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Research article

The influence of alkali and alkaline earth metal compounds on pyrolysis of peanut shell

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ABSTRACT: This article aims at studying the influence of alkali and alkaline earth species on the pyrolytic performances of peanut shell. The biomass sample was washed with 5 wt% acids (H_2SO_4 and HCl) and deionized water, respectively. The concentrations of metallic elements in the original and washed peanut shells were determined with inductively coupled plasma-atomic emission spectrometry. The pyrolysis experiment was performed on a thermogravimetric analyzer (TGA) at a heating rate of 10 °C/min and N_2 flow rate of 100 mL/min. It can be observed that the derivative thermogravimetric (DTG) curves of demineralized peanut shell were obviously shifted to higher temperature and the char yields increased greatly. With the addition of 1 wt% or 10 wt% K_2CO_3 or dolomite to the original and acid-washed biomass samples, the DTG curves of the original peanut shell were shifted to low temperature and this effect was more distinct for the acid-washed peanut shell. K_2CO_3 displayed much greater effect than dolomite on the alteration of the pyrolysis behavior. The first-order kinetic analysis showed that the activation energy increased greatly with demineralization. © 2011 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: pyrolysis; peanut shell; metallic element; demineralization

INTRODUCTION

Biomass is one of the most promising renewable energy resources in the world. The thermochemical conversion of biomass provides a viable route for the production of fuels and chemicals to substitute the fossil fuels and reduce greenhouse gas emissions[1]. Pyrolysis is not only a thermal conversion process, but is also a first step in the gasification or combustion process[2]. In the past decades, many researches have been performed to improve the understanding of biomass pyrolysis behavior[3]. The pyrolysis product distributions and product properties are mainly determined by the conversion conditions (temperature, pressure and heating rate) and biomass properties (chemical composition, ash content and composition, particle size and shape, density, moisture content, etc.)[4].

There are significant amounts of alkali and alkaline earth metal compounds (mainly K, Na, Mg and Ca) present in biomass, which play important roles in the pyrolysis process[5–7]. In particular, potassium has a marked influence on the pyrolysis behavior of biomass, modifying both the yield and distribution of reaction products[8]. Liu *et al*.[9] used a thermogravimetric analysis coupled with a Fourier transform infrared spectroscopy to investigate the catalytic effect of potassium salts on cellulose pyrolysis. They found that potassium salts catalyzed the dehydration and depolymerization reactions in the initial pyrolysis stage, enhanced the release of oxygenated gases, intensively catalyzed the formation of char and restrained the production of volatiles. In our previous work[10], the influence of mineral matter on the pyrolysis of palm oil wastes was investigated and it was found that most of the mineral additives (KCl, Na_2CO_3, $CaMg(CO_3)_2$, Fe_2O_3 and Al_2O_3) demonstrated negligible effects on the pyrolysis of palm oil wastes, while K_2CO_3 was not only found to inhibit the pyrolysis of hemicellulose but also promote the degradation of cellulose.

At present, increasing attention has been paid to improve the quality of pyrolysis products, such as bio-oil and char, by demineralization or impregnation pretreatment[7,11]. China is a major producer of peanuts and the yield of peanut shell is abundant annually; therefore, it is worthy to convert peanut shell into high-value biofuels through thermochemical methods such as pyrolysis[12]. However, there is not much information available about the pyrolysis behavior of peanut shell[13,14]. Moreover, little has been reported on the influence of alkali and alkaline earth metal

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compounds since peanut shell has a high content of mineral matter, especially K[6].

In this article, different demineralization pretreatment methods including acid washing (HCl and H_2SO_4) and deionized water (DI water) washing are applied to peanut shell samples. Then, typical inorganic salts (K_2CO_3 and dolomite) are added to original and acid-washed biomass samples. Pyrolysis characteristics of those untreated and pretreated samples are investigated with a thermogravimetric analyzer (TGA) and their kinetic properties are determined according to the first-order reaction mechanism, which is conducive to the understanding of peanut shell pyrolysis.

EXPERIMENTAL

Materials

Peanut shell of smaller than 0.15 mm (100 mesh) was chosen for demineralization and salt-added pretreatments. The results of proximate and ultimate analysis are shown in Table 1.

