Research article

Practical estimation of reaction heat during the pyrolysis of cedar wood

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A R T I C L E   I N F O

A B S T R A C T

Variation of reaction heat of cedar wood pyrolysis with the variation of product distribution was estimated by means of heat balance calculation. For estimating the reaction heat of pyrolysis, heat balance was calculated with heating values of gas products, oil and char. Heating values of char and oil, except for gas product, were estimated with an estimation equation using only elemental composition of the products. The above heat balance indicated that the reaction heat of pyrolysis distributed in a wide range from −0.5 to 1.5 MJ/kg with the variation of product yields. The thermal decomposition of char and oil vapor to permanent gas during pyrolysis contributes to the endothermicity of reaction heat, while the production of the oil vapor from cedar pyrolysis contributes to the exothermicity of reaction heat. The gas composition also affects reaction heat distribution. Decrease in CO yield results in exothermicity of reaction heat. Increase in CH_4 contributes to exothermicity of reaction heat.

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1. Introduction

Pyrolysis reaction of biomass or other carbonaceous solid fuels is one of the key technologies to convert such carbonaceous resources to fuel and/or chemicals. For designing a reactor for such conversion, the heat of reaction, as well as kinetics, is one of the most important parameters for designing a reactor. Pyrolysis reaction has been recognized as an endothermic reaction because pyrolysis reaction consists of decomposition reaction. Several studies have reported the reaction heat from the pyrolysis of biomass and/or related materials [1–14]. The values reported for the reaction heat for pyrolysis were distributed in a wide range depending on the experimental conditions as well as the type of feedstock. Tang and Neill [1] have reported that the pyrolysis of cellulose is an endothermic reaction with a reaction heat of 0.369 MJ/kg. Rogers and Ohlemiller [2] have also reported that the reaction heat for the pyrolysis of cellulose is 0.337 MJ/kg. On the other hand, Roberts [3] has reported that values of the reaction heat for the pyrolysis of cellulose and lignin are −0.8 and −0.08 MJ/kg, respectively. Milosavljevic et al. [4] have summarized that the reaction heat for the pyrolysis of cellulose is distributed in a wide range from −2.1 to 2.5 MJ/kg. The heat of reaction from pyrolysis exhibits a significant variation depending on the experimental conditions even for cellulose, which has a structure rather simple as compared with that of biomass feedstock. In spite of such distribution in the reaction heat of pyrolysis, no reasonable explanation has been presented in any reports.

Several researchers reported the variation of reaction heat during biomass pyrolysis with product yield. Mok and Antal [5] have

investigated the effects of pyrolysis pressure and purge gas flow rate on the heat demands for the pyrolysis of cellulose. They have reported that a high pressure and low purge gas flow rate result in an increase in the char yield and a decrease in the heat demand. Notably, they have also reported an interesting result: the reaction heat of pyrolysis is related to char yield. The reaction heat of pyrolysis decreases almost linearly with increasing char yield. The reaction heat of pyrolysis was switched from endothermic to exothermic when the yield of char exceeded 17 wt%, although they provided no reason for this trend. Milosavljevic et al. [4] have investigated the reaction heat of pyrolysis under atmospheric pressure. They observed the similar trends as observed by Mok and Antal [5]: the reaction heat of pyrolysis linearly decreases with increasing char yield, although they did not observe an exothermic phenomenon. Despite the fact that the range of char yield is almost similar to that reported by Mok and Antal [5], the reaction heat values are completely different. Basile et al. [11] have investigated the effect of pressure on the reaction heat for the pyrolysis of biomass. They also observed a linear relationship between the reaction heat of pyrolysis and char yield. The reaction heat exhibited an exothermic phenomenon at high char yield. These studies have revealed that the char yield affects the reaction heat of pyrolysis. If the yield of char affects the reaction heat of pyrolysis, the yield of oil and gas should also affect the reaction heat. However thermal analysis methods cannot reflect properly the effect of oil and gas yield on the reaction heat.

Almost all the above-mentioned studies have been conducted by employing thermal analysis methods such as differential thermal analysis (DTA) [1,3,6,10] and differential scanning calorimetry (DSC) [2,4,5,7–11]. By these analyses, the heat of reaction can be directly obtained for a reaction occurring in a solid or liquid phase, while the heat of reaction in the homogeneous gas phase cannot be obtained by these

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methods, thereby demonstrating a limitation for the direct observation of reaction heat.

Another method for determining the reaction heat is the calculation of heat balance. Daugaard and Brown [12] have investigated the heat required for the pyrolysis of biomass in a pilot-scale fluidized bed reactor. They have measured the heat input to and output from the reactor and evaluated heat loss. From the difference of these values, they have concluded that the heat required for the pyrolysis of biomass varies from 0.78 to 1.64 MJ/kg depending on the type of biomass resource. Yang et al. [13] have calculated the reaction heat of pyrolysis by estimating enthalpy. Thus far, it has been difficult to determine the enthalpy of the oil fraction produced from the pyrolysis of biomass because the identification and qualification of the oil fraction, which consists of thousands of compounds, were difficult. They have proposed an estimation method for calculating the enthalpy of the oil fraction only using elemental composition. According to their calculation, the estimated heat of pyrolysis ranges from 1.1 to 1.6 MJ/kg depending on the type of biomass. These reports proved that the calculation of heat balance could reflect the effect of product distribution on the reaction heat of pyrolysis. Therefore the heat balance calculation must be proper to estimate the variation of the reaction heat and can estimate the distribution of reaction heat of pyrolysis with product yield.

