

Short communication

Catalytic effects of six inorganic compounds on pyrolysis of three kinds of biomass

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Abstract

Six inorganic compounds, i.e., Na₂CO₃, NaOH, NaCl, Na₂SiO₃, TiO₂ and HZSM-5, have been investigated with regard to their catalytic effects on pyrolysis of three biomass species, i.e., pine wood, cotton stalk and fir wood by thermal analysis experiments. The results show that Na₂CO₃, NaOH, Na₂SiO₃ and NaCl made devolatilization occur at lower temperature regions in the pyrolysis of the three kinds of biomass, whereas TiO₂ and HZSM-5 made that occur at higher temperature regions in the pyrolysis of cotton stalk and had no obvious effects on pyrolysis temperatures of pine wood and fir wood. The basic catalysts NaOH, Na₂CO₃ and Na₂SiO₃ decreased the maximum weight loss rates while NaCl and HZSM-5 increased them and TiO₂ had no obvious effects on them. The four sodium compounds made pyrolysis of the three kinds of biomass more exothermic, which might be due to more char formation, whereas TiO₂ and HZSM-5 had minor effects on reaction heat. The catalytic effects in all aspects were roughly correlated with one another and their relationship with the basicity and acidity of the catalysts were preliminarily described and analyzed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Catalytic effects; Biomass; Thermal analysis; Pyrolysis

1. Introduction

Biomass can be converted into fuels, chemicals and high quality carbon products such as activated carbon by pyrolysis process [1–5]. Pyrolysis is also the initial stage of gasification and combustion of biomass [4,6]. So studies of pyrolysis are of great importance in many aspects. However, pyrolysis is a very complex process and is subjected to influences of many factors such as texture structures of the biomass, water content, inherent minerals, heating rates, reactor patterns and additives. Adding additives is a flexible method to regulate pyrolysis process. Desired products yields or selectivity might be obtained by catalytic pyrolysis with appropriate additives. Since biomass exists in large varieties thus having different components and structures, pyrolysis of different biomass species might need different additives to optimize the process. Seeking proper additives

is a laborious job. Many researches regarding this are available in the literature [7–9], however, they were usually carried out under different conditions. Therefore, it is hard for us to compare the catalytic effects of additives on pyrolysis of biomass on the same basis. Fortunately, thermal analysis can provide a fast preliminary evaluation of catalytic effects of additives on pyrolysis. In addition, this method has the advantage of needing very small amount of samples.

Here, we have investigated the catalytic effects of six inorganic compounds (Na₂CO₃, NaOH, NaCl, Na₂SiO₃, TiO₂ and HZSM-5) on pyrolysis of three kinds of biomass (pine wood, cotton stalk and fir wood) by thermal analysis under the same conditions thus providing a comparative study in terms of catalyst types and biomass species.

2. Experimental

2.1. Biomass and catalysts

Sawdust of pine wood (*P. massoniana* Lamb.), fir wood (*M. glyptostriboides* Hu et Cheng) and cotton stalk were employed

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Table 1
Proximate analysis of three different biomass species

	M_{ad} (%)	V_d (%)	A_d (%)	FC_d (%)	$Q_{b,d}$ (MJ/kg)
PW	8.27	81.98	2.16	15.86	19.92
CS	7.65	74.75	7.51	17.73	18.68
FW	7.54	80.86	1.98	17.16	21.82

PW: pine wood; CS: cotton stalk; FW: fir wood.

in this study. Proximate analysis was presented in Table 1, where M_{ad} (moisture) was weight loss percentage on air dry basis at 75 °C, A_d (ash) was the residue percentage on dry basis after complete combustion at 800 °C, V_d (volatile) was weight loss percentage on dry basis after devolatilization at 700 °C for 10 min under scarce oxygen atmosphere and FC_d (fixed carbon) was calculated by difference. $Q_{b,d}$ was bomb calorific value on dry basis.