Table 1. Proximate and ultimate analyses of peanut shell.

Proximate analysis (wt%, ad)				Ultimate analysis (wt%, daf)				
M	V	A	FC	C	H	N	S	O[a]
8.84	68.48	4.69	17.99	46.15	3.07	1.27	0.07	49.44

ad, air dry basis; daf, dry air-free basis; M, moisture; V, volatile; A, ash; FC, fixed carbon.

[a] Calculated by difference.

Experimental setup

Pretreatment methods

Demineralization. About 20 g of peanut shell was put in the beaker and immerged with 500 mL DI water or 500 mL acid (5 wt% HCl or H_2SO_4), respectively. The beaker was put in the water bath of 80 °C to accelerate the dissolution of minerals from biomass. The sample was stirred for 2 h and then filtered. The pH value of the filtrate was tested, which was in the range of 2.0–3.0 (strongly acidic). Therefore, the solid residue was washed with DI water repeatedly until the pH value of the filtrate was ~7.0 to make sure the sample was acid free. Finally, the solid residue was collected and dried in the oven at 105 ± 5 °C for 24 h.

Inorganic salts addition. The three dominant metallic elements in peanut shell are Mg, Ca and K. Taking account of the influence of different cations, K_2CO_3 and $CaCO_3 \cdot MgCO_3$ (dolomite) were added into both original and acid-washed samples (including H_2SO_4 washing and HCl washing). The concentration of additive in original peanut shell sample was 10 wt% (on the basis of biomass), while the concentrations in acid-washed samples were 1 and 10 wt%, respectively.

Concentrations of metallic elements in samples

The biomass ash was first prepared for measuring the concentrations of metallic elements in peanut shell. The empty crucible was put in muffle furnace and burnt at 550 ± 20 °C to a constant weight and the crucible was cooled in a desiccator. Then, about 5 g of sample was added into the cooled crucible and burnt in muffle furnace at 550 ± 20 °C to a constant weight. The residue was regarded as biomass ash. The second step was to digest the biomass ash. About 0.1 g of ash was dissolved in a mixture of 2 mL of concentrated nitric acid and 2 mL of hydrofluoric acid. The mixture was digested by placing in the microwave for 22 min and then cooled for 30 min. Then, 25 mL of boric acid was added into the digested solution and then subjected to the microwave radiation for 3 min. The final digested solution was diluted with DI water to 250 mL. Finally, the major metallic elements such as Fe, Mg, K, Na, Ca and Al were analyzed by inductively coupled plasma-atomic emission spectrometry.

Pyrolysis procedure

Biomass pyrolysis experiment was carried out using a TGA (STA 409, Netzsch, Germany). About 20 mg of the sample was used in each trial and the flow rate of carrier gas (N_2) was set at 100 mL/min. The sample was first heated up from the ambient temperature to 150 °C at 10 °C/min and kept for 10 min to remove moisture. Then, it was heated up to 800 °C at 10 °C/min and kept isothermal for 3 min. Duplicate experiments were performed to make sure the reproducibility and accuracy of analysis.

Kinetic analysis

A kinetic analysis of the pyrolysis process is beneficial for understanding the influence mechanisms of alkali and alkaline earth metal compounds. The first-order reaction is appropriate to describe the experimental data obtained by TGA[15]. Then, the following equation can be used to calculate the kinetic parameters according to the Arrhenius law:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha) \qquad (1)$$

where α is the mass conversion ratio and is given as $\alpha = (m_o - m_t)/(m_o - m_f)$, m_o, m_t and m_f representing original, current (at time t) and final sample weight, respectively; A the pre-exponential factor, E the activation energy, R the gas constant and T the absolute temperature.

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For a constant heating rate β during pyrolysis, $\beta = \mathrm{d}T/\mathrm{d}t$, Eqn (1) can be transformed into

$$\frac{\mathrm{d}\alpha}{1-\alpha} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)\mathrm{d}T \qquad (2)$$

Using the Coats–Redfern method[16], the following relation is yielded:

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

A plot of $\ln[-\ln(1-\alpha)/T^2]$ *vs* $1/T$ will yield the values of A and E from the intercept and the slope[15].

