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# Insight into the kinetic analysis of catalytic combustion for biomass after alkaline metals loaded pretreatment

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## HIGHLIGHTS

- AM content affected the catalytic combustion process both at the pyrolysis process, more notably, the oxidization process.
- During pyrolysis process, the activity energy decreased with AM loading pretreatment, and decreased with the increasing of AM content; For oxidization process, the oxidizing rate increased with AM loading pretreatment, and increased with the increasing of AM content.
- The kinetic model described the catalytic combustion for biomass after AM loaded pretreatment was established.
- The evolution of pyrolysis rate subordinated to the normal distribution model; The oxidization rates of acid-washing biomass followed the first order homogeneous reaction model; The oxidization rates of biomass-AM samples accorded well with RPM.

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## ABSTRACT

Biomass combustion was important for a wide range of scientific and industrial processes, and played a key role in biomass utilization. This study was aimed to research the catalytic combustion kinetics of biomass after alkali metals (AM) loaded pretreatment. Firstly, this paper investigated the behavior of catalytic combustion for biomass after AM loaded pretreatment. Without considering the evaporation of moisture, the thermal events of catalytic combustion for biomass could be divided into two mass loss steps. The first process was the loss of volatile compounds and the formation of semi-coke. The second process was volatile compounds and the semi-coke were oxidized, and released a lot of heat. Secondly, this paper evaluated the performance of catalytic combustion for different kinds of AM. With the increment of AM loading ratio, the initial pyrolysis temperatures reduced, whereas the devolatilization index, the comprehensive combustibility index, the semi-coke yield index and the differential thermal peak area showed an opposite variation trend. Additionally, at the same concentration, the same kind of AM had different catalytic influences on various type of biomass. Thirdly, this paper established the kinetic model to described the catalytic combustion for biomass after AM loaded, which accurately described catalytic combustion for biomass after AM loaded.



## 1. Introduction

Recently, in view of environmental protection around the world, there has been renewed interest in the biomass utilization, which provided a marked potential way to reduce greenhouse emissions [1]. Biomass combustion was important for a wide range of scientific and industrial processes, and played a key role in biomass utilization [2]. There is increasing concern that the momentousness of catalytic combustion [3–6]. Nevertheless, the behavior of catalytic combustion for coal [7], black carbon [8], or coal soot [9] has been massively researched over many years by mixing different inorganic compounds. For instance, Jiménez et al. [10] studied the catalytic combustion of coal soot with adding AM on CaO-MgO physical mixtures. It was now well established from a variety of researches, that it was advantageous to enhance the performance of coal combustion by mixing alkaline earth, alkali metals in the form of oxides or salts, such as raising oxidation rates and declining ignition temperature [11–13]. Admittedly, as a number of heterogeneous and homogenous reactions are involved in the catalytic combustion, the mechanism of catalytic combustion turn to elaborate [14]. As the metal oxides have the facility to store oxygen and redox properties, some researchers suggested that the oxygen transfer improved by mixing alkaline earth, alkali

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and transition metals. Compared to coal, biomass contains more volatiles. Nonetheless, few studies have investigated that the catalysts of coal combustion whether are suitable for biomass combustion.

A considerable literature has grown up around the theme of the catalytic combustion of biomass [15–17]. For instance, Wang et al. [17] investigated the catalytic combustion of wheat straw by incorporating TiO, CuO and MnO, notwithstanding the price of TiO, CuO and MnO were expensive. Accordingly, there is rarely engineering application of TiO, CuO and MnO as the catalyst of combustion. Relatively, the price of alkali or alkaline earth is cheap, further, alkali or alkaline earth is widespread. Alkaline earth has been investigated in previous researches as catalysts for wheat straw, rice and municipal solid wastes [18]. Nonetheless, a large volume of published studies taken a simple approach to research the catalytic combustion for biomass fuels, e.g. mixing alkali or alkaline earth with biomass fuels. Actually, biomass also contains a small amount of potassium (K), calcium (Ca), magnesium (Mg), sodium (Na) and other elements. Those alkali metals usually consist in biomass with the form of oxides or salts. Jiang et al. [19] demonstrated that those alkali metals could affected the pyrolysis and combustion of shale char. Consequently, those alkali metals possible have catalytic effects on the biomass combustion. However, there is lack of information on the catalytic combustion for biomass by those alkali metals. Removing those alkali metals from biomass plays an important role in the investigation of this research area. Srinivasan et al. [20] demonstrated that inorganic matters could be removed by acid-washing pretreatment. Compared to water-washing pretreatment, acid-washing pretreatment is more effective in removing inorganic matters from biomass. Furthermore, the initial content of alkali metals is usually various in different biomass species. Therefore, the content of alkali metals probably is one of important factors in biomass combustion. Kawamoto et al. [21] pointed out that $K^+$ as well as $Na^+$, $Ca^{2+}$, $Mg^{2+}$ could promoted the generation of solid char, small molecular compound and $H_2O$ in cellulose pyrolysis. Jensen et al. [22] confirmed that the yields of tar and gases were between those from the raw and washed straw by adding 2 wt% (daf) KCl to the washed straw, and suggested that the added potassium salt did not behave in the same way as the inherent potassium salt in the straw. Hence, for biomass combustion, the type of alkali metals probably is another important factor. Many studies demonstrated that biomass combustion process included four parts, drying process, pyrolysis process, oxidization process and reduction process [23,24]. As illustrated in Fig. 1I, flue gas as well as semi-coke was generated from the dried biomass after pyrolysis process, then these productions were oxidized by oxygen, and released lots of heat. Finally, the semi-coke was converted into ash. As previously described, some researchers indicated that there had obviously catalytic effects on biomass pyrolysis with the addition of some alkali metal salts, besides the yield of solid char and gas production increased, as presented in Fig. 1II.

