



Effect of potassium on thermogravimetric behavior and co-pyrolytic kinetics of wood biomass and low density polyethylene



Limin Zhou ^{a, b, *}, Hongbin Zou ^a, Yun Wang ^a, Zhanggao Le ^a, Zhirong Liu ^a, Adesoji A. Adesina ^b

^a State Key Laboratory for Nuclear Resources and Environment, East China University of Technology, 418 Guanglan Road, 330013, Nanchang, PR China

^b School of Chemical Sciences and Engineering, University of New South Wales, Sydney, 2035, Australia

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ABSTRACT

The effect of potassium on the thermogravimetric behavior and co-pyrolytic kinetics of wood sawdust (WS) and low density polyethylene (LDPE) was investigated using a thermogravimetric analyzer. It was found that the co-pyrolysis behavior of the potassium-treated WS/LDPE mixtures were different from the combination of WS and LDPE, and the maximum weight loss between the experimental and calculated values (ΔW) was up to -24.2% . Potassium has a great influence on the pyrolysis of WS/LDPE mixtures, leading to the decrease of the characteristic decomposition temperature (T_{p1}) and the increase of char yield with increasing potassium content. The simulation of possible structures indicates that $[K\text{-cellobiose}]^+$ complexes have different configurations and potassium may facilitate the cracking of the glycosidic linkage and the ring-opening reaction. The kinetic analysis indicated that the co-pyrolysis of the potassium-treated WS/LDPE mixtures could be described by three independent first-order reactions. The increase of the potassium contents in the WS/LDPE mixtures causes an increase trend for E and A values in the first decomposition stage but leads to a decreasing trend in the second stage. Furthermore, the kinetic compensation effect (KCE) has been observed in each decomposition stage for the co-pyrolysis of potassium-treated WS/LDPE mixtures.

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1. Introduction

The co-pyrolytic process could have potential application in the environmentally friendly conversion of biomass and plastic wastes into valuable products [1–4]. Plastics have high hydrogen contents and can provide hydrogen during co-pyrolysis with biomass, resulting in the increase of liquid production [2,3]. Schematically, biomass could promote the degradation of plastics leading to an increase of the yield of light liquids [4]. Many research works have focused on the improvement of the liquid fraction [2–4]. However, the co-pyrolysis of biomass and plastic may also help to obtain high quality chars with higher calorific values compared to bio-chars produced in the pyrolysis of biomass alone [1,5].

Thermogravimetric analysis (TGA) is an important method for the investigation the co-pyrolysis of different solid materials such

as coal, biomass and plastic. The co-pyrolytic kinetics of these materials could be described by single or multiple-step first-order reactions [6,7]. The clarification of the co-pyrolytic behavior and kinetics is important for the operation of the industrial co-pyrolysis processes [7].

The effects of potassium on biomass pyrolysis have been reported by some researchers [8–10]. It was reported that potassium present in biomass could act as a catalyst for biomass pyrolysis [8–11]. Nowakowski et al. [8] found that potassium-catalyzed pyrolysis of short rotation willow coppice increased the char yields greatly. Potassium has also been found to have a catalytic effect on the combustion of the biomass, resulting in the higher combustion conversion [12].

However, very limited information could be found for the influence of potassium on the co-pyrolytic behavior and kinetics of biomass and plastic, thus it is important to investigate this for the co-pyrolytic utilization of both materials. This work clarified the influence of potassium content on the co-pyrolytic characteristics and kinetics for SW/LDPE co-pyrolysis, which is very important for the modeling of the co-pyrolytic process. The results from this work

* Corresponding author. State Key Laboratory for Nuclear Resources and Environment, East China University of Technology, 418 Guanglan Road, 330013, Nanchang, PR China.

E-mail address: lmzhou@ecit.cn (L. Zhou).

indicated that potassium treatment (or impregnation) could be a useful way for facilitating the conversion of biomass/plastic mixtures through co-pyrolytic process due to its catalytic effect.

2. Experimental

2.1. Raw materials

The wood sawdust biomass (WS) is from a local sawmill in Fuzhou, China. Low density polyethylene (LDPE, Tianjin Petrochemical Company, China) is used as the typical plastic. The WS was dried and grounded previously, and then sieved to obtain 140–200 μm biomass particles. After that it was treated with hydrofluoric acid for demineralization according to the procedure as described in Ref. [13]. The treated WS was then impregnated with potassium acetate solution to obtain the potassium-treated WS samples (potassium content 1.25–5.0 wt%). The preliminary experiments for the co-pyrolysis of potassium-treated WS/LDPE mixtures with different mass ratio have shown that the interaction between WS and LDPE is very strong in mass ratio of 1:1, which is similar to the experimental results obtained by Sharypov et al. [3] for the co-pyrolysis of biomass and plastic. Thus the WS/LDPE mixtures were homogenized by mixing in mass ratio of 1:1 for the experiments and labeled with different potassium contents (for instance, the WS impregnated with 1.25% K and LDPE mixture is labeled as WS/LDPE-1.25% K). Some characteristics of WS and LDPE are listed in Table 1.

