Gas- and coke/soot-forming reactivities of cellulose-derived tar components under nitrogen and oxygen/nitrogen

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ABSTRACT

Eight types of cellulose-derived primary volatile product, i.e., levoglucosan, glycolaldehyde, furfural, 5-hydroxymethylfurfural (5-HMF), hydroxyacetone, acetic acid, formic acid, and MeOH, were pyrolyzed separately under N_2 and O_2/N_2 at 500–600 °C for 10 min in a closed ampoule, to clarify their gas- and coke/soot-formation behaviors. Under N_2, levoglucosan and glycolaldehyde gave coke through liquid-phase reactions after they melted, whereas coke formation from furfural, 5-HMF, and acetic acid was observed all over the reactor wall. The latter type of coke was formed through gas-phase reactions after vaporization of the starting compound and its pyrolysis products. The compositions of the product gases were found to be related to the functional groups of the primary volatile products, and their formations were reasonably explained by homolytic cleavage of the weakest bonds, followed by radical reactions. The addition of O_2 (0.3 M equiv with respect to the stoichiometric amount required for combustion) greatly altered the reactivities of furfural, 5-HMF, and acetic acid, although the effects were not large for the other components; the addition of O_2 significantly increased the gas yields from the furans and acetic acid at 500 °C, but greatly reduced the gas yields at 600 °C. Soot formation from the furans was also significantly enhanced by the presence of O_2. These unexpected results can be explained by the proposed pyrolysis pathways, in which O_2 acts as a biradical for H abstraction or radical-coupling reactions.

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1. Introduction

Gasification is attracting much interest as a technique for converting woody biomass to fuels and useful chemicals. The product gas can be used in efficient power-generation systems with gas engines or gas turbines. Synthetic petroleum and its related chemicals can be produced via syngas ($CO + H_2$) by Fischer–Tropsch (FT) reactions. In gasification, however, "tar trouble" is a challenging issue that needs to be solved for practical applications of gasification processes. The condensation of tarry products and deposits of coke/soot materials cause problems such as pipeline fouling of the gasifier, engine damage in the power plant, and deactivation of the FT catalyst.

Much effort has been made to solve tar trouble. Most studies have focused on the elimination of tar by catalytic tar cracking [1–5], water or oil scrubbing [6], and other physicochemical procedures. However, only a few studies have focused on the formation and elimination of coke/soot [7,8]. The mechanisms of coke

and soot formation from wood gasification are therefore not well understood, although such information is important in controlling gasification reactions to give tar-free clean gasification.

It has been suggested that coke and soot are produced through secondary reactions of the primary volatile products from wood constituents [8,9]. Hosoya et al. [10] compared the coke-formation reactivities of wood polysaccharides (cellulose and hemicellulose) and lignin. They reported that cellulose and hemicellulose gave coke mainly through liquid-phase reactions after condensation of the volatile products on the reactor wall at temperatures lower than their dew points, whereas coke was produced from lignin all over the reactor wall. The latter coke is formed through gas-phase reactions during vaporization of the primary pyrolysis products. They suggested that these differences originated from different coke-forming reactivities in the liquid and gas phases. Cellulose- and hemicellulose-derived primary products, which form coke through liquid-phase reactions, would be stable in the gas phase, whereas the lignin-derived primary products are reactive even in gas-phase coking reactions.

The mechanisms of coke formation from lignin have been investigated using reactivity data for model compounds. Hosoya et al. [11] proposed a role for *o*-quinone methide intermediates, which

are formed through the radical-induced *ipso* rearrangement of methoxyl groups above 400–450 °C, in gas-phase coke formation from lignin. Asmadi et al. [12] reported that larger amounts of coke were formed from syringyl-type aromatic nuclei with two methoxyl groups than from guaiacyl-type nuclei with only one methoxyl group; they concluded that the reactions arising from the methoxyl groups directly controlled coke formation from lignin. Hosoya et al. [13] reported that these coke-forming reactivities were suppressed in the presence of hydrogen donors such as cellulose-derived primary volatile products. This implies that the coking reactions of the lignin-derived products are influenced by coexisting wood-polysaccharide-derived products during wood pyrolysis/gasification.

The major chemical components of the primary volatile products from cellulose pyrolysis, which occurs rapidly at temperatures above 300–350 °C, have been identified [10,14–17]. These include water, anhydrosugars, aldehydes, ketones, acids, furans, and alcohols. The pyrolysis reactivities of simple compounds such as acetic acid [18–21] and formic acid [22–26] have been well studied in relation to the combustion mechanisms of hydrocarbons as fuels. Shin et al. [27] studied the secondary reactions of levoglucosan, 5-hydroxymethylfurfural (5-HMF), and acetic acid as model cellulose pyrolysis products, using molecular beam mass spectrometry to detect the products. However, they did not discuss the coke/soot-formation behaviors. Only on levoglucosan many papers are reported [28–32] dealing with the condensation reaction and subsequent coke formation, which starts at a relatively low pyrolysis temperature of 250 °C. Recently, it was reported that such condensation and coke formation during levoglucosan pyrolysis were effectively suppressed in aprotic solvents [33,34] as well as in the gas phase [30]. In spite of these extensive investigations, there have been no systematic studies on coke/soot-formation reactivities of various primary pyrolysis products from cellulose. Furthermore, the relationships between the chemical structure and the product gas composition have not been well discussed for these primary products.

