



Hydropyrolysis characteristics and kinetics of potassium-impregnated pine wood



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ABSTRACT

Pine wood biomass (WB) samples impregnated with different potassium contents have been investigated to determine the influence of potassium on their hydropyrolysis behavior. The experiments were carried out using a thermogravimetric analyzer under both N₂ and H₂ atmosphere, and at the heating rate of 10 °C/min from room temperature to 700 °C. Results demonstrated that potassium effected on the biomass pyrolysis significantly, as evidenced by the changes in char content and characteristic parameters such as the maximum weight loss rates and the corresponding peak temperatures. The mass of char remaining after pyrolysis significantly increased with the impregnation of potassium acetate, but it did not increase proportionately to the potassium content. The temperature at which the maximum degradation rate occurs shifted to lower temperature, and this effect was more prominent for potassium-impregnated biomass pyrolysis under H₂. It was also shown that the potassium had significant catalytic influence on the biomass pyrolysis, but this ability varied with the potassium content. The kinetic analysis indicated that both unimpregnated and potassium-impregnated biomass exhibited two-stage characteristics which could be kinetically described by two consecutive first order reactions. Moreover, the apparent kinetic compensation effect (KCE) has been observed for biomass pyrolysis under both N₂ and H₂.

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1. Introduction

In the past decades biomass has become more attractive to industry since it is a low CO₂, alternative energy source, which can therefore make significant contributions to meeting renewable energy obligations [1]. Processes such as combustion, gasification and pyrolysis have been identified as possible routes for energy and transport fuel production. The inorganic constituents of biomass can include more than 19 metals (including alkali metals), some of which act as catalysts that can determine the rate of degradation and yield of char in pyrolysis. It has been shown that certain chemical elements which affect pyrolysis degradation are sodium, potassium, magnesium and silicates [2]. Furthermore, in combustion, sulfur, sodium, chlorine and potassium in particular, influence the ash chemistry and hence dictate corrosion, slagging and fouling characteristics [3].

Of all the metals present in biomass, it is potassium that has the greatest influence on its thermal conversion properties, catalyzing both the pyrolysis and the combustion/gasification stage [4,5]. Potassium

catalyses both volatile combustion and char burn-out reactions, at least under low temperature combustion [6].

Transformation and release of potassium have been studied during the pyrolysis processes of biomass [7]. The results reveal that the potassium evolves during decomposition of the organic matrix at 200–400 °C from the original binding sites and may redeposit as discrete particles (mainly potassium) or disperse in the organic char matrix. Further evaporation of potassium to the gas phase occurs at approximately 700 °C, and evaporation of deposited potassium particles contributes to this.

The effect of alkali and other metals on the decomposition behavior of biomass have been investigated by some researchers [3–10]. Most of them suggested that the inorganic species present in biomass (which are necessary for plant growth) became one of the decisive factors which determined the behavior of biomass under thermal degradation, and this in turn affected the kinetic and conversion during pyrolysis, combustion, and gasification. Nowakowski et al. [4] reported that potassium-catalyzed pyrolysis increased the char yields greatly. Shimada et al. [8] claimed that alkali and alkaline earth metal chlorides affected cellulose pyrolysis in different ways. Pan and Richards [9] examined the effect of ion-exchanged cations on wood pyrolysis and reported that potassium, but not calcium, acted as a catalyst in pyrolytic reactions. A catalytic effect due to the presence of potassium in the biomass samples (willow SRC, wheat straw) was observed during combustion experiments in a DTA and methane-air flame [3].

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Alkali metals' catalytic effects on biomass pyrolysis have been known from early times, but have not been as much clarified in terms of the reaction mechanism as in the case of no alkali presence. Nishimura et al. [11] argued that K^+ acts as an initiator for biomass pyrolysis. The main components of biomass such as hemicelluloses and cellulose, are composed of numerous glucose units connected by glycosidic linkage with covalent bond of 300–400 kJ/mol and have crystalline structures stabilized by OH...O hydrogen bonds. When the temperature for biomass pyrolysis reaches over 200 °C, the degradation of hemicellulose and cellulose is initiated from the cleavage of the glycosidic linkage in its amorphous phase, where the weaker hydrogen bonds (about 25 kJ/mol) are present relative to its crystal phase (about 75 kJ/mol) [12]. The cleavage of glycosidic linkage is followed by the ring-opening of the glucose units. It is then possible that the ring-opening of $-C-O-C-$ bonds in the glucose unit is accelerated by the addition of K salts [11].

Since the presence of potassium plays important roles during biomass pyrolysis, it is important to clarify the influence of potassium on the pyrolysis behavior of biomass. On the other hand, the accurate knowledge of the reaction kinetics is essential for modeling of the pyrolysis process as well as designing a suitable reactor. For this reason the present work focuses on the kinetics of biomass pyrolysis in the presence of potassium.

