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Experimental investigation of intraparticle secondary reactions of tar during wood pyrolysis

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HIGHLIGHTS

- ▶ This study can clarify intraparticle secondary reactions of tar.
- ▶ Intraparticle reactions occur during the pyrolysis of large wood particle.
- ▶ Polymerization of tar (intraparticle reactions) progresses at approximately 380 °C.
- ▶ Intraparticle tar decomposition to secondary gas progresses at approximately 400 °C.
- ▶ Char works as a catalyst and lowers the reaction temperature of tar cracking.

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ABSTRACT

This study experimentally investigated intraparticle secondary reactions of tar during the pyrolysis of woody biomass. For this, pyrolysis products (gas, char, and tar) derived from Japanese cypress sawdust (particle size < 1 mm) and Japanese cypress wood cylinders (8 mm in diameter and 9 mm long) were compared. The samples were pyrolyzed in a thermobalance under argon atmosphere. The final reactor temperature was 600 °C, and the heating rate was 0.5 K/s. Under these conditions, the difference between the sawdust and wood cylinder is the intraparticle secondary reactions of tar. The tar yield of the wood cylinder decreases, whereas its total gas and char yields increase when compared with those of the sawdust. These results indicate that intraparticle secondary reactions of tar, which include intraparticle tar decomposition to form gases and polymerization to form char, occur during the pyrolysis of the wood cylinder. It is found that the intraparticle tar decomposition progresses between 400 and 500 °C, which is lower than the homogeneous cracking temperature of tar. This observation suggests that the intraparticle tar decomposition can occur heterogeneously on the surface of the microporous char which acts as a catalyst. This study shows that the intraparticle secondary reactions of tar play an important role in the pyrolysis of large wood particles. Moreover, these reactions have the potential to achieve tar reduction in biomass gasification without any additional tar removal process.

1. Introduction

Biomass, especially wood, is expected to be developed as a renewable energy resource to deal with global warming and the depletion of fossil fuels. Biomass is a carbon neutral fuel and hence it differs from fossil fuels [1,2]; moreover, it may offer additional advantages of low sulfur and nitrogen content [2,3]. Biomass can be converted to energy forms through various processes, such as thermochemical conversion and biochemical conversion. Gasification and pyrolysis are the most promising thermochemical conversion processes [4]. The energy efficiency of gasification is higher than that of combustion [2,5]. The primary reaction of gasification is pyrolysis, which produces three main products: gas, char, and tar. However, tar is an undesirable product that causes many operational difficulties in biomass gasifiers. Tar formation and condensation in a gasification system lead to blockage and foul of process equipment such as engines and turbines [2,6,7]. Therefore, many researchers have been developing technologies for controlling or suppressing the tar formation during biomass pyrolysis [8–10].

When biomass is pyrolyzed, volatile matter, which includes several tar and gas species, is released by thermal scission of chemical bonds; char is also formed. These reactions are considered as the primary reactions of pyrolysis. Next, a portion of the tar undergoes secondary reactions consisting of its decomposition to secondary gas and secondary tar, and polymerization to secondary

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char. Secondary tar decomposition may occur homogeneously in the vapor phase and heterogeneously on the surfaces of the pyrolyzing solid or other beds. Moreover, secondary tar decomposition can also occur within (intraparticle) or outside (extraparticle) the biomass particles [11,12]. Extraparticle tar decomposition reactions include homogeneous vapor phase cracking and heterogeneous conversion over the surface of the char or other beds. Boroson et al. [13] studied the homogeneous vapor phase cracking of wood pyrolysis tar using a two-stage reactor and reported 5–88% tar conversions at temperatures of 773–1073 K with residence times of 0.9–2.2 s.

The biomass feedstock used in commercial gasifiers has a relatively large particle size such as that of woodchips and wood pellets, because biomass materials unlike pulverized coal cannot be economically processed into fine sizes. Wood pellets measure 6–8 mm in diameter according to Swedish standards [14]. During the pyrolysis of large biomass particles, it was frequently mentioned that intraparticle secondary reactions, including intraparticle tar decomposition, are significant and affect product yields [11,15]. Large biomass particles may provide sufficient residence time for tar cracking reactions inside the particles. Thus, tar may be cracked during transport in the pores of large biomass particles or the char layer. Many researchers have reported positive effects of biomass char on the tar cracking reaction in a two-stage reactor [1,3,16–19]. However, there is little information and evidence regarding intraparticle secondary reactions of tar. We recently investigated intraparticle tar decomposition experimentally and numerically [20]. A calculation in our previous research indicated the possibility of intraparticle tar decomposition; however, this calculation did not consider heterogeneous reactions because their kinetic parameters were not available. In addition, the gas species produced through intraparticle tar decomposition have not been clarified. Further experimental studies should be conducted to investigate the intraparticle secondary reactions of tar.

