



Thermogravimetric characteristics and kinetics analysis of oil cake and torrefied biomass blends



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HIGHLIGHTS

- Thermogravimetric and kinetic analysis of torrefied biomass were studied.
- Torrefaction can increase the maximum DTG and smooth the DTG curve.
- CAS can improve the efficient heat transfer during pyrolysis.
- Torrefaction can enhance the activation energy which can be lowered by the CAS.
- 270 °C torrefaction and 30% CAS are conservatively selected as optimum conditions.

ARTICLE INFO

Article history:

Received 5 July 2015

Received in revised form 28 January 2016

Accepted 30 January 2016

Available online 6 February 2016

Keywords:

Biomass

Oil cake

Torrefaction

Co-pyrolysis

Kinetics

ABSTRACT

The pyrolysis characteristics and kinetics of the blends produced from the mixture of torrefied camphorwood and castor bean cake (CAS) were determined by thermogravimetric analysis. Kissenger–Akahira–Sunose (KAS) and Coats–Redfern methods were applied for kinetic analysis. The results show that torrefaction can increase the maximum decomposition rate and smooth the pyrolysis reaction at 250–330 °C in the differential thermogravimetry (DTG) curves, and the additive of CAS can reduce the high maximum decomposition rate caused by torrefaction. The kinetic results suggest that the activation energy can be enhanced by torrefaction, while this can be lowered by the additive of CAS. It was found that the activation energy dropped dramatically for CAM torrefied at 300 °C by Coats–Redfern method, whereas KAS method showed the contrary trend. The pre-exponential factors by Coats–Redfern method were decreased by the processes of torrefaction and co-pelletization with CAS. In consideration of heating value and activation energy, 270 °C torrefaction and 30% CAS is conservatively selected as the optimum condition.

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1. Introduction

Current awareness of environmental pollution and fossil energy shortage has resulted in the exploitation of clean and renewable energy. Biomass is considered as a sustainable and environmental energy resource, which contributes to the reduction of net CO₂ emission [1,2]. By virtue of great concerns on the sustainable and environmental energy resource, the development of applied technologies and methods for bio-energy has become a crucial topic. Pelletization is one of the most important methods to make its

density 4–10 times higher than raw material, which significantly reduces the transportation/storage costs [3,4]. However, the defective characteristics of biomass pellets hinder its large-scale application, such as high hygroscopicity, low energy density and low higher heating value (HHV). Several technologies have been considered to improve the characteristics of biomass pellets [3,5,6]. In our previous research, the defective characteristics of biomass pellets can be improved with the aid of torrefaction and co-pelletization [7].

Torrefaction is a thermal pretreatment process carried out at temperatures ranging from 200 to 300 °C under nitrogen condition [8]. It is well known that the torrefied biomass possesses the following properties: (1) the particles have strong hydrophobicity;

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(2) fine grindability is obtained after torrefaction; (3) the HHV of torrefied biomass is higher than that of raw biomass; (4) the moisture content drops markedly. Despite the numerous advantages of torrefied biomass, torrefaction has adverse effects on the energy consumption during pelletization and pellet density. In our previous study, co-pelletization of torrefied biomass and castor bean cake (CAS) can improve the characteristics of pellets and eliminate the unfavorable sides of torrefaction by means of the residual oil and protein in castor bean cake [7].

In reviewing recent studies of biomass fuel, most researches focused on the energy consumption, pellet density, hydroscopicity, pellet strength and heating value of biomass pellets [3,7,9–11]. Meanwhile, thermogravimetric analysis has been carried out extensively to investigate the thermal decomposition and kinetics during pyrolysis of biomass [12,13]. A detailed knowledge of thermogravimetric decomposition and kinetics is of vital importance for its thermal use and further upgrading the heat treatment process [14]. Also, it is well known that co-pyrolysis helps to produce high quality fuel, increase the solid retention time and reduce the char deposition [15,16]. It was reported that the kinetic analysis was performed to better understand the pyrolysis properties of oak tree and propose reaction mechanism [15]. Oyedun et al. examined the thermal decomposition and kinetics of co-pyrolysis of biomass and plastic blends and found that the pyrolysis characteristics and reactivity of blends varied [16]. However, the degradation of blends is a complex process that involves the decomposition of various components and mutual reactions between biomass and the additives. Until now, the thermogravimetric behavior and mechanisms to the co-pyrolysis of blends have not been fully studied. To our best knowledge, few studies focus on the mutual effects on the pyrolysis process and kinetic factors that exist between torrefied biomass and oil cake blends, so it is necessary to illustrate the interaction of torrefaction and co-pelletization with oil cake on the decomposition rates and activation energy in the co-pyrolysis process.