Purity and properties of the catalysts are as following: Na_2CO_3 , C.P; NaOH, A.P; NaCl, A.P; Na_2SiO_3 , C.P, liquid product, provided by Huainan Inorganic Chemical Plant; TiO_2 , anatase, average particle size = 30 nm, specific area > 12 m²/g, purchased from Hehai Nanotechnology Co. Ltd.; HZSM-5, 0.5–1.5 μm, $SiO_2/Al_2O_3 = 59$, specific area = 400–600 m²/g, purchased from Shanghai Huaheng Chemical Plant.

2.2. Sample preparation

The sawdust of the three kinds of biomass with size less than 1 mm was air dried until constant weight for use. Two kinds of samples were prepared. One was the bare samples (untreated) and the other was catalysts treated samples. The treated samples were prepared according to the following procedure. Two grams of certain catalyst was mixed with 50 ml distilled water to make dilute solution or suspension (in the case of Na_2SiO_3 , the total solid content of its liquid product used was made to be 2 g and total solution volume was made to be 50 ml). Twenty grams of certain biomass sawdust was then mixed with the solution or suspension followed by vigorous stirring for about 5 min at room temperature. The catalysts treated samples were dried at 75 °C together with the three untreated samples until constant weight.

2.3. Operating conditions

A thermal analyzer (STD 2960, V3.0F, TA Co., America) was used to analyze the thermal characteristics of the biomass. Ca. 10 mg sample of each kind of biomass was pyrolyzed with a heating rate of 10 K min⁻¹. The volatiles were carried out by nitrogen gas with a flow rate of 100 ml min⁻¹.

3. Results and discussion

3.1. Catalytic effects on pyrolysis temperatures

It can be seen from Figs. 1–6 that all sodium compounds made three biomass samples devolatilize at lower temperatures. The temperature reduction effects follow the order of

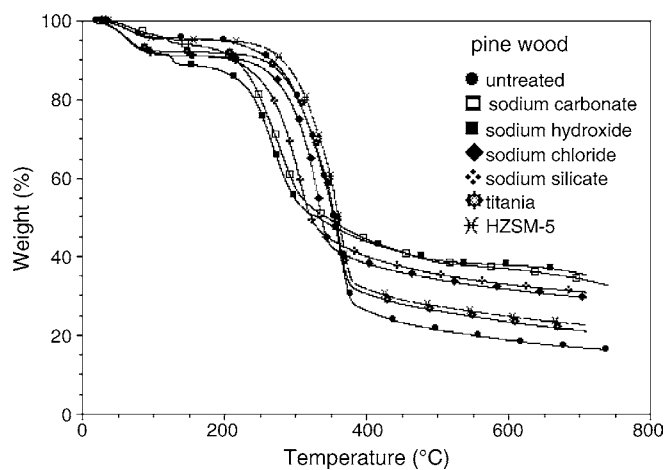


Fig. 1. TG curves of pine wood treated with different catalysts (heating rate: 10 K min⁻¹).

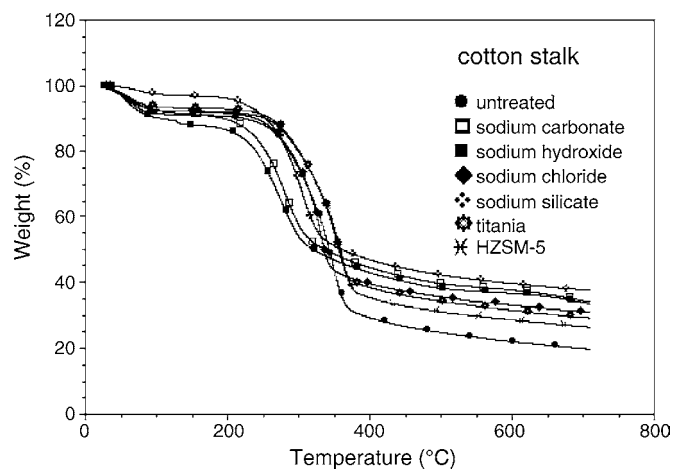


Fig. 2. TG curves of cotton stalk treated with different catalysts (heating rate: 10 K min⁻¹).