The kinetic parameters might be different with pyrolysis temperature, therefore they should be determined by stages and the weight mean activation energy (E_m) can be calculated by Cumming's method[17]:

$$E_\mathrm{m} = (F_1 \times E_1) + (F_2 \times E_2) + \cdots + (F_n \times E_n) \qquad (4)$$

where E_1 through E_n is the activation energy of every stage (1 through n), F_1 through F_n is the corresponding relative weight loss amount.

RESULTS AND DISCUSSION

Influence of demineralization on pyrolysis

The contents of the major metallic elements in original and washed biomass samples are shown in Table 2. It can be observed that the K in peanut shell was dissolved most easily by DI water and Na, Mg was next. However, Fe, Ca and Al were difficult to dissolve in water, as a result, their relative concentrations increased with the decrease of ash content (due to partial demineralization). Acids are more effective in dissolving K, Na, Mg and Ca. Neither water nor acid solutions had significant influence on the content of Al or Fe. The HCl solution had a higher ability of demineralization than the H_2SO_4 solution, probably because the former solution had a stronger acidity than the latter solution. In addition, the demineralization pretreatments had small effects on the organic components in biomass[18]. As a result, their influences on biomass pyrolysis are negligible compared to that of inorganic matter.

Table 2. The contents of metallic elements in the original and washed peanut shells (mg/g-ash).

Sample	Fe	Mg	K	Na	Ca	Al
Original biomass	2.31	47.88	6.62	5.35	13.04	4.68
Washed with DI water	3.24	35.48	1.16	3.45	13.69	6.60
Washed with H_2SO_4	3.85	20.39	1.41	4.20	4.86	8.33
Washed with HCl	1.81	7.82	0.82	1.45	2.45	6.38

The pyrolysis curves of peanut shell samples with and without demineralization pretreatment are plotted in Fig. 1. It can be observed that demineralization increased the yield of pyrolytic char, which was attributed to the gasification of char by CO_2 and H_2O, the primary products of pyrolysis[6]. Moreover, the metallic elements, such as K, Na and Ca, play an important role in catalyzing the biochar gasification reaction[19]. Thus the demineralization pretreatment reduced the char-consuming gasification reaction. The derivative thermogravimetric (DTG) curves of three washed biomass samples were similar. Compared to that of original biomass, the DTG curves of washed biomass were shifted to high temperature zone. It might result from the catalysis of mineral compounds, which were decreased due to washing. From Table 2, it was known that only concentrations of K decreased a lot in both DI water and acid demineralization biomass. Hence, it can be deduced that K might have the main catalytic effect on peanut shell pyrolysis.

It can be seen that the maximum pyrolysis rate of demineralized peanut shell increased a lot, as mineral matter or mineral species was removed. Demineralization not only removed alkali and alkaline earth metals, but also removed many other impurities, which provided more pathways for the release of volatile.

Figure 1 shows that peanut shell pyrolysis occurs mainly between 230 and 380 °C. The kinetic parameters of original and pretreated biomass samples in this temperature range are listed in Table 3. It can be seen that the mean activation energy (E_m) of washed samples were larger than that of original biomass. The order of E_m of four 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 presented great catalytic effects on pyrolysis behavior. With water and acid washing, metallic elements were reduced significantly from biomass samples, which inhibited the pyrolysis of peanut shell, therefore the activation energy increased remarkably.

Influence of inorganic salts addition on pyrolysis

The pyrolysis curves of acid-washed biomass samples with K_2CO_3 addition are 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;