In this study, camphorwood (CAM) was torrefied at three torrefaction temperatures (240 °C, 270 °C and 300 °C). The raw and torrefied CAM were pelletized with castor bean cake (CAS), one kind of high-production oil cake, at three different proportions of 100%, 85% and 70%. This study provides comprehensive experimental data concerning the effects of torrefaction temperature and blending ratio on the co-pyrolysis of biomass. The specific objective of this study is to investigate the thermal decomposition behaviors and thermogravimetric kinetics concerning the mutual effects of torrefaction and co-pelletization with CAS.

2. Materials and methods

2.1. Materials

Camphorwood (CAM) is abundant in Hunan province, China, which was chosen as the experimental biomass in this study. The selected biomass was torrefied at 240 °C, 270 °C and 300 °C with a nitrogen flow of 100 mL/min as a carrier gas. Prior to torrefaction, the biomass sawdust was ground into fractions of particle size below 1 mm and then dried at 40 °C for 48 h. As shown in Table 1, the extractives content in torrefied biomass was lower than that in raw biomass, which resulted in high friction and weak binders during pelletization. Castor bean cake (CAS), waste of oil expression process, has high fatty compounds and protein contents among the various wastes. In the process of pelletization, the additive (CAS) was added into raw and torrefied samples with the proportion of 0%, 15% and 30%. The loaded sample (around 1 g) was compressed at a rate of 2 mm/min until the pressure was 4000 N. When torrefied biomass and castor bean cake are blended, the

Table 1
The proximate and ultimate analysis of raw and torrefied samples.

		CAM				CAS
		Raw	240 °C	270 °C	300 °C	
Proximate analysis (%)	VM	85.51	82.62	79.20	70.91	69.80
	FC	13.42	16.21	19.36	26.55	21.41
	A	1.07	1.17	1.44	2.54	8.79
Elemental analysis (%) ^a	C	48.18	51.02	53.05	61.94	44.21
	H	6.09	6.19	6.06	5.02	5.93
	O	45.03	42.37	40.60	32.81	41.94
	N	0.70	0.41	0.30	0.23	7.92
Fiber analysis	Hem ^b	20.82	18.39	9.70	4.63	28.98
	Cel ^c	38.87	48.47	52.69	40.22	20.73
	Lig ^d	24.40	23.77	27.77	49.58	23.75
	Ext ^e	15.91	9.37	9.84	5.57	26.54
O/C ratio		0.93	0.83	0.77	0.53	0.95
HHV (MJ/kg)		18.86	18.90	20.45	22.35	19.12

^a Elemental analysis (dried and ash-free base).

^b Hemicelluloses.

^c Cellulose.

^d Lignin.

^e Extractives.

defective friction and weak binder during pelletization can be removed by the fatty compounds and protein in CAS. Therefore, castor bean cake obtained from the expression process of castor bean can be used for this fuel blend study.

2.2. Thermogravimetric analysis

The pyrolysis characteristics of the samples were conducted using a thermogravimetric analyzer (DTG-60). The analyzer provides continuous recording of the thermogravimetry (TG) and the differential thermogravimetry (DTG) in terms of temperature increment per second. In each experimental run, around 15 mg sample from pellet loaded into a platinum crucible was placed inside the thermal analyzer. Then the experiment run was carried out at heating rates of 10, 20, 30 and 40 °C/min with temperature ranging from 30 °C to 800 °C. Once the heating temperature reaching 105 °C, it was hold for 5 min to remove the free moisture in sample and provide a dry basis for thermal analysis. To maintain the inert environment, nitrogen was used as the carrier gas during thermal analysis. The flow rate of carrier gas was fixed at 100 mL/min. Based on the distributions of sample weight, it was possible to carry out the TG and DTG curves of sample. The experiment under given condition was carried out more than twice for the sample counterparts from different parts of the pellet.

2.3. Pyrolysis kinetics

The pyrolysis kinetics parameters were obtained as follows. Generally, the reaction rate is expressed by the decomposition rate of samples given by Eq. (1):

$$\frac{dx}{dt} = k(T)f(x) \quad (1)$$

where $f(x)$ represents reaction model of degradation and rate constant, x is conversion given by Eq. (2):

$$x = (W_0 - W_i)/(W_0 - W_f) \quad (2)$$

where W_0 , W_i and W_f refer to initial, instantaneous and final weights, respectively. The k is the rate constant that is expressed by Arrhenius equation as Eq. (3):

$$k(T) = A \exp(-E/RT) \quad (3)$$

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