$NaOH > Na_2CO_3 > Na_2SiO_3 > NaCl$. This coincides with their basicity sequence. These effects may be caused by the catalytic role of the sodium compounds during pyrolysis or by swelling role during the impregnation of biomass samples or by both [10].

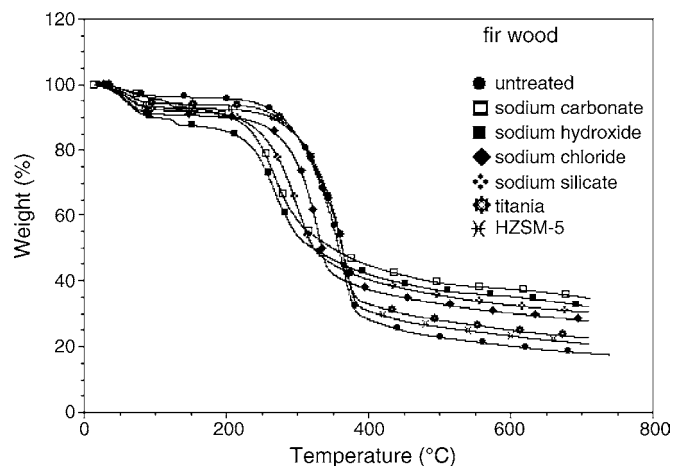


Fig. 3. TG curves of fir wood treated with different catalysts (heating rate: 10 K min⁻¹).

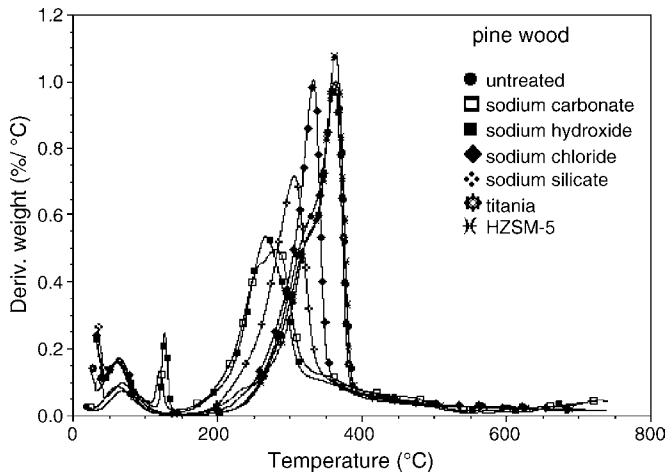


Fig. 4. DTG curves of pine wood treated with different catalysts (heating rate: 10 K min^{-1}).

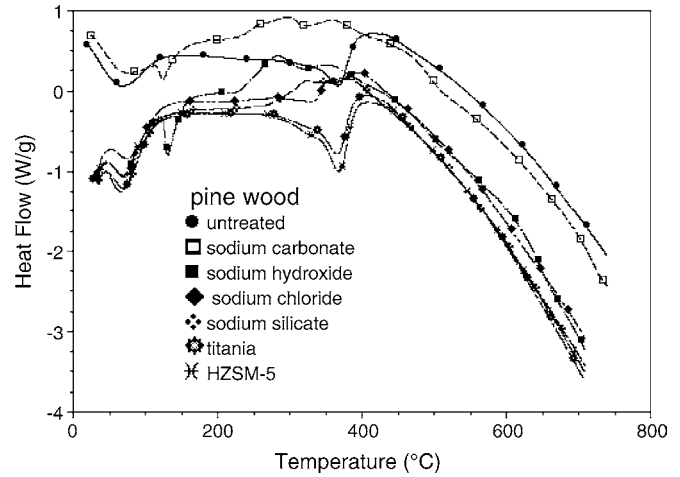


Fig. 7. DSC curves of pine wood treated with different catalysts (heating rate: 10 K min^{-1}).