Bamboo (BB) forests supply important ecosystem services and play an important role in terrestrial carbon cycling [25]. Compared to other countries, China has plentiful bamboo resources in terms of number of area and species (>500 species in 39 genera), and has long been known as the "Kingdom of Bamboo" [25]. Bamboo could be applied to produce bamboo-fiber, bamboo-flavone, bamboo-charcoal, bamboo-flooring, bamboo-plywood, etc. A lot of bamboo chips will be produced in practical production. The utilization of bamboo chips plays a critical role in development of bamboo industry. Much researches on the utilization of bamboo chips has focused on the pyrolysis behaviors of bamboo chips [26–28]. Actually, combustion is more suitable for utilizing bamboo chips. The benefit of this approach is that combustion heat can be applied in bamboo industry. Meanwhile, the transporting costs of bamboo-waste could be reduced. Therefore, the utilizing efficiency of bamboo could be improved. As mentioned above, it was advantageous to enhance the performance of solid fuels combustion by mixing alkaline earth, alkali metals. Up to now, far too little attention has been paid to investigate the catalytic combustion of bamboo chips. Rice is one of main food crop in the world, of which 90% of rice is produced in Asia, and consumed by the developing countries in Asia. Similar to bamboo, rice husk (RH) is one of main biomass resource. Investigating the catalytic combustion of those biomass will enhance our understanding how to utilize those biomass wastes with high efficiency.

The combustion kinetics of biomass is an important characteristic to describe the effect of the operating parameters, such as reaction temperature, heating rate and residence time, on the conversion rate of biomass-to-bioenergy. A major advantage of kinetic analysis is that the reaction rate of biomass combustion can be predicted. Simultaneously, the mechanism of biomass combustion as well as the process of biomass combustion could be deeply comprehended by kinetic analysis. The existing literature on kinetic analysis of combustion is extensive and focuses particularly on coal combustion [29], biomass combustion [30], coal char combustion [31], biomass char combustion [32] and coal-biomass char blends combustion [33]. However, there is a relatively small body of literature that is concerned with the catalytic combustion of biomass by AM loaded pretreatment.

The purpose of this investigation is to explore the catalytic combustion kinetics of biomass after AM loaded pretreatment by an experimental and theoretical study. The main issues addressed in this paper are: a) investigate the behavior of catalytic combustion for biomass after AM loaded by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC); b) comprehensive evaluate the performance of catalytic combustion for different kinds of AM, the evaluating index contains the devolatilization index, the comprehensive combustibility index, the semi-coke yield index and the differential thermal peak area; and c) establish the kinetic model of catalytic combustion for biomass after AM loaded.

## 2. Materials and methods

### 2.1. Materials

Rice as the main source of carbohydrate for most Asians and is grown in all Chinese provinces. In addition, bamboo is one of the most important forest resources in China with wide distribution and large amount [25]. So rice hull and bamboo was selected as the ideal biomass of this study. The raw rice hull was obtained from local farm, and bamboo was attained from local manufactory. They were shredded to 60–80 mesh, dried at 105 °C for 3 h in the oven and then stored in a desiccator. The proximate, ultimate and component analyses for the BB and RH are listed in Table 1. As listed in Table 1, the volatile content of BB and RH were significantly higher than coal [9]. In addition, the ash content of RH was obviously higher than BB, these results was similar to other researches [34–36]. However, the cellulose content of BB was higher than that of the RH, similar results was reported by other researchers [28,37,38].

To evaluate the inhibition of biomass ash and more easily study the effects of AM on biomass combustion, acid washing as well as AM loading were performed. The deashing biomass (form-AW) was originated from the raw biomass (form-RAW) by: acid (38% HCl) washing 24 h, hot water (60 °C) rinsing 24 h, then hot air drying (105 °C) 24 h. The AM loading biomass (form-AM) was originated from the deashing biomass (form-AW) by: acid (38% HCl) washing 24 h, then AM loading (with various content of AM for