Hydropyrolysis is an important technique for improving the quality of bio-oil produced from biomass pyrolysis. Preliminary work with *Euphorbia rigida* wood [13], pine wood chips [14] has established that bio-oils can be obtained in higher yield and with lower oxygen contents via hydropyrolysis compared to normal pyrolysis. Hydrogen is a reducing gas and the cracking of biomass in the presence of hydrogen can reduce the oxygen content in bio-oil [14]. Hydropyrolysis has also been described as a potentially rapid procedure for obtaining lignin-enriched residues from wood pyrolysis for either simply estimating lignin content or for performing stable isotope ratio measurements [15]. Therefore, it is interesting to investigate the hydropyrolysis characteristics and kinetics of biomass. It should be noted that the pyrolysis process refers not only to the thermal decomposition of the initial biomass but also to the secondary reactions among the primary pyrolysis products. Fig. 1 shows the decomposition routes for biomass pyrolysis [16].

The aims of the present work are to examine the influence of potassium on the pyrolysis characteristics and kinetics of biomass pyrolysis. A comparative study of nitrogen (inert) and hydrogen (10% H_2 in N_2) as a carrier gas was conducted using a thermogravimetric analyzer. The thermal events taking place during pyrolysis of biomass were identified and the kinetic data were obtained to fit thermogravimetric data, the global processes being considered as two consecutive first order reactions according to the initial fast pyrolysis and the subsequent slow pyrolysis.

2. Experimental

2.1. Materials

Pine wood sawdust (collected from New South Wales, Australia) was used as biomass feedstock. The wood biomass was dried at

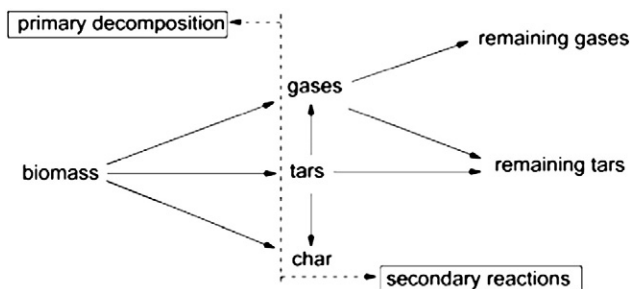


Fig. 1. The decomposition routes for the biomass pyrolysis.

105 °C and ground previously, sieved to obtain a 90–140 μm fraction. The proximate analysis, ultimate analysis, lower heating rate (LHV) and biochemical composition (determined by Klason sulfuric acid digestion procedure [17]) are listed in Table 1.

2.2. Impregnation of the wood biomass (WB)

One gram of biomass (pine wood) samples was demineralized using hydrochloric acid treatment according to the method reported in other literature [5]. The original content of K in the pine wood is 3.8 mg/g, and after HCl washing the K content is <0.1 mg/g. The washed pine wood was then impregnated by potassium (as potassium acetate) to yield a 1.25 wt.%, 2.5 wt.%, 3.75 wt.% and 5.0 wt.% K-impregnated sample. A certain amount of potassium solution (K content 10 mg/mL) was added into the biomass sample, and then the final solution volume for impregnating the biomass was fixed at 10 cm^3 by adding de-ionized water. The biomass samples were mixed for 2 h and then oven dried at 70 °C to constant weight. These samples were labeled according to the salt concentration in which they were impregnated (e.g. WB – 2.5% K).

2.3. Pyrolysis

Pyrolysis was carried out in a ThermoCahn TGA 2121 system. The balance can record accurately the weight loss of 0.001 mg and temperature of 0.1 °C and has provision for passing reactant/inert gas around the sample and heating the sample at heating rates ranging from 1 to 100 °C/min. In the present study, about 10 mg of sample was pyrolyzed under N_2 or H_2 (90% N_2 + 10% H_2 mixture) atmosphere (gas flow 50 mL/min) at heating rate of 10 °C/min from room temperature to 700 °C. The small amount of sample and the slow heating rate ensure that the heat transfer limitations can be ignored. The evolution with temperature of weight loss (TG) and the weight loss rate (DTG) were obtained for pyrolysis. The weight loss rate was calculated by the expression:

$$\frac{dW}{dt} = -\frac{1}{W_0} \left(\frac{dW_t}{dt} \right) \quad (1)$$

The pyrolysis conversion, x , can be calculated by

$$x = \frac{W_0 - W_t}{W_0 - W_f} \quad (2)$$

where W_0 is the original mass of the test sample; W_t is the mass at time t and W_f is final mass at the end of pyrolysis.

3. Results and discussion

3.1. TG curves

For pyrolysis of the biomass materials, the weight loss curves are shown in Fig. 2. It can be seen that the pyrolysis of biomass under both N_2 and H_2 is characterized by an initial rapid decomposition followed by a slow process. The first stage is attributed to the fast decomposition of hemicellulose and cellulose, while the second stage is caused by the slow decomposition of lignin of biomass [10]. In the first stage (<280–300 °C under N_2 and <250–280 °C under H_2), the TG curves have almost overlapped for both the potassium-impregnated and un-impregnated biomass materials under N_2 , while these curves have shifted to lower temperature under H_2 after impregnating potassium. In the second stage (>280–300 °C), the final weight loss decreased by 13–17% under N_2 and 11–15% under H_2 , respectively, as the potassium content in the biomass increased from 1.25% to 5.0%.

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