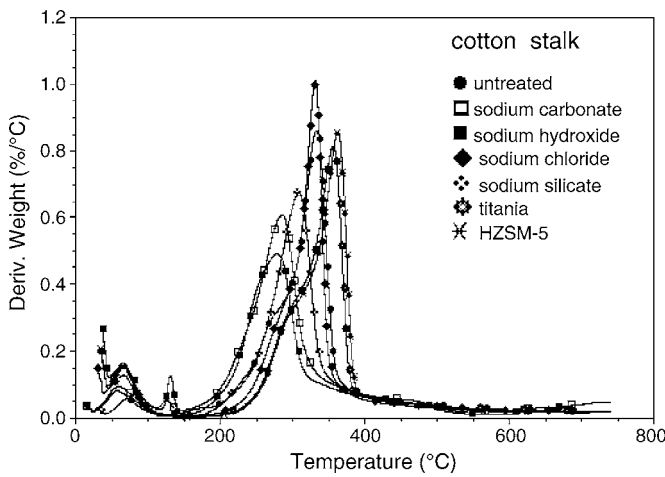


Fig. 5. DTG curves of cotton stalk treated with different catalysts (heating rate: 10 K min^{-1}).

Sodium ion is very small and it can penetrate into the biomass textures and break the intermolecular hydrogen bridges under swelling or heating. As a result, devolatilization occurs earlier. Moreover, strong sodium base can extract some low molecular compounds in the biomass. It can also react with hemicellulose, cellulose and lignin. For example, sodium hydroxide can react with cellulose through active alcohol groups of cellulose as illustrated in formula (1) [11]. In addition, a small peak at around 120°C occurs on each DTG curve of sodium hydroxide and sodium carbonate treated samples. Accordingly, a small endothermic peak at around 120°C also occurs on each DSC curve of sodium hydroxide and sodium carbonate treated samples (see Figs. 7–9). This phenomenon does not occur for pyrolysis of sodium silicate and sodium chloride treated samples. This might be due to the more basic characteristics of the former two sodium compounds, which extract some low molecular compounds in the biomass and they vaporize at around 120°C [12].

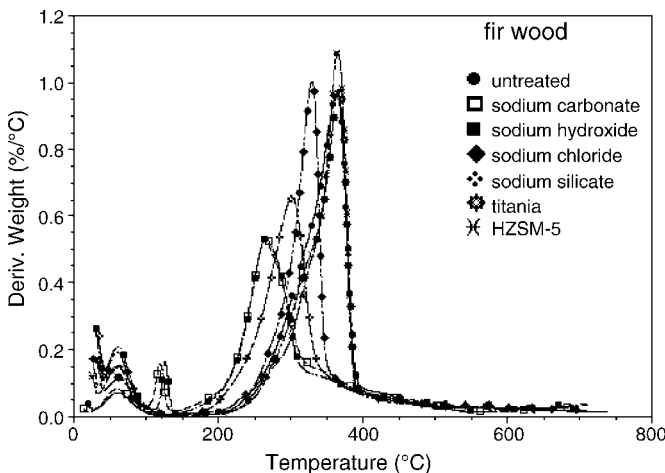
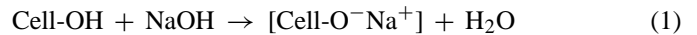


Fig. 6. DTG curves of fir wood treated with different catalysts (heating rate: 10 K min^{-1}).

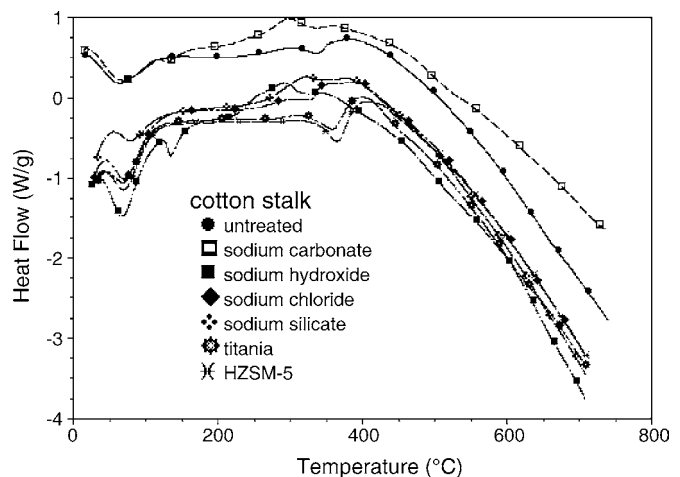


Fig. 8. DSC curves of cotton stalk treated with different catalysts (heating rate: 10 K min^{-1}).

