salts is much greater than that of original

biomass.

(3) Simple reaction mechanism was applied to the calculation of pyrolysis kinetic properties. Fitting were carried out in separated sections and the reaction order was 1. Demineralization and K_2CO_3 addition increased the activation energy of peanut shell, but dolomite had unobvious impact on it.

Acknowledgments

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