Bioresource Technology 247 (2018) 217–225

Contents lists available at ScienceDirect

Bioresource Technology

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

Influence of catalysts on co-combustion of sewage sludge and water hyacinth blends as determined by TG-MS analysis

Limao Huang[a], Candie Xie[a], Jingyong Liu[a,*], Xiaochun Zhang[a], KenLin Chang[a], Jiahong Kuo[a], Jian Sun[a], Wuming Xie[a], Li Zheng[a], Shuiyu Sun[a], Musa Buyukada[b], Fatih Evrendilek[b]

[a] *School of Environmental Science and Engineering, Institute of Environmental Health and Pollution Control, Guangdong University of Technology, Guangzhou 510006, China*

[b] *Department of Environmental Engineering, Abant Izzet Baysal University, Bolu 14052, Turkey*

ARTICLE INFO

Keywords:
Sewage sludge
Water hyacinth
Catalysts
Co-combustion
TG-MS

ABSTRACT

Effects of the three metal carbonates (K_2CO_3, Na_2CO_3, and $MgCO_3$) were quantified on catalytic co-combustion of the sewage sludge and water hyacinth (SW) blend using a thermogravimetric-mass spectrometric (TG-MS) analysis and kinetics modeling. The main dominating steps of the catalysts were the organic volatile matter release and combustion stage. Weighted mean values of activation energy (E_m) were estimated at 181.18 $KJ \cdot mol^{-1}$, 199.76 $KJ \cdot mol^{-1}$, 138.76 $KJ \cdot mol^{-1}$, and 177.88 $KJ \cdot mol^{-1}$ for SW, SW + 5% K_2CO_3, SW + 5% Na_2CO_3, and SW + 5% $MgCO_3$, respectively. The lowest E_m occurred with SW + 5% Na_2CO_3. Overall, catalyst effect on co-combustion appeared to be negligible as indicated by Gibbs free energy (ΔG). The normalized intensities of SW + $MgCO_3$ were strongest. The addition of Na_2CO_3 and $MgCO_3$ to SW increased flue gases emissions (CO_2, NO_2, SO_2, HCN, and NH_3) of SW, whereas the addition of K_2CO_3 to SW reduced flue gases emissions from the entire combustion process.

1. Introduction

With the growth of the global economy and human population, cumulative energy demand on fossil fuels, and associated emissions of greenhouse gases have increased significantly (Gangulya et al., 2012; Edward et al., 2017; IPCC, 2014). Actual and potential impacts of global climate change on the environment stipulate the pursuit of socio-economic policies that encourage the use of alternative energy sources. Increased production of biofuels is expected to contribute to the development of sustainable energy systems in industrialized and industrializing countries (Vamvuka et al., 2009; Xu and Chen, 2013).

There is an increasing amount of feedstock devoted to obtain energy from biomass such as wood, agricultural waste, coffee ground, sewage sludge, and water hyacinth (Chen et al., 2017; Huang et al., 2016). The rapidly growing rate of global urbanization has recently increased the quantity of sewage sludge (SS) from urban waste water treatment plants (Cieslik et al., 2015). Mean annual SS output was estimated at about 30 million t (with 80% moisture content) in China in 2015 (Liu et al., 2015). Since SS is laden with toxic metals, organic pollutants, and pathogens, the emissions of flue gas from SS combustion can pose harmful effects on public and environmental health (Batistella et al., 2015). On the other hand, water hyacinth (WH) (*Eichhornia crassipes*) was reported as one of the world's top ten "invasive grasses" due to its rapid and difficult-to-control proliferation (Villamagna and Murphy, 2010). However, its rapid growth paves the way for biofuel production (Zimmels et al., 2009), bioremediation (Gangulya et al., 2012), bioethanol and gas production (Aswathy et al., 2010; Mishima et al., 2008), feed production and adsorbent preparation (Guerrero-Coronilla et al., 2015), and co-combustion or pyrolysis (Huang et al., 2016; Luo et al., 2011). Many studies have focused on the hydrogen or methane production and pyrolysis gas (Luo et al., 2011; Lin et al., 2017; Barua and Kalamdhad, 2017); however, a few studies have investigated gaseous emissions during the co-combustion with water hyacinth.

Several emission reduction methods used for SS combustion included the optimization of combustion process (Han and Bollas, 2016), and the uses of catalysts (Sutton et al., 2001), adsorbents, or the dilution of the feedstock with other less pollutant materials (Xu et al., 2017). Although emissions from catalytic co-combustion of the sewage sludge and water hyacinth blend (SW) are expected to be lower than those from fossil fuels, it needs to be quantified whether or not SS-related emissions increase human exposure to health-damaging air pollutants (Batistella et al., 2015). In so doing, kinetics behaviors of emissions during the entire co-combustion process based on the chemical composition of the biomass and the reaction conditions should be

---

[*] Corresponding author.
E-mail address: www053991@126.com (J. Liu).

http://dx.doi.org/10.1016/j.biortech.2017.09.039
Received 13 July 2017; Received in revised form 4 September 2017; Accepted 6 September 2017

taken into account using a combined analysis technique of thermogravimetry and mass spectrometry (TG-MS) (Zhao et al., 2011; Huang et al., 2011; Miranda et al., 2012). There are a few studies about gaseous emissions from the co-combustion to improve understanding of the kinetic behaviors and gas emission characteristics of the alternative biomass under different catalysts. Therefore, the objective of this study is to quantify the thermal, kinetic and flue gas characteristics of the catalytic co-combustion of the SW blend in response to the three metal carbonates (K_2CO_3, Na_2CO_3, and $MgCO_3$) using a TG-MS analysis and non-isothermal analyses based on the Ozawa-Flynn-Wall (OFW) kinetic iso-conversional models.

