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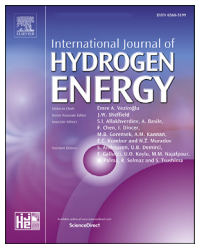

Study on catalytic properties of potassium carbonate during the process of sawdust pyrolysis

Weihong Zhou [a,b], *Bin Bai* [b], *Guanyi Chen* [a,c,**], *Longlong Ma* [d], *Dengwei Jing* [e,*], *Beibei Yan* [a]

[a] *School of Environmental Science and Engineering/State Key Lab of Engines, Tianjin Engineering Center of Biomass-derived Gas and Oil, Key Laboratory of Efficient Utilization of Low and Medium Grade Energy (Ministry of Education), Tianjin University, Tianjin, 300072, China*

[b] *School of Civil Engineering, University of Science and Technology Liaoning, Liaoning Anshan, 114051, China*

[c] *School of Science, Tibet University, No.36 Jiangsu Street, Lhasa, 850012, Tibet Autonomous Region, China*

[d] *Guangzhou Institute of Energy Conversion Guangzhou, Guangdong, 510640, China*

[e] *State Key Laboratory of Multiphase Flow in Power Engineering (SKLMF), Xi'an Jiaotong University, 28 Xianning West Road, Xi'an, 710049, China*

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ABSTRACT

In order to investigate the effect of potassium carbonate on biomass pyrolysis properties, sawdust was used as raw material and different amounts of K_2CO_3 were added by impregnation method to carry out thermogravimetric and pyrolysis experiments. The effects of pyrolysis temperature and the amount of K_2CO_3 addition on the pyrolysis of sawdust were studied using a self-made fixed-bed pyrolysis furnace. Calculation of pyrolysis kinetics shows that the existence of K_2CO_3 catalyst changes the pyrolysis path of sawdust, so that the activation energy of pyrolysis sawdust decreases at low temperature and increases at high temperature. The pyrolysis experiments shows that the addition of K_2CO_3 and the increase of pyrolysis temperature both reduce the yield of the pyrolysis oil of sawdust and increase the yield of the pyrolysis syngas. However, K_2CO_3 catalyst promotes the yield of char, the increase of pyrolysis temperature decreases the yield of char. Analysis of the pyrolysis products finds that the addition of K_2CO_3 and the increase of pyrolysis temperature both improve quality of the pyrolysis oil, form more microporous surface of char, and increase the hydrogen content in the pyrolysis syngas. It is considered that the optimal process for producing pyrolysis syngas is 900 °C of pyrolysis temperature and 10% of K_2CO_3 addition.

* *Corresponding author.*
** *Corresponding author.* School of Environmental Science and Engineering/State Key Lab of Engines, Tianjin University, Tianjin 300072, China.
E-mail addresses: chen@tju.edu.cn (G. Chen), dwjing@xjtu.edu.cn (D. Jing).

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Introduction

In recent years, with the increasing consumption of fossil fuels, the shortage of energy and the environmental pollution seriously restrict the economic and social development. As a clean, efficient and renewable energy resource, biomass energy arouses attentions around the world. Biomass is transformed into many forms of energy products by pyrolysis technology. However, conventional pyrolysis technology has the problems of low efficiency and poor product quality, hindering the further utilization of products. The presence of catalytic pyrolysis technology has better solved these problems [1–3]. Scholars have carried out a large number of studies on the catalytic pyrolysis of biomass.