2.2. Thermogravimetric analysis (TGA)

The pyrolysis of WS, LDPE and WS/LDPE mixtures was investigated using a Shimadzu TGA-50H thermogravimetric analyzer (Japan). Around 10 mg sample was heated under the protection of N_2 flow (30 mL/min). The sample was held at 105 $^{\circ}\text{C}$ for 30 min for the removal of moisture, and then it was heated at 10 $^{\circ}\text{C}/\text{min}$ to 700 $^{\circ}\text{C}$. All the experiments are repeated at least two parallel runs and the relative errors are less than 5%.

2.3. Kinetic analysis

The pyrolysis conversion (x) of the materials can be calculated by the following expression:

$$x = \frac{W_0 - W_t}{W_0 - W_f} \quad (1)$$

where W_0 (mg) is the original mass of the material; W_t is the mass of the sample at time t (min); W_f (mg) is final mass of the material.

The kinetic parameters, activation energy and pre-exponential factor, of biomass and plastic pyrolysis were determined by the Coats-Redfern approach [14]. It is assumed that the pyrolysis of solid fuels (such as biomass, plastic and coal) is a first-order reaction and could be expressed as the following formula [14,15]:

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-x) \quad (2)$$

where x is pyrolysis conversion, t (min) is time, E (kJ/mol) is activation energy, A (min^{-1}) is pre-exponential factor, R (J/mol K) is universal gas constant, T (K) is pyrolytic temperature.

For a constant heating rate (H), $H = dT/dt$, Eq. (2) could be integrated as:

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\frac{AR}{HE}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (3)$$

The kinetic parameters (E and A) can be calculated from the slope and the intercept of the plots of $\ln[-\ln(1-x)/T^2]$ versus $1/T$, respectively.

3. Results and discussion

3.1. Thermogravimetric (TG) curves

Fig. 1 shows the TG curves for the pyrolysis of the potassium-treated WS (Fig. 1(a)) and the potassium-treated WS/LDPE mixtures (Fig. 1(b)) with different potassium contents.

It can be seen from Fig. 1(a) that the pyrolysis of all the biomass samples is characterized by an initial rapid decomposition followed by a slow process. The initial stage (250–380 $^{\circ}\text{C}$) is attributed to the fast decomposition of hemicellulose and cellulose, while the latter process (380–700 $^{\circ}\text{C}$) is mainly caused by the slow decomposition of lignin in biomass [10]. The weight loss for WS materials decreased (char increased) after potassium treatment, decreased by 2.2–6.8 wt% at 700 $^{\circ}\text{C}$, as the potassium contents in the biomass increased from 1.25 to 5.0 wt%. The reason for the increase in the char yield after potassium treatment will be further discussed (in Section 3.4).

As shown in Fig. 1(b), the molecular structure of LDPE is not as complicated as WS but is more stable, thus LDPE is decomposed at higher temperature and the pyrolysis process is completed in a short-time period [3]. Moreover, the co-pyrolysis of the potassium-treated WS/LDPE mixtures with different potassium contents is different from the behavior of individual components. Since WS is decomposed at lower temperature than LDPE, the weight loss of the potassium-treated WS/LDPE mixtures at the low temperature region (<400 $^{\circ}\text{C}$) is mainly contributed to the decomposition of WS.

3.2. Derivative thermogravimetric (DTG) curves and the effects of potassium contents

The DTG results for the WS, LDPE, and the potassium-treated WS/LDPE mixtures with different potassium contents are shown in Fig. 2, and Fig. 3, respectively. For comparison, the DTG results for the potassium-treated WS are also presented (as shown in Fig. S1). The main characteristic parameters are summarized in Table 2, including the initial decomposition temperature (T_i), the final decomposition temperature (T_f), the maximum weight loss rate (dW_i/dT)_{max}, and its corresponding pyrolytic temperature (T_p) [7].

Table 1
Proximate and ultimate analyses of biomass and plastic samples.

Sample	Proximate analysis (wt%)			Ultimate analysis (wt% daf)				
	Ash (dry basis)	Volatile matter (daf)	Fixed carbon (daf)	C	H	N	O _{diff}	S
WS	2.6	82.8	17.2	48.2	6.2	1.5	43.8	0.3
LDPE	0.3	99.7	0.3	85.2	14.1	—	0.5	0.2

Diff: by difference; daf: dry ash free.

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