2. Methods and materials

2.1. Sampling procedures

Sewage sludge samples were collected at intervals of 0.5 and 8 h through continuous acquisition from a terminal conveyor belt in a wastewater treatment plant in Guangzhou, Guangdong Province, China. Water hyacinth samples were collected from canals surrounding Guangzhou University Mega Center, Guangzhou, Guangdong Province, China. One week after all SS and WH samples were allowed to dry naturally at room temperature in the laboratory, they were milled and sieved using a 74-μm sieve. They were then subjected to oven drying at 105 °C to reach a constant weight and stored in a desiccator for subsequent testing. The moisture contents of SS and WH were 7.57% and 9.95%, respectively. The ultimate, proximate, calorific value and ash composition analyses of SS and WH are presented in Table 1.

The three metal carbonates of K_2CO_3 (purity ≥ 99.0%), Na_2CO_3 (purity ≥ 99.8%) and $MgCO_3$ (purity: 83.68–98.32%) were chosen as the catalysts owing to their inexpensive, colorless and tasteless characteristics. These catalysts were directly purchased from commercial shops. Based on a previous study on the co-combustion of SW blend ratios (Huang et al., 2016), the SW blend ratio of 80% SS to 20% WH was chosen in this study.

2.2. Experimental set-up procedures

Thermogravimetric analyses were conducted at the three heating rates of 10, 20 and 40 °C min^{-1} at a flow rate of 50 ml min^{-1}, using a simultaneous DSC–TGA equipment (NETZSCH STA 409 PC) from 30 to 1000 °C under the air atmosphere. Approximately 8 ± 0.5 mg of the sample was used in alumina crucibles in each analysis. Prior to the start of the experiment, several preliminary experiments without the samples were conducted to obtain the baseline against which the systematic errors of the instrument itself were in turn eliminated when the experiments with the samples were started. Furthermore, the samples selected randomly in the same batch were repeated for three times in an experiment to confirm the repeatability and authenticity of the generated data, and the resultant errors were within ± 2%. The NETZSCH–T4–Kinetic 2 software was used to provide TG and derivative TG (DTG) curves. A Vario EL Cube elemental analyzer (Elementar Analysen Systeme Gmbh, Germany) and a WZR-1T-CII Microcomputer Calorimeter (Bent Instrument Co., Ltd., Chain) were used for the ultimate analysis and higher heating values of the samples.

Emissions at the heating rate of 20 °C min^{-1} were monitored using a mass spectrometer (MS) (Rigaku Thermo Mass Photo, Japan) coupled to a TGA under 20% O_2/80% He atmosphere, at a flow rate of 300 ml min^{-1}. Data were normalized so that each m/z had its own response factor (Otero et al., 2011) and the intensities of the same parent molecules (CO_2, NO_2, NO, SO_2, HCN, NH_3 and H_2O) may be compared to the different samples.

2.3. Kinetic behaviors

Kinetic data from solid-state combustion were obtained using a TGA. Solid state reactions are the complex processes involving a superposition of several elementary processes such as nucleation, adsorption, desorption interfacial reaction, and surface/bulk diffusion. The approach used in the present study to compute combustion kinetic rates was based on Arrhenius equation. The rate of transformation from solid to volatile state is generally described thus:

$$\frac{d_\alpha}{d_t} = k(T)f(\alpha) \tag{1}$$

According to Arrhenius equation:

$$k(T) = Ae^{(-E_\alpha/RT)} \tag{2}$$

where α was conversion degree; t was time; T was the reaction temperature; A was the pre-exponential factor; E_α was the apparent activation energy; and R was the universal gas constant (8.314 J/K mol^{-1}).

α was expressed as follows (Huang et al., 2016):

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{3}$$

where m_0 and m_∞ were the initial and final masses of the samples, respectively. m_t was the mass of the samples at time t.

Eqs. (1) and (2) were combined into the following equation:

$$\frac{d_\alpha}{d_t} = Ae^{(-E_\alpha/RT)}f(\alpha) \tag{4}$$

when heating rate (β) was introduced (°C s^{-1}):

Table 1

The ultimate, proximate, calorific value and ash composition analyses of SS and WH on an air-dried basis.

Sample	Ultimate analyses (wt%)						Proximate analyses (wt%)				$Q_{net,d}$[a] (MJ kg^{-1})
	C	H	O[b]	N	S		M[c]	V[d]	A[e]	FC[f]	
SS	24.13	3.94	12.49	4.50	0.74		7.57	40.22	46.63	5.58	10.79
WH	36.62	5.28	27.49	3.01	0.25		9.95	56.30	17.40	16.35	14.77
Ash composition analyses (wt%)											
	Na_2O	MgO	P_2O_5	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	
SS	0.14	0.25	0.23	1.59	2.81	0.04	11.20	0.20	0.05	14.28	
WH	0.18	/	0.35	0.18	0.41	14.11	0.23	0.01	0.05	0.10	

[a] $Q_{net,\ d}$, higher heating value on an air-dried basis.
[b] O, calculated by O = 100%–C–H–N–S–M–A.
[c] M, moisture.
[d] V, volatile matters.
[e] A, ash.
[f] FC, fixed carbon.