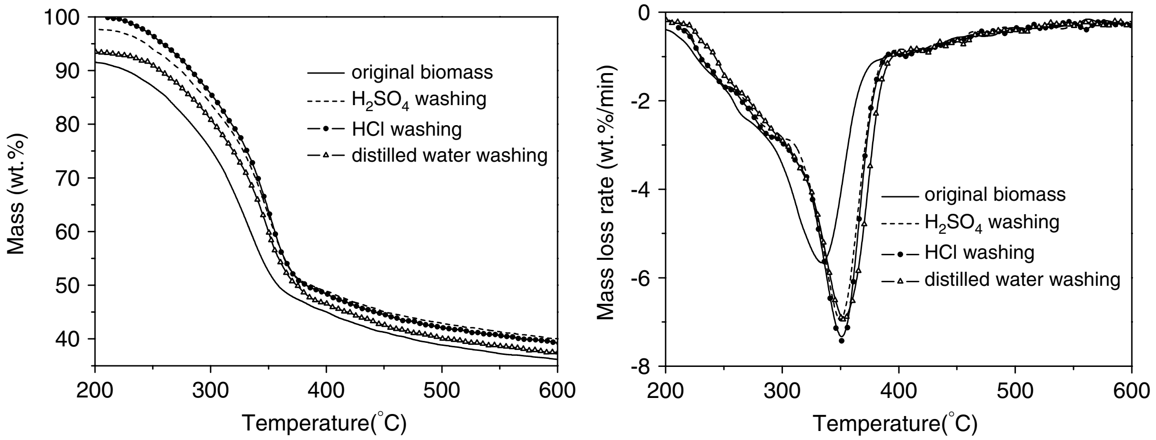

Figure 1. Pyrolysis curves of original and washed peanut shells.

Table 3. Kinetic properties of original and demineralization peanut shells.

Sample	Temperature (°C)	CR	E (kJ/mol)	A (s^{-1})	Weight loss (%)	E_m (kJ/mol)
Original biomass	231–371	0.98863	37.16	1.77×10^2	42.14	37.16
Washed with DI water	245–330	0.99845	34.81	64	20.69	51.49
	330–385	0.99433	64.18	4.32×10^4	27.2	
Washed with H_2SO_4	232–327	0.99768	48.58	1.45×10^3	20.72	60.88
	327–377	0.99572	71.16	1.89×10^5	24.81	
Washed with HCl	236–331	0.98961	66.77	7.58×10^4	23.13	71.84
	331–376	0.99477	76.68	5.57×10^5	24.29	

CR, correlation coefficient.

(3) the maximum pyrolysis rate was decreased with the concentration of K_2CO_3 increasing and (4) K_2CO_3 made the DTG curves of original biomass shift to lower temperature by ~15 °C, but the DTG curves of acid-washed biomass shift to higher temperature. It indicates that adding a small quantity of K_2CO_3 into biomass may promote pyrolysis and there are obvious differences between original biomass and acid-washed biomass with K_2CO_3 addition in the pyrolysis behavior.

The pyrolysis curves of acid-washed biomass samples with dolomite addition are shown in Figs 4 and 5. The effect of dolomite on peanut shell pyrolysis are list as follows: (1) the maximum pyrolysis rate was increased slightly; (2) dolomite made the DTG curves of original biomass shift to lower temperature, but that of acid-washed biomass shift to higher temperature and (3) char yield of peanut shell increased greatly with dolomite addition (except H_2SO_4-washed biomass with 1 wt% dolomite). It indicates that dolomite has less effect on biomass pyrolysis.

Kinetic calculations were also carried out based on the assumption of the first-order reaction mechanism in main pyrolysis zone. The main pyrolysis stage was separated according to the pyrolysis peaks on DTG curves. Calculation results are listed in Table 4. It showed that K_2CO_3 increased the activation energy of original peanut shell but decreased that of acid-washed sample, which might be attributed to the fact that excessive K_2CO_3 would hinder the release of volatile compounds. Dolomite had no obvious effect on the activation energy of original peanut shell. Dolomite decreased the activation energy of H_2SO_4-washed biomass but increased that of HCl-washed biomass. In comparison with dolomite addition, K_2CO_3 addition exhibited much greater effect on activation energy.

CONCLUSION

The peanut shell samples with different washing methods have similar pyrolysis curves. Demineralization increased the char production of peanut shell pyrolysis and made the DTG curves shift to higher temperature. Inorganic salts made the DTG curves of original peanut shell shift to lower temperature but the DTG curves of acid-washed biomass shift to even higher temperature. K_2CO_3 had much more effect on pyrolysis than that of dolomite. Demineralization and K_2CO_3 addition increased the activation energy of peanut shell and dolomite had an unobvious impact on it.

