

ASUKA FUKUTOME  
HARUO KAWAMOTO  
SHIRO SAKA

Graduate School of Energy  
Science, Kyoto University,  
Yoshida-honmachi, Sakyo-ku,  
Kyoto, Japan

SCIENTIFIC PAPER

UDC 547.458.81:66.092-977:66.07

DOI 10.2298/CICEQ160325018F

## MOLECULAR MECHANISMS FOR THE GAS-PHASE CONVERSION OF INTERMEDIATES DURING CELLULOSE GASIFICATION UNDER NITROGEN AND OXYGEN/NITROGEN

### Article Highlights

- Levoglucosan is the major volatile intermediate (max. 69.3%, C-based) of cellulose pyrolysis
- Levoglucosan intermediate fragments at 600 °C and is completely gasified at 900 °C
- Gas/tar formation is mostly explained by the gas-phase reactions of levoglucosan
- Benzene, furans and anhydrofuranose originate from molten-phase pyrolysis
- Synergetic effects of oxygen and volatiles accelerate the conversion of volatiles into gases

### Abstract

*Gas-phase conversions of volatile intermediates from cellulose (Avicel PH-101) were studied using a two-stage experimental setup and compared with those of levoglucosan (1,6-anhydro-β-D-glucopyranose). Under N<sub>2</sub> or 7% O<sub>2</sub>/N<sub>2</sub> flow, vapors produced from the pyrolysis zone (500 °C) degraded in the secondary reaction zone at 400, 500, 600 or 900 °C (residence time: 0.8–1.4 s). The 69.3% (C-based) of levoglucosan was obtained at 400 °C under N<sub>2</sub> flow along with 1,6-anhydro-β-D-glucofuranose (8.3%, C-based), indicating that these anhydrosugars are the major volatile intermediates from cellulose pyrolysis. Levoglucosan and other volatiles started to fragment at 600 °C, and cellulose was completely gasified at 900 °C. Most gas/tar formations are explained by gas-phase reactions of levoglucosan reported previously, except for some minor reactions originating from the molten-phase pyrolysis, which produced benzene, furans and 1,6-anhydro-β-D-glucofuranose. Synergetic effects of O<sub>2</sub> and volatiles accelerated fragmentation, and cellulose gasification was completed at 600 °C, which reduced benzene and hydrocarbon gas productions. The molecular mechanisms including the action of O<sub>2</sub> as a biradical are discussed. These lines of information provide insights into the development of tar-free clean gasification that maintains high efficiency.*

*Keywords: cellulose gasification, volatiles, pyrolysis, levoglucosan, gas-phase reactions, molecular mechanism.*

Gasification is a promising way to utilize biomass resources for renewable energy and chemicals. The producer gas can be used for power generation in gas turbines/engines, and the production of petroleum and chemicals through Fischer-Tropsch react-

ions. However, issues related to tar formation inhibits the establishment of reliable systems. Tar clogs the gasifier outlet and can damage engines and turbines used for power generation by condensing and coking on the walls. Understanding the chemistry involved in biomass gasification provides insights into the development of tar-free clean gasification that maintains high efficiency.

This paper focuses on the gas-phase secondary reactions mechanisms of the volatile intermediates

Correspondence: H. Kawamoto, Graduate School of Energy Science, Kyoto University, Yoshida-honmachi, Sakyo-ku, Kyoto 606-8501, Japan.

E-mail: [kawamoto@energy.kyoto-u.ac.jp](mailto:kawamoto@energy.kyoto-u.ac.jp)

Paper received: 25 March, 2016

Paper accepted: 31 March, 2016

during the gasification of cellulose, the major constituent of lignocellulosic biomass. Biomass gasification proceeds as a two-stage process, in which the volatiles and solid char intermediates are gasified in a secondary reaction stage. Cellulose produces relatively large amounts of the volatile intermediates compared with that of the other constituents, hemicellulose and lignin. Thus, the gas-phase secondary reaction stage is important in the gasification of cellulose. Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose, LG) is a major volatile intermediate of a high yield (up to around 70%) from cellulose pyrolysis [1,2].

Although many papers describe the pyrolysis of cellulose, studies of the gas-phase secondary reaction stage of the volatile intermediates have been limited [3-8]. Evans and Milne [4] studied gas-phase conversions during the pyrolysis of biomass-consisting polymers including cellulose using a two-stage pyrolyzer directly coupled with a molecular-beam mass spectrometric (MS) analyzer. They estimated the formation of aromatic species including furan, benzene, toluene and phenol along with CO and CO<sub>2</sub> from the MS data. With a similar system, Shin *et al.* [5] compared the gas-phase reactions of LG, 5-hydroxymethyl furfural (5-HMF) and hydroxyacetone as cellulose-derived volatile intermediates. Li *et al.* [6] analyzed CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and formaldehyde using real-time evolved gas analysis by infrared (IR) spectrometry instead of MS. However, because of restrictions in the experimental apparatus, these studies use only MS or IR data of the pyrolysis mixtures for product identification.

