



Thermogravimetric investigation on characteristic of biomass combustion under the effect of organic calcium compounds



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HIGHLIGHTS

- Thermal behavior of organic calcium compounds and its blended fuels were studied.
- Co-burning was controlled by OCCs' additive amount and its volatile matter contents.
- Combustion performance indexes decrease with increases of Ca/S ratio.
- OCCs improve most biomass burning, and co-burning of OCCs and biomass is feasible.

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ABSTRACT

Experiments were conducted in a thermogravimetric analyzer to investigate thermal behavior of different organic calcium compounds (OCCs) and its blended fuels with three kinds of biomass. The effectiveness of synthesized method for OCC was assessed by the pyrolysis test. Effect of the mole ratio of calcium to sulfur on co-combustion characteristics was studied. Results indicated that preparation method of modified calcium acetate (MCA) had high precision and accuracy. Co-combustion characteristic of OCCs blended with biomass was controlled by OCCs' additive amount and the content of volatile matter which is mainly composed of small hydrocarbon molecules. Combustion performance indexes for peanut shell and wheat straw impregnated by OCCs were improved, however, an inverse trend was found for rice husk because of lower additive amount of OCCs. The blended fuel show higher combustion performance indexes compared with combustion of individual biomass, and these indexes decrease with increases of Ca/S ratio.

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1. Introduction

Biomass is the world's fourth-largest energy source, and its reserves are abundant (Demirbas, 2004; Forbes et al., 2014). Biomass with high volatile matter (VM) and low ash content features can achieve zero CO₂ emissions in the whole life cycle (Fernández et al., 2012), it has the dual nature of renewable and environmentally friendly. One of the most promising technologies for energy conversion of these biomass fuels is direct combustion. To achieve the same heating output of combustor, more biomass is needed because of the lower calorific value in biomass. Although the sulfur and nitrogen contents of biomass are low, the total pollutant emissions from biomass combustion can be significant. Meanwhile, as the environmental regulations become more serious, its pollutants emissions such as SO₂, NO_x, and PM_{2.5} in the process of

combustion cannot be neglected (Werther et al., 2000). Khan et al. (2009) provided an overview of the emission limits applied in the Netherlands. NO_x emission limit is dependent on the electricity equivalent efficiency. Brassard et al. (2014) compared the gaseous and particulate matter emissions from the combustion of agricultural and forest biomasses, they found that the quantity and quality of emissions were closely related to fuel characteristics; and they concluded that NO_x and SO₂ emissions limits could be included in the Quebec regulations.

The SO₂ and NO_x are the main pollutant emissions which are critically related to the biomass properties and are generated during combustion. High NO_x emissions (up to 1000 mg/m³) can be generated in laboratory units and large scale plants during the biomass combustion (Werther et al., 2000). For fluidized-bed combustion, the oxidation of fuel-N is the major source of NO_x emissions which can be attributed to the low operating temperature (750–950 °C) that prevents the formation of the thermal NO_x during the combustion process (Duan et al., 2014; Permchart and

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Table 1
Ultimate and proximate analyses and calorific values of biomass.

Material	Ultimate analysis (wt.%, db)					Proximate analysis (wt.%, db)			Calorific (MJ/kg, db)
	C	H	O*	N	S	VM	FC	A	
PS	41.75	6.10	38.53	0.52	0.54	70.47	16.97	12.55	17.69
RH	39.83	4.16	41.07	0.93	0.15	67.91	18.23	13.86	14.28
WS	42.19	4.63	37.95	0.61	0.21	68.67	16.92	14.42	16.18

db, Dry basis.

* Calculated by difference on dry ash-free basis.

Kouprianov, 2004). NO_x generated from high nitrogen content biomass is usually very high because of lower char content and therefore NO_x has little char available for reduction by CO (Savolainen, 2003). SO₂ from biomass combustion sources is also one of the causes for acid rain. Test runs and evaluations based on material balances have shown that 40–90% of the total sulfur input by the biomass is bound in the ash, the rest is mainly emitted as SO₂ with the flue gas (Oberberger et al., 1997). However, most of the available technologies, which have been run in the large scale facility, are focused on separate pollutant controlling. The investment and running costs are much higher, and this compromises the economical efficiency of power plant (Niu et al., 2011a). More attentions have been paid to simultaneously reduce NO_x and SO₂. The ability to simultaneously remove these pollutants using OCCs has been recognized (Atal, 1995; Cheng et al., 2004; Nimmo et al., 2004; Steciak et al., 1995). OCCs can release plenty of carboxylic and hydrocarbonyl radical during the thermal decomposition process and these intermediates can reduce NO emission under proper condition, but also have combustible characteristics. Calcium oxide as the residual solid products is effective in desulphurization. The use of OCCs such as calcium propionate (CP) as preservatives is well known in the food industry. The thermal behaviors of CP and calcium magnesium acetate (CMA) have been reported (Han and Sohn, 2002; O'Connell and Dollimore, 2000).

