

Contents lists available at ScienceDirect

[Thermochim](dx.doi.org/10.1016/j.tca.2010.11.006)ica Acta

journal homepage: www.elsevier.com/locate/tca

Investigation on catalyzed co[mbustion](http://www.elsevier.com/locate/tca) [of](http://www.elsevier.com/locate/tca) [wheat](http://www.elsevier.com/locate/tca) [stra](http://www.elsevier.com/locate/tca)w by thermal analysis

Lili Wang, Yupeng Guo, Yanchao Zhu, Yuning Qu, Ying Li, Chunguang Rong, Zichen Wang, Yanhua Liu[∗]

College of Chemistry, Jilin University, No. 2699, Qianjin Street, Changchun 130012, China

article info

Article history: Received 2 May 2010 Received in revised form 25 September 2010 Accepted 2 November 2010 Available online 11 November 2010

Keywords: Thermal analysis Catalyzed combustion Combustion characteristic Devolatilization Index

1. Introduction

Since the energy crisis in the mid-1970s, the energy utilization of biomass resources had received considerable attention. Biomass was a kind of renewable energy source [1,2]. The utilization of biomass rather than existing fossil fuels could offer more environmentally acceptable process for energy production and aid in conserving the limited supplies of fossil fuels [3]. It was well-known that wheat straw was a potential source of energy and value-added by-products among the vario[us](#page-3-0) [biom](#page-3-0)asses. In Denmark, wheat straw was the main biomass, which was used in the production of heat and power [4]. At present, the utilization efficiency of wheat straw was very low, so the high-e[fficie](#page-3-0)nt and clean technologies for the utilization of wheat straw were greatly encouraged [5].

During the last decade, more studies on coal combustion have been performed [6,7]. Wheat straw combustion was different from coal [and](#page-3-0) [c](#page-3-0)arbon due to its higher volatiles, therefore it was important to study the combustion of wheat straw [8]. The conversion technologies of biomass to energy are mainl[y](#page-3-0) [com](#page-3-0)bustion, pyrolysis and gasification, biomass can be converted into useful forms of ener[gy](#page-3-0) [effic](#page-3-0)iently using such processes [9–11]. Some authors had studied to promote combustion efficiency. The concentrations of alkali (K, Na), chlorine, CaO and Fe₂O₃ [mi](#page-3-0)nerals in the fly ashes were reduced using kaolinite and clinochlore as fuel additives [12].Wang had studied the behavior of wheat straw with the addition of coal during combustion by therm[ogravime](#page-3-0)tric [13], and Cai had studied

ABSTRACT

Combustion of wheat straw incorporating $TiO₂$, CuO and $MnO₂$ was investigated by means of thermal analysis carried out at 20 ◦C/min in the temperature range from 50 ◦C to 900 ◦C. Combustion characteristic indexes had been put forward to describe wheat straw combustion characteristics. All the results showed that the catalysis of the catalysts to the wheat straw combustion had been embodied in facilitation of the volatile matters release from wheat straw, which reduced the temperature of the maximum combustion rate, and the relative active sequence of catalysts to the ignition characteristic could be improved remarkably. The catalysis of different catalysts to the Devolatilization Index could be described as follows: $MnO₂ > TiO₂ > CuO$, and the relative active sequence of catalysts to the Combustion Characteristic Index could be described as follows: $CuO > TiO₂ > MnO₂$.

© 2010 Elsevier B.V. All rights reserved.

the oxidative pyrolysis kinetics of wheat straw by thermogravimetric analysis (TGA) under oxygen dynamic atmosphere [14]. In order to make use of wheat straw widely in energy field, the research for combustion characteristics of wheat straw was necessary.

Thermal analysis techniques had been widely used for combustion and pyrolysis of biomass [15,16]. The main objective of this study was to investigate combustion chara[cterist](#page-3-0)ics of wheat straw incorporating $MnO₂$, TiO₂ and CuO by thermal analysis. In this article, the catalysts were used in the process of biomass combustion, which changed the process of combustion, leading to the energy release in short tim[e](#page-3-0) [and](#page-3-0) [avo](#page-3-0)iding the behavior of agglomeration. It is propitious to the use of energy. On the basis of the results, the effects of different catalysts on pyrolysis of biomass would be investigated, so the liquid (termed bio-oil or bio-crude), solid and gaseous fractions would be changed, the effective catalysts could be selected in order to obtain more termed bio-oil or bio-crude. Therefore, the results of this work would be the base of biomass catalytical thermo-chemical conversion.

2. Experimental

2.1. Materials

The experimental materials of wheat straw came from a resident area of Changchun. The proximate analysis of wheat straw is presented in Table 1. TiO₂, CuO and MnO₂ were used as catalysts in the experiments. Wheat straw and catalysts were measured and mixed together. The samples with 2%, 5% and 10% of catalyst weights were prepared in the experiments.