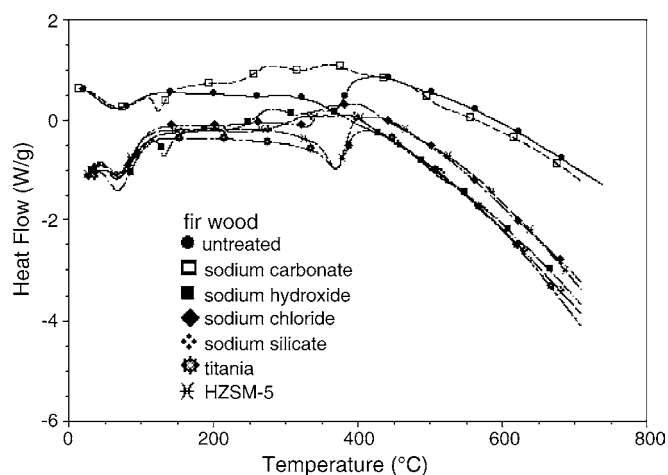


Fig. 9. DSC curves of fir wood treated with different catalysts (heating rate: 10 K min^{-1}).

As for TiO_2 and HZSM-5 treated samples, pyrolysis temperatures depend on biomass species. TiO_2 and HZSM-5 had no apparent effects on pyrolysis temperatures for pine wood and fir wood. However, their presence made the pyrolysis of cotton stalk move to higher temperature regions (see Fig. 5). From Table 1, we know that ash content of cotton stalk is much higher than that of pine wood and fir wood. More ash means more minerals in biomass hence more effective catalytic role during pyrolysis, especially in terms of temperature reduction effect. This justifies the lower pyrolysis temperature region of cotton stalk compared with pine wood and fir wood. TiO_2 and HZSM-5, whose surface is acidic, might have deactivated the basic minerals in the cotton stalk by acid–base interaction thus inhibited pyrolysis of cotton stalk.

3.2. Catalytic effects on weight loss rates

Catalysts have different effects on weight loss rates. It can be found from Figs. 4–6 that NaOH, Na_2CO_3 and Na_2SiO_3 have dramatically lowered the maximum weight loss rates. On the contrary, NaCl has slightly increased the maximum weight loss rates for pine wood and fir wood and increased the maximum weight loss rate by ca. 15% for cotton stalk. HZSM-5 had increased the maximum weight loss rate by ca. 10% for both pine wood and fir wood while has no obvious effect on that for cotton stalk. TiO_2 has no obvious effect on the maximum weight loss rates. Note that surfaces of TiO_2 and HZSM-5 are both acidic and the later is more acidic than the former. The acidic sites on the surface of HZSM-5 can absorb some reactants and form carbocations hence promotes more volatiles formation. On the contrary, although alkaline catalysts can make vapors evolve earlier at low temperatures; it can also suppress yields of volatile and promote charring at higher temperatures [10].

3.3. Catalytic effects on char formation

Table 2 shows the final char residue weights at 700°C and Table 3 shows the net char residue weights (ash and added catalyst deducted). We can find that sodium compounds have

Table 2
Char residue weight (%)

	Untreated	Na_2CO_3	NaOH	NaCl	Na_2SiO_3	TiO_2	HZSM-5
PW	17	34	36	30	31	21	23
CS	26	30	34	31	38	29	27
FW	18	35	32	28	31	23	21

increased the net char weight percentages (some exceptions occur in the case of cotton stalk). TiO_2 and HZSM-5 seems to decrease the net char weight percentages for all the three biomass, yet it should be noted that this is dubious. Because both TiO_2 and HZSM-5 are water insoluble and hence are difficult to disperse uniformly in biomass sawdust during sample preparation process. This might have introduced considerable errors in calculating net weight char residue. Therefore, effects of TiO_2 and HZSM-5 on char formation could not be drawn so far.