Existence of interactions between biomass and OCCs during co-combustion can lead to variations of fuel reactivity and burnout characteristics because co-combustion performance may not necessarily demonstrate synergistic interactions or simple additive behaviors as expected (Idris et al., 2010). Our knowledge of using OCCs as an additive for biomass combustion to simultaneously remove SO₂ and NO_x is still deficient. At present, extensive experiments in test rigs and power plants have been made to investigate the co-combustion behavior of OCCs and different coals. Niu et al. (2011a) studied the co-combustion behavior using thermogravimetric analysis (TGA) method, and they concluded that the coal combustion course can be optimized with the addition of OCCs. Atal and Levendis (1993) found that the addition of CMA inhibited swelling of the coal-water fuel. However, fragmentation of the chars containing CMA can occur occasionally during the volatile combustion stage, and thus the char's reactivity was improved. However, the VM content of biomass is much higher than that of OCCs. The VM content of blended fuel decreases with the additional amount of OCCs, which may have negative effect on the combustibility characteristics of blended fuel. Therefore, it is meaningful to screen OCC of good fuel quality for co-combustion with different biomass at a wide range of Ca/S ratio before designing co-combustion scenarios. Meanwhile, commercially available CMA is expensive (about \$1300/ton) due to the relatively high cost of producing acetic acid from natural gas and due to its limited markets. Therefore, we used low-cost raw materials in this study to produce CMA by chemical synthesis. The CMA obtained through synthetic method is named MCMA. Modified OCCs were synthesized following the same procedure reported in the literatures (Niu et al., 2011b; Valor et al., 2002).

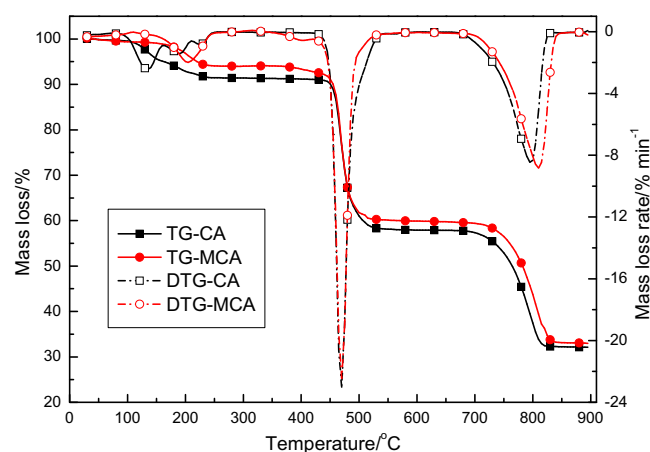


Fig. 1. TG and DTG curves for the thermal decomposition of CA and MCA (CA = calcium acetate, MCA = modified calcium acetate).

In this study, peanut shell (PS), wheat straw (WS) and rice husk (RH) are selected as biomass fuel; calcium acetate (CA), CP, and MCMA are respectively added to different kinds of biomass according to the mole ratio of calcium to sulfur (Ca/S ratio) from 1 to 3. The main objectives of this study are to (1) compare the decomposition behavior of MCA and pure CA by pyrolysis test; (2) compare combustion behaviors of three different biomass fuels with OCCs; (3) analyze the co-combustion behaviors for peanut shell and three different OCCs with a wide range of Ca/S ratio; and (4) calculate the kinetic parameters using the Coats–Redfern method.

2. Experimental section

2.1. Materials

Three different biomass fuels including PS, WS, and RH used in this study were collected from South-East China, which are the most common agricultural residues. Ultimate and proximate analyses and calorific values of biomass are given in Table 1. The higher heating values (HHVs) of all the biomass samples were measured through IKA C2000 CONTROL bomb calorimeter. Three different OCCs (i.e. CA, CP, and MCMA) were used to blend with biomass. The co-combustion profiles of blended fuels were evaluated. Modified CA (MCA) obtained by using synthetic method and analytic pure CA are analyzed by pyrolysis test to compare their decomposition behavior. The effectiveness of the synthesized method for OCC was assessed by the pyrolysis test. Prior to characterization, all the OCCs and biomass samples were ground into less than 0.15 mm fine powders using a rotary mill.

2.2. Preparation of OCC and biomass blends

Different Ca/S ratios, i.e. 1:1, 2:1, and 3:1, were selected. To guarantee a uniform distribution of OCCs in biomass, according

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