Among many kinds of inorganic salts in biomass which have less content but significant impact on pyrolysis of biomass [4,5], potassium salt attracts scholars' attention with its excellent catalytic properties [6–10]. The existing researches focus more on the high-quality bio-oil and bio-char from the catalytic pyrolysis of biomass. Mishal [11] studied the effect of potassium salt on the pyrolysis of poplar at 427 °C. It was found that the addition of potassium salt has a significant effect on the conversion time and the exothermic peak temperature shift. It was believed that K_2CO_3 promotes the pyrolysis of poplar wood to form char more effectively than KCl. Chen [12] studied microwave pyrolysis of sawdust with eight kinds of inorganic salts at 470 °C. It was found that inorganic salts greatly increase the yield of solid product, reduce the yield of gas product, and have no obvious effect on the yield of liquid product. Lu [13] studied the catalytic effects of K_3PO_4 on poplar, pine, corn stalk, cellulose and hemicellulose at 300 °C–600 °C using Py-GC/MS. It was found that K_3PO_4 inhibits the volatilization of holocellulose to form organic volatile components, but promotes the decomposition of lignin to form phenols. Hwang [14] studied the pyrolysis of potassium-impregnated poplar at the temperature of 450 °C, 500 °C and 550 °C. It was found that potassium increases the yield of char and affects the properties of the pyrolysis oil. Mohamed [15] studied the influence of catalyst consisting of clinoptilolite, bentonite and K_3PO_4 on the pyrolysis of switchgrass at 400 °C. It was found that microwave absorptivity is improved and the quality of biomass oil and char is enhanced. From the above researches, it can be seen that the pyrolysis temperatures used in these studies are relatively low, and there are few studies on the catalytic pyrolysis of biomass at high temperatures. As for the existing literature of high-temperature catalytic pyrolysis of biomass, most scholars used online detection methods to study pyrolysis processes and intermediated pyrolysis products of biomass, such as TG-FTIR, Py-GC/MS, etc. Besides, they set up pyrolysis reaction device of biomass for pyrolysis experiments and discussed the variation of partial pyrolysis products, rather than a comprehensive analysis of the whole three pyrolysis products, including pyrolysis syngas, pyrolysis oil and char. Hu [16] studied the effects of inherent alkali/alkaline earth metal salts (AAEMS) on the pyrolysis of biomass at 500 °C–900 °C, focusing on the variation of gas products and tar. Nowakowski [17] used TG-FTIR and Py-GC/MS techniques to investigate the effect of potassium salts on short rotation willowcoppice. Xing [18] used thermogravimetry and Py-GC/MS techniques to compare the effects of potassium and copper on the pyrolysis of sawdust. Lv [19] studied the influence of cellulose, lignin and alkali/alkaline earth on the pyrolysis of six biomass, and mainly analyzed the variation of char and pyrolysis product yield. Therefore, it is necessary to carry out experiment on catalytic pyrolysis of biomass with potassium salt under high temperature conditions. By comprehensively analyzing the yield and compositional changes of the three pyrolysis products, the authors investigated the catalytic pyrolysis behavior of potassium salts at high temperature, which provides inspiration and guidance for further gas production.

Thermogravimetric analysis (TGA) is an important research method in the field of biomass pyrolysis. Through pyrolysis kinetic analysis, the pyrolysis process and the pyrolysis rules of biomass are investigated. Because the kinetic parameters obtained from different kinetic analysis methods vary greatly, we conducted a kinetic study on the pyrolysis of biomass [20] and compared the results among different calculation methods in earlier stage. It was found out that the multi-scan rate method - Starink method avoids the hypothesis difference of the reaction mechanism function, ensuring the calculation result more accurate and convincing. Many existing kinetic pyrolysis studies [21–23] also showed that the calculation results obtained from the multi-scan rate method give a better description of the pyrolysis process of biomass. Therefore, Starink method has been adopted to carry out pyrolysis kinetic analysis in this experiment.

In summary, the potassium salt catalyst has a good catalytic effect in the pyrolysis process of biomass. In this paper, thermogravimetric analysis and fixed-bed pyrolysis furnaces were used for experimental studies. Using K_2CO_3 as catalyst and pine sawdust as raw materials, the influence of K_2CO_3 on pyrolysis yields and compositions of syngas, char and pyrolysis oil under high temperature pyrolysis conditions was fully analyzed through experiments. Kinetic analysis of K_2CO_3 catalytic pyrolysis was conducted by Starink method.

Materials and methods

Material

The pine sawdust (SD) used in the experiment was taken from the Anshan, Liaoning. Before carrying out the experiment, the sawdust was crushed and sieved as particle size of was 5–10 mm. After grinding and screening, the sawdust was selected as the thermogravimetric test sample which had the comminution granularity was within the range of 0.074 mm and 0.125 mm. These experimental samples were dried at 105 °C in the oven. The results on proximate analysis and ultimate analysis of sawdust are shown in Table 1.

Sample preparation

The chemical reagents used in the experiment were analytical grade and purchased from Sinopharm Chemical Reagent CO., Ltd. Catalyst solution was made up of potassium carbonate and deionized water. The mass ratio of catalyst and sawdust