A reasonable explanation on the distribution in the reaction heat of pyrolysis has not been reported anywhere, despite many studies on the heat of pyrolysis were reported. Understanding of the distribution of reaction heat will provide a direction to the design of reactors and also processes. Therefore quantitative estimation of the distribution in the reaction heat of pyrolysis must be useful practically.

In this study, the distribution in the reaction heat of woody biomass, cedar, pyrolysis was estimated by heat balance for clarifying the contribution of pyrolysis products to the reaction heat. For calculating the heat balance, the heating values of the pyrolysis products were required. The authors have already proposed the equation for estimating the heating value for hydrocarbon fuels within 10% error utilizing only elemental composition [15]. The elemental composition of products should vary with their yield because of thermal decomposition of functional groups and molecules. Hence, pyrolysis experiments were performed to obtain the relationship between the product yield and elemental composition of each product. Finally, heat balance was calculated for evaluating the contribution of each product on the reaction heat of pyrolysis to clarify heating values of the pyrolysis with extent of pyrolysis.

2. Cedar pyrolysis to determine relationship between product yield and elemental composition

2.1. Procedure to determine pyrolysis products

Pyrolysis experiment was performed in a fluidized bed reactor to determine the relationship between product yield and the elemental composition. Biomass sample used herein was cedar chips, which had a particle size of less than 2 mm. The sample property is listed in Table 1. Silica sand was used as the bed material with a particle size ranging from 50 to 200 μm.

Fig. 1 shows the schematic of the experimental apparatus, consisting of two screw feeders, a fluidized bed reactor, hot filter, condenser, and two cold traps. The fluidized bed reactor was heated up to a certain temperature, 723, 823 or 923 K, using an electronic furnace. Cedar chips

Table 1
Properties of cedar chip and product oil.

	Cedar chip	Oil
C, mass%-dry	52.0	62.0
H, mass%-dry	5.9	7.0
O, mass%-dry	42.2	31.0
LHV, MJ/kg	20.1	25.7

were continuously fed into the reactor from the top at a feeding rate of 0.5 g/min. Silica sand was also continuously fed into the reactor at a feeding rate of 5 g/min. Cedar chips were rapidly pyrolyzed in the fluidized bed reactor for producing volatiles and char. The volatiles were swept away from the reactor by the fluidization gas (N_2), while the char overflowed from the reactor with the silica sand. Hence, a steady state was achieved in the fluidized bed reactor. The volatiles evolving from the reactor were then sequentially cooled to 383 K, 268 K, and 200 K for condensing the liquid products. Gaseous products such as CO, CO_2, H_2, and hydrocarbon gases were intermittently analyzed by gas chromatography (3000 Micro GC Gas Analyzer, Inficon). After feeding the biomass feedstock for 60 min, the feeding of the feedstock and silica sand was terminated, and the reactor was cooled down to room temperature. A mixture of char and silica sand was recovered from the solid container connected to the fluidized bed reactor. The liquid product was recovered from the hot filter and condenser. The weights of the char and liquid product were measured for calculating the product yield. The weight of char was measured by a combustion method. The mixture of char and silica sand was subjected to combustion, and the weight decrease was analyzed. The weight decrease was assumed to correspond to the weight of char. The liquid product in the hot filter was recovered using a solvent (tetrahydrofuran). The solution was then evaporated under a vacuum of around 200 Pa for evaporating the solvent. The residue after evaporation as well as the recovered liquid in the condenser was treated as the liquid product. The amount of gaseous products was calculated by the integration of the gas flux and the concentration of each component. Elemental compositions of the char and liquid product were analyzed using an elemental analyzer (Flash2000, Thermo Fisher Scientific). The water content in the liquid product was analyzed by Karl–Fischer titration (EBU-610-KF, Kyoto Electronics Manufacturing). The yield of each product was calculated on dry basis by the following equations.

$$Y_{water} = \frac{A_{water} - A_{moisture}}{A_{biomass} - A_{moisture}} \tag{1}$$

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$$Y_i = \frac{A_i}{A_{biomass} - A_{moisture}} \tag{2}$$

Here, Y_{water} and Y_i represent the yields of the water and product i (gas, char and oil, except water), respectively. A_{water}, $A_{biomass}$, $A_{moisture}$, and A_i represent the amount of water, biomass on wet basis, moisture, and product i, respectively. The amount of the oil was calculated from the amount of the liquid product subtracted by the amount of water. A recovery of around 95% was achieved in this experiment.

2.2. Variation of product yield and elemental composition

In this section, the relationship between the product yield and elemental composition of the products is clarified. Fig. 2 shows the variation of the product yield with pyrolysis temperature. The yield of oil exhibited the maximum value at 823 K. On the other hand, with increasing pyrolysis temperature, the yield of gas increased, while that of char decreased. The yield of water was almost constant throughout the pyrolysis temperature. The tendency of the product distribution exhibited good consistency with that reported previously [16,17]. Fig. 3 shows the variation of the elemental composition of oil with pyrolysis temperature. The elemental composition of oil was almost constant despite the variation of the yield with the pyrolysis temperature. Fig. 4 shows the variation of H/C and O/C with the char yield according to the elemental composition of char. A char yield of 100% corresponds to the original cedar chip. The trends of H/C and O/C exhibit a logarithmic relationship with the char yield. The cross sections with the X-axis were 9.2 and 14.9 for H/C and O/C, respectively, indicating that the minimum