[∗] Corresponding author. Tel.: +86 431 8515 5358; fax: +86 431 85155358. E-mail address: Liuyanh@jlu.edu.cn [\(Y.](#page-3-0) [Liu](#page-3-0)).

^{0040-6031/\$ –} see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.tca.2010.11.006

Table 1 Proximate analysis of wheat straw.

	Chemical analysis (%)				Elemental analysis (%)			
		Water Volatile Fix matter	carbon	Ash C		H.	N	
Wheat straw 7.34		68.80	19.20		4.66 39.68 9.68 10.42 39.35			

2.2. Experimental methods

The combustion characteristics of wheat straw with or without catalysts were performed on Mettler Toledo simultaneous thermal analyzer (TGA/SDTA851 e) with system interface device and a computer workstation. The prepared compound was about 5 g, and 5 mg compound was used to carry out the next experiments. Air was the purge gas and its flow rate was 20 ml/min, and the range of furnace temperature was from 50 ◦C to 900 ◦C, with heating rate 20 ◦C/min.

2.3. Methods of determination of Devolatilization Index (D) and Combustion Characteristic Index (S)

In this study, such indexes were determined by the equati[ons](#page-2-0) as follows:

$$
D = \frac{(d_m/d_t)_{\text{max}}}{T_{\text{max}} \Delta T}
$$

$$
S = \frac{(d_m/d_t)_{\text{max}}(d_m/d_t)_{\text{mean}}}{T_e^2 T_h}
$$

 $(d_w/d_t)_{max}$ was the maximum combustion rate, $(d_w/d_t)_{mean}$ was the average combustion rate, T_e was the ignition temperature, T_f was the burnout temperature and T_{max} was the temperature of the maximum combustion rate (T_{max} – the corresponding temperature of the first peak for DTA profile). ΔT was determined by the equation as follows: $\Delta T = T_{max} - T_e$. In the equations, D was used to evaluate the performance of volatile matters release, and S was used to evaluate the characteristic of wheat straw combustion.

3. Results and discussion

The combustion profiles of different blends with different catalysts and the pure wheat straw had been compared. Fig. 1 shows the TG–DTA profiles of wheat straw, and the curves reveal that combustion of wheat straw has been mainly divided into two stages. In the temperature range 100° C–500 $^{\circ}$ C, there were two exothermal peaks in the DTA curve. The first step in the combustion of wheat

Fig. 1. TG-DTA of wheat straw combustion.

straw (100–350 °C) showed an exothermal peak and the mass loss was about 64%. The second step of the mass loss was about 32% in the TG curve (350–500 $°C$), with an exothermal peak in the DTA curve.

The additive quality of the catalysts was 0%, 2%, 5% and 10%, respectively. The DTG curves are shown in Fig. 2a–c, and the results indicate that ignition temperature and T_{max} are lower than the case without catalysts in air atmosphere. When additive quality of catalysts was 10%, the catalyzed efficiency was higher than others. Fig. 3 shows the DTG profiles of wheat straw with 10% different catalysts. As shown in Table 2 and Fig. 3[,](#page-2-0) [the](#page-2-0) [te](#page-2-0)mperature of the maximum combustion rate has been decreased from 325 ◦C to 273 ◦C due to the existence of the catalysts.

3.1. Devolatili[zation I](#page-2-0)ndex (D) of wheat straw with different c[atalysts](#page-2-0)

Table 2 shows the characteristic parameters of the blends with different catalysts and pure wheat straw, obtained from the burning profiles (Fig. 3). Table 2 and Fig. 3 indicate that T_e and T_{max} of pure wheat straw are 287 °C and 325 °C, respectively, which are decreased to a certain degree with the catalysts used in experiments. The parameter $(d_m/d_t)_{max}$ increased from 2.11 mg/min to a certain degree. Among $(d_m/d_t)_{max}$ of the blends containing different c[atalysts,](#page-2-0) $MnO₂$ $MnO₂$ had [preferab](#page-2-0)le catalyzed performance to the maximum combustion rate of wheat straw. The phenomena showed that catalysts could facilitate wheat straw combustion. Furthermore, the Devolatilization Index D had been put forward to describe the performance of volatile matter release. With the increasing value of D, the temperature of volatile matter release became lower and $(d_m/d_t)_{max}$ became larger, which facilitated the release of the volatile matters. Table 2 indicates that $D(10^{-6})$ of pure wheat straw is 1.1, and incorporating with catalysts in experiments can increase D to a certain degree. D of the samples with 10% MnO₂, TiO₂ and CuO increased to 4.1, 3.1 and 3.0, respectively. The results showed that MnO₂ had preferable catalyzed action to the release process of the whe[at](#page-2-0) [straw](#page-2-0) [vo](#page-2-0)latile matters, but all the kinds of catalysts had made D increased. For Devolatilization Index of wheat straw, the relative active sequence of catalysts was described as: $MnO₂ > TiO₂ > CuO$.