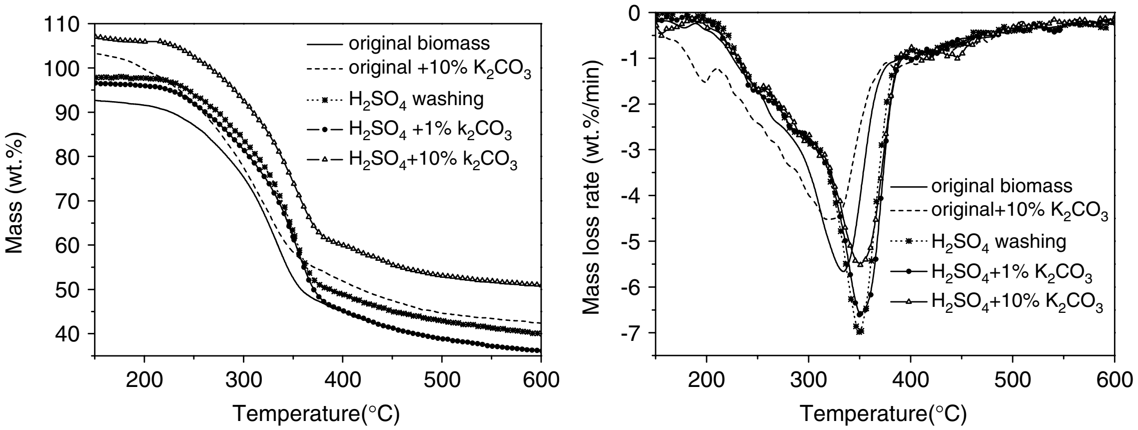

Figure 2. Pyrolysis curves of H_2SO_4-washed peanut shell with K_2CO_3 addition.

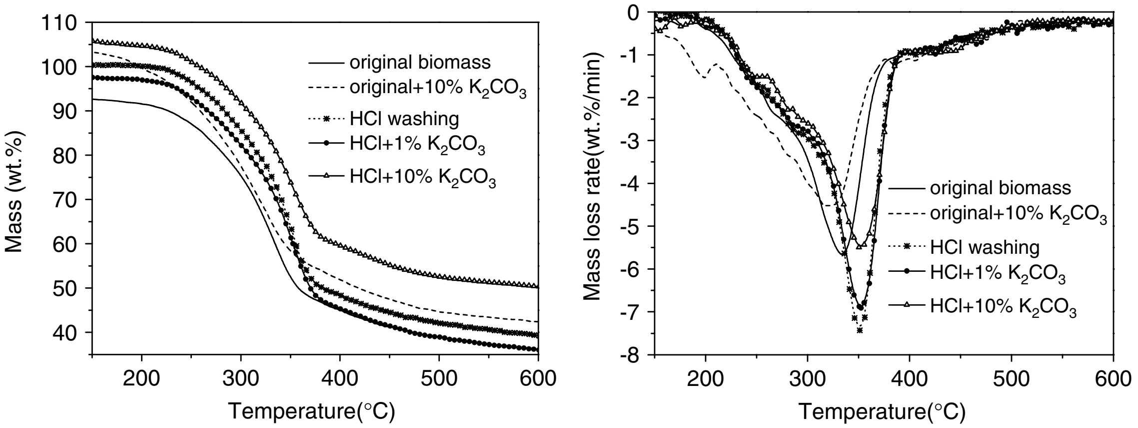

Figure 3. Pyrolysis curves of HCl-washed peanut shell with K_2CO_3 addition.