In the pyrolysis of fine biomass particles, these reactions are negligible because of the short residence time of the traveling tar inside the particle. A simulation conducted by Di Blasi [11] showed that in small particles (less than 6 mm), intraparticle degradation of tar is negligible. Bryden and Hagge [21] reported that char does not provide additional holding time within the particles for secondary pyrolysis reactions in thermally thin particles (Biot number < 0.2). The characteristics of intraparticle secondary reactions of tar can be clarified according to the differences in such reactions between fine and large biomass particles by comparing the yields of pyrolysis products between fine and large particles.

The purpose of this study is to clarify intraparticle secondary reactions of tar experimentally by comparing the yields of pyrolysis products between the sawdust and wood cylinder, which represent fine and large biomass particles, respectively. Pyrolysis characteristics of both the samples under our experimental conditions were investigated by examining the temperature distribution of biomass particles, ultimate analysis of chars, and the weight fraction histories. Next, we discussed the effects of intraparticle secondary reactions of tar on the product yields and the reaction temperature.

2. Experimental

2.1. Sample preparation

The samples used in this study were Japanese cypress sawdust and Japanese cypress wood cylinders. The properties of Japanese cypress wood (trunk) are shown in Table 1. The wood cylinder was milled and then sieved to produce sawdust with particles less than 1 mm in size. The initial weight of the sawdust for each experiment was approximately 50 mg. The wood cylinder had a diameter of 8 mm, length of 9 mm, and initial weight of approximately 180 mg.

Table 1
Proximate and ultimate analyses of Japanese cypress wood (trunk).

Proximate analysis (wt%)	
Volatile matter	78.7
Fixed carbon	13.2
Ash	0.2
Moisture	7.9
Ultimate analysis (wt%, daf)	
C	51.5
H	6.2
O	42.2
N	0.1
S	–

2.2. Pyrolysis experiments

Fig. 1 shows a schematic diagram of the experimental apparatus that consists of a gas supply system, thermobalance (ULVAC TGD-9600), tar trap, and gas sampling bag. Pyrolysis experiments on the sawdust and wood cylinder were performed in the thermobalance. A sample was placed in a platinum crucible on a thermocouple (thermometric point). The height of the sawdust sample in the crucible was approximately 4 mm at which secondary tar decomposition on the char surface of other sawdust particles can be neglected [17]. Air inside the experimental setup was purged by a vacuum pump and then replaced by argon. Before pyrolysis, both the sawdust and wood cylinder samples were dried at 110 °C for 10 min. This drying period was long enough to dry both samples. Then, pyrolysis was performed at a heating rate of 0.5 K/s in an argon atmosphere flowing at 0.3 l/min. The heating rate was controlled at the thermometric point. Argon was used to sweep volatile matter from the reaction zone in order to prevent extraparticle reactions, which include secondary tar decomposition in the vapor phase. A calculation using the kinetic mechanism and parameters proposed by Boroson et al. [13] showed that extraparticle tar decomposition in the gas phase can be neglected in our experiment. The wood samples were heated at a constant rate to a final temperature of 600 °C measured at the thermometric point and were held at this temperature for 5 min. Tar was collected by an ice-cold trap containing a glass fiber filter (GC-90, ADVANTEC) downstream of the reactor, and the total weight of the trapped tar was measured after pyrolysis was complete. The weight change of the downstream tube was measured after experiment to determine an amount of tar depositing in the tube. In this study, tar is defined as condensable compounds attached to the filter in the tar trap and inside the downstream tube. Residual matter from the samples in the crucible was considered to be char and it was weighed after pyrolysis was complete. The final product yields shown in this paper were average from three repeated experiments, and the error bars which indicate 95% confidence intervals were also shown.

2.3. Measurements within the wood cylinder

The temperature within the wood cylinder was measured in the radial direction at three locations: the center ($r = 0$ mm), an intermediate position ($r = 1$ mm), and an outer position ($r = 2$ mm), at a depth of 6 mm from the top of the cylinder using *K*-type thermocouples with a diameter of 0.5 mm. These thermocouples were inserted through holes drilled into the wood cylinder. Fig. 2 shows the installation of thermocouples inside the wood cylinder. Tem-