3.2. Combustion Characteristic Index (S) of wheat straw with different catalysts

The ignition and burnout temperature could not directly reflect the combustion characteristics of wheat straw, but Combustion Characteristic Index S was used to evaluate the characteristic of combustion. In other words, with the increasing value of S, the ignition temperature became lower and the performance of combustion became better. Table 2 shows that $S(10^{-10})$ of pure wheat straw is 28.2. Compared with the combustion characteristics of wheat straw with different catalysts, it had been shown that the wheat straw Combustion Characteristic Index S of the samples with 10% MnO₂, TiO₂ and CuO had increased to 124, 142 and 157, respect[ively.](#page-2-0) [For](#page-2-0) Combustion Characteristic Index, the relative active sequence of catalysts was described as: $CuO > TiO₂ > MnO₂$. It indicated that all the catalysts had catalytic actions to the combustion of wheat straw, and the combustion performance had been greatly improved with CuO used in the experiment. Finally, CuO showed markedly catalytic activity to combustion.

The previous study reported the catalyzed combustion of high ash coal by thermogravimetric analysis $[6]$, MnO₂ had better effect on ignition performance and $Fe₂O₃$ had better effect on burnout performance, the ignition index and burnout index increased obviously due to addition of the catalysts. Compared with the previous study, $MnO₂$ and CuO were the effective catalysts to the combustion of wheat straw, which [had](#page-3-0) [sh](#page-3-0)owed markedly catalytic activity

Fig. 2. DTG of different amounts of catalysts: (a) CuO, (b) MnO₂, and (c) TiO₂.

Notes: 1, wheat straw; 2, wheat straw + 10% MnO₂; 3, wheat straw + 10% TiO₂ and 4, wheat straw + 10% CuO.

Fig. 3. DTG of wheat straw with 10% catalysts gr2.

to combustion and made Combustion Characteristic Index increase largely in this article.

4. Conclusions

The combustion of wheat straw could be divided into two stages. One was volatile matter release and combustion, and the other was the combustion of residual volatile matters and fixed carbon. The existence of catalysts could enhance the release of volatile matters for the first stage, which made the ignition and the maximum combustion rate of wheat straw happen at lower temperatures than that without catalysts. In the second stage, the action of catalysts for fixed carbon combustion might be as the carrier of oxygen, which supplied oxygen to the char easily. Therefore the combustion of wheat straw became more fully due to the addition of these catalysts. The energy released in a short time was propitious to the use of it. The results might be used to understand the characteristics and also provide a useful basis for further application of wheat straw in energy field.

References

- [1] M. Becidan, Ø. Skreiberg, J.E. Hustad, J. Anal. Appl. Pyrol. 78 (2007) 207–213.
- [2] L. Núñez-Regueira, J. Proupĭın-Castiñeiras, J.A. Rodrĭıguez-Añón, Thermochim. Acta 420 (2004) 29–31.
- [3] C. Acikgoz, O.M. Kockar, J. Anal. Appl. Pyrol. 78 (2007) 406–412.
- [4] M. Stenseng, A. Jensen, K. Dam-Johansen, J. Anal. Appl. Pyrol. 58-59 (2001) 765–780.
- [5] H. Luik, I. Johannes, V. Palu, L. Luik, K. Kruusement, J. Anal. Appl. Pyrol. 79 (2007) 121–127.
- [6] B.G. Ma, X.G. Li, L. Xu, K.Wang, X.G.Wang, Thermochim. Acta 445 (2006) 19–22.
- [7] R. Barranco, A. Rojas, J. Barraza, E. Lester, Fuel 88 (2009) 2335–2339.
- [8] M.Q. Chen, J. Wang, M.X. Zhang, M.G. Chen, X.F. Zhu, F.F. Min, Z.C. Tan, J. Anal. Appl. Pyrol. 82 (2008) 145–150.
- [9] H.B. Vuthaluru, Bioresour. Technol. 92 (2004) 187–195.
- [10] C. Wang, Z.K. Du, J.X. Pan, J.H. Li, Z.Y. Yang, J. Anal. Appl. Pyrol. 78 (2007) 438–444.
- [11] E. DeOliveira, R.L. Quirino, P.A.Z. Suarez, A.G.S. Prado, Thermochim. Acta 450 (2006) 87–90.
- [12] D. Vamvuka, D. Zografos, G. Alevizos, Bioresour. Technol. 99 (2008) 3534–3544.
- [13] C.P.Wang, F.Y.Wang, Q.R. Yang, R.G. Liang, Biomass Bioenergy 33 (2009) 50–56.
- [14] J.M. Cai, S. Alimujiang, Ind. Eng. Chem. Res. 48 (2009) 619–624.
- [15] B.X. Shen, C.F. Wu, L. Qin, Energy 31 (2006) 2900–2914.
- [16] J. Reina, E. Velo, L. Puigjaner, Thermochim. Acta 320 (1998) 161–167.