3.4. Catalytic effects on heat flow

Each of DSC curves for the three untreated biomass samples shows an obvious endotherm between 350 and 400°C followed by an obvious exotherm between 400 and 500°C (see Figs. 7–9). The endotherm is correlated mainly to the decomposition of cellulose in the biomass and the exotherm is attributed to the recombination of the degradation products of lignin, e.g., phenols and phenolic derivatives, which led to char formation. The above analysis can be confirmed by the DSC of the pure cellulose and lignin. We know from Pappa et al. [12] that DSC of pure cellulose showed an endotherm at 341°C followed by no exotherm and the DSC of pure lignin showed an exotherm at 400°C without a preceding endotherm. Due to the cement-like role of lignin to cellulose, the endotherm and exotherm of our untreated biomass samples occurs at higher temperatures.

DSC curves for the samples treated with TiO_2 and HZSM-5 show no apparent change in terms of shape in contrast to the corresponding DSC curves for the untreated biomass samples. But both the endotherm area and the exotherm area for the treated samples are a little larger than those of untreated samples. This indicates that the added catalysts have played some roles in the pyrolysis process, which are not very clear so far.

A wide camel back-like exotherm peak occurs between 250 and 400°C on each of DSC curves for the samples treated with NaOH and Na_2CO_3 . The endotherm corresponding to the

Table 3
Net char residue weight (%)

	Untreated	Na_2CO_3	NaOH	NaCl	Na_2SiO_3	TiO_2	HZSM-5
PW	15	23	25	19	20	10	12
CS	19	15	18	16	22	14	11
FW	16	24	22	17	20	12	10

Ash and added catalyst deducted. For untreated samples: net char residue weight (%) = char residue weight (%) – ash (%); for treated samples: net char residue weight (%) = char residue weight (%) – $(1/11) \times 100 - (10/11) \times$ ash (%).

decomposition of cellulose seems to have been masked by this wide exotherm. The exotherm is due to charring reaction and it indicates that NaOH and Na₂CO₃ have greatly promoted char formation. From analysis of Section 3.3, we know that NaOH and Na₂CO₃ indeed tend to increase char formation. As for samples treated with Na₂SiO₃ and NaCl, the exotherm peaks are between 300 and 400 °C and are not so wide as those for NaOH and Na₂CO₃ treated samples. Therefore, the preceding endotherm peaks are exposed. Each DSC curve shows an endotherm between 50 and 100 °C, which corresponds to moisture vaporization process.

4. Conclusions

From thermal analysis of three kinds of biomass species and investigation of catalytic effects of six inorganic compounds on their pyrolysis we found that the catalytic pyrolysis behaviors varied with the basicity and acidity of the additives. The following conclusions can be drawn:

- (1) The sodium catalysts can make pyrolysis of the three biomass species take place at lower temperatures. The temperature reduction effects follow the order of NaOH > Na₂CO₃ > Na₂SiO₃ > NaCl, which is in the same sequence of their basicity. TiO₂ and HZSM-5 have no obvious effects on pyrolysis temperatures of pine wood and fir wood, whereas they are able to make pyrolysis of cotton stalk occur at higher temperatures and the temperature increasing effects follow the order of HZSM-5 > TiO₂, which is in order of decreasing acidity.
- (2) The basic catalysts NaOH, Na₂CO₃ and Na₂SiO₃ can decrease the maximum weight loss rates while NaCl and HZSM-5 tend to increase the maximum weight loss rates. All the sodium catalysts tend to promote char formation.

- (3) Sodium catalysts can make the pyrolysis more exothermic while TiO₂ and HZSM-5 have minor effects on reaction heat.

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