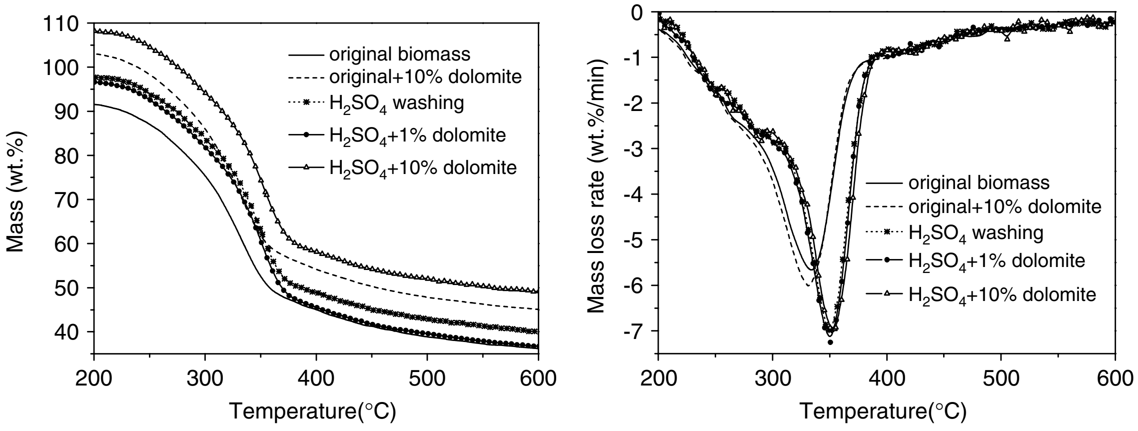

Figure 4. Pyrolysis curves of H_2SO_4-washed peanut shell with dolomite addition.

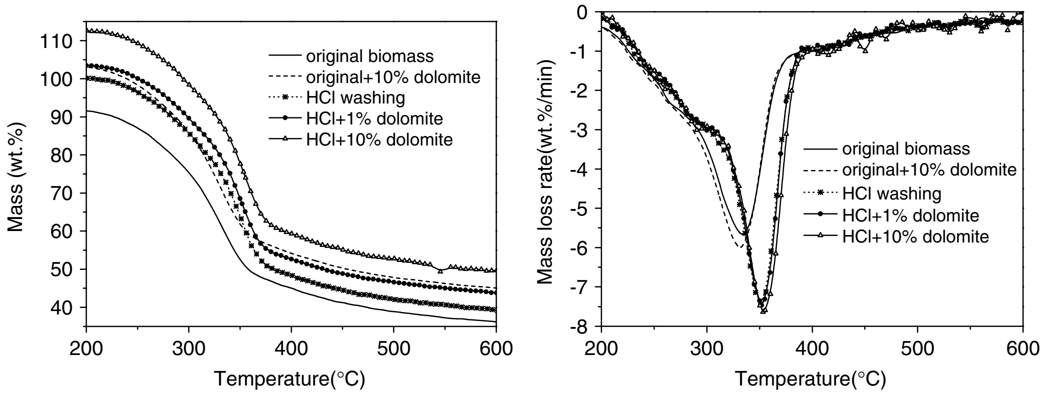

Figure 5. Pyrolysis curves of HCl-washed peanut shell with dolomite addition.

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

Sample	Temperature (°C)	CR	E (kJ/mol)	A (s^{-1})	Weight loss (%)	E_m (kJ/mol)
Origin + 10% dolomite	230–360	0.9877	37.17	2.22×10^2	39.51	37.17
Origin + 10% K_2CO_3	230–355	0.9979	50.56	3.56×10^3	42.25	50.56
H_2SO_4 + 1% dolomite	231–331	0.9995	42.54	3.83×10^2	23.33	56.61
	331–376	0.9960	70.46	1.65×10^5	23.70	
H_2SO_4 + 10% dolomite	235–335	0.9993	43.26	4.29×10^2	23.69	55.75
	335–380	0.9936	68.82	1.09×10^5	22.65	
H_2SO_4 + 1% K_2CO_3	231–331	0.9998	37.95	1.35×10^2	22.78	52.12
	331–381	0.9962	65.28	5.41×10^4	24.51	
H_2SO_4 + 10% K_2CO_3	236–331	0.9991	35.86	88	21.28	47.07
	331–381	0.9975	58.23	1.28×10^4	21.38	
HCl + 1% dolomite	255–330	0.9850	81.80	1.71×10^6	19.29	83.08
	330–375	0.9965	84.09	2.38×10^6	24.61	
HCl + 10% dolomite	245–330	0.9866	74.22	3.44×10^5	21.14	76.69
	330–380	0.9958	78.62	7.40×10^5	27.15	
HCl washing + 1% K_2CO_3	231–331	0.9994	42.30	3.54×10^2	23.11	54.59
	331–381	0.9951	67.03	7.75×10^4	22.84	
HCl washing + 10% K_2CO_3	236–331	0.9971	30.06	23	20.52	43.73
	331–381	0.9977	56.92	9.65×10^2	21.26	

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