In this study, we selected eight compounds, i.e., levoglucosan (an anhydrosugar), glycolaldehyde (a hydroxyl aldehyde), furfural and 5-HMF (furans), hydroxyacetone (a hydroxyl ketone), acetic acid and formic acid (acids), and MeOH (an alcohol) as the major volatile primary pyrolysis products from cellulose. Their pyrolytic reactivities under N_2 at 500–600 °C in a closed ampoule reactor are discussed, focusing on coke/soot formation and the product gas composition. Coking reactions in the liquid and gas phases were clearly distinguished from the positions at which the coke was deposited. The influences of O_2 addition, which is believed to act as an accelerating agent for gasification, on gas and coke/soot formation are also discussed.

2. Experimental

2.1. Materials

Levoglucosan (**1**), glycolaldehyde dimer (**2**), hydroxyacetone (**3**), furfural (**4**), 5-HMF (**5**), acetic acid (**6**), formic acid (**7**), and MeOH (**8**) were used as the primary volatile products from cellulose. Compounds **1** and **4** were purchased from the Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Compound **3** was purchased from the Sigma–Aldrich Co. LLC (St Louis, MO, USA). Other chemicals were purchased from Nacalai Tesque Inc. (Kyoto, Japan). These chemicals were used without further purification. The glycolaldehyde dimer (**2**; boiling point: 312.4 ± 42 °C [35]) was considered to evaporate as the monomer during pyrolysis, because it gave an equilibrium mixture with the glycolaldehyde monomer, which has a lower boiling point (131.3 ± 23.0 °C [35]) after melting of **2**.
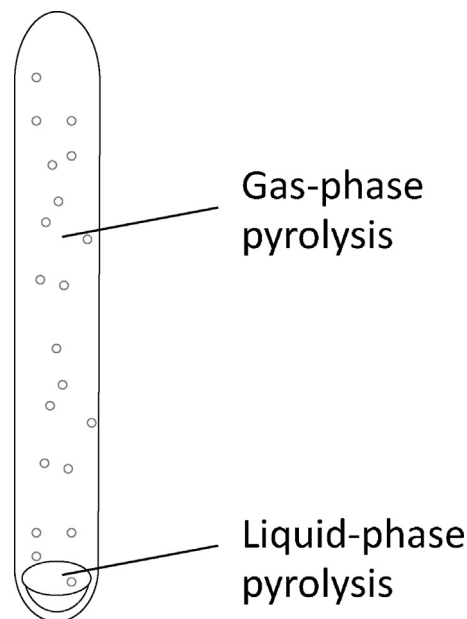

Fig. 1. Liquid- and gas-phase pyrolysis reactions in closed ampoule reactor.

2.2. Pyrolysis and product analysis

Pyrex glass ampoule reactors (internal diameter: 8.0 mm, length: 80 mm, wall thickness: 1.0 mm) (Fig. 1) were used for pyrolysis. Coking reactions in the liquid and gas phases were clearly distinguished by the positions at which the coke was deposited. Compounds **1**–**8** were each placed at the bottom of an ampoule reactor; therefore, the coke deposited at the bottom (defined as primary coke) was suggested to be formed through liquid-phase reactions, which competed with evaporation of the starting compound during pyrolysis. Primary coke is related to coking on a cold line of an actual gasifier through liquid-phase reactions after condensation of the primary volatile products at the temperatures below their boiling points. In contrast, the coke deposited all over the reactor wall (defined as secondary coke) would be formed through gas-phase reactions after evaporation of the starting compound and its pyrolysis products. The ampoule was uniformly heated in the present experiment and volatiles did not condensed on the ampoule reactor wall after vaporization. Thus, secondary coke is not the products from volatile's condensation.

Compounds **1**–**8** (6.0 mg) were each placed at the bottom of a Pyrex glass tube in a glove box, in which the air had been completely exchanged with N_2. The glass tube was sealed with a rubber septum, and then the glass tube was removed from the glove box. The glass ampoule was sealed using a burner with a small N_2 bag attached to the tube through the rubber septum to control the inside pressure. For pyrolysis in the presence of O_2, an adequate amount of O_2 was added to the glass tube using two gas-tight syringes through the rubber septum before it was sealed. The concentration of O_2 was adjusted to 0.3 M equiv with respect to the stoichiometric amount required for complete oxidation to CO_2 and H_2O. The ampoule reactor was then heated in an upright orientation for 10 min by insertion of the whole ampoule into a muffle furnace preheated to 500–600 °C through a small hole in the top. As shown in the temperature profiles reported by Asmadi et al. [12], it took about 120 s for the inside temperature to reach the furnace temperature. Pyrolysis of MeOH and formic acid in O_2/N_2 could not be performed, because these compounds with low boiling points tended to react with O_2 during sealing of the ampoule.

After pyrolysis, the ampoule was immediately cooled in flowing air for 1 min and then in cold water. It was then connected to a