Morf *et al.* [7] developed two-stage pyrolysis equipment to recover the tar and gaseous products from the gas-phase secondary reactions during biomass gasification. They reported the tar yield decreasing linearly with an increase in the temperature from 600 to 900 °C, along with the yields of some tar components including hydroxyacetone and acetic acid, which started to decrease around 600 and 900 °C, respectively. Furthermore, Norinaga *et al.* [8] determined 25 products including gas and tar components by the direct analysis of the mixtures using gas chromatography (GC), although the products from the char pyrolysis are also included in the product stream.

The research group of the authors has focused on the reactivity of LG, as an intermediate, and the pyrolysis reactions of carbohydrates, including LG, are different in the gas and liquid phases [9,10]. In the liquid (molten) state, LG polymerizes around > 250 °C along with dehydration into furans and char (coke), whereas LG is stable up to around 500 °C in the gas

phase and selectively fragments into C1-C3 aldehydes and ketones [10]. Intermolecular hydrogen bonding acting as an acid catalyst has been proposed to explain the enhanced transglycosylation (polymerization) and dehydration reactivities in the liquid phase [11-14].

Fukutome *et al.* [10] reported the details of pyrolytic reactions of the gaseous LG by the careful control of the evaporator conditions to prevent liquid-phase reactions. They also proposed molecular mechanisms, in which radical chain reactions contribute greatly, from the kinetic analysis data [15] and the gas-phase reactions of model compounds [16,17] including polyalcohols such as glycerol and glyceraldehyde/1,3-dihydroxyacetone. Further discussion with the results of theoretical investigations [15] suggest that heterolysis reactions of the gaseous LG are limited because of the strain of the bicyclic ring, compared with simple polyalcohols. One type of cyclic Grob fragmentation with the calculated activation energy ( $E_a$ ) of 57.3 kcal mol<sup>-1</sup> may be involved in the gas-phase heterolysis of LG. Developing these lines of information, the roles of LG gas-phase reactions as the intermediate on cellulose gasification can be discussed in depth.

In this paper, the gas-phase reactions of cellulose-derived volatiles formed at temperatures lower than 500 °C are studied in the temperature range up to 900 °C using a two-stage experimental setup containing primary pyrolysis and gas-phase secondary reaction zones. Similar investigations are conducted for LG, which included liquid-phase reactions competing with direct evaporation. The results are compared with previous results of the pyrolysis of gaseous LG. Effects of oxygen are discussed to understand the cellulose gasification under partial oxidation conditions.

## EXPERIMENTAL

The reagents used for the pyrolysis trials were purchased from the following companies: cellulose (Avicel PH-101) from Aldrich (Saint Louis, MO, USA); levoglucosan from Carbosynth Ltd. (Berkshire, UK). These chemicals were used as received without further purification. The water content of the cellulose sample was around 8 wt.%.

### Two-stage tubular reactor

The two-stage tubular reactor (Figure 1) was composed of two cylindrical electric furnaces (internal diameter: 35 mm, length: 160 mm, Asahi Rika Seisakusho Co., Ltd.), which served for primary pyrolysis of cellulose or LG and secondary reactions of the

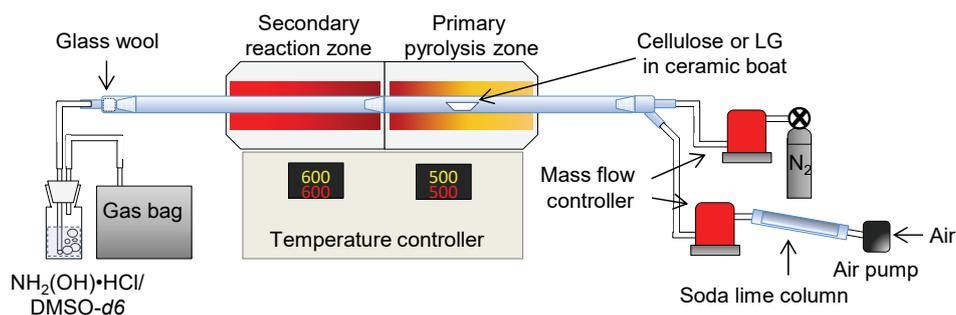


Figure 1. A flow-type two-stage tubular reactor that consists of primary pyrolysis, gas-phase secondary reaction zones along with product-recovery units.

volatile intermediates, respectively. Each furnace included a quartz glass tube (internal diameter: 15 mm, wall thickness: 1.5 mm), and these tubes were connected. The right end of the reactor was divided into 2 branches, one of which was attached to a nitrogen cylinder through a mass flow controller (Horiba SEC-400MK3), and the other one was attached to an air pump through a mass flow controller (Horiba SEC-400MK3). A soda lime column was used to remove the  $\text{CO}_2$  in air. During the trials under inert conditions, the end was only connected to an  $\text{N}_2$  cylinder. The left end of the quartz glass tube was connected to a gas wash bottle through a glass-wool filter and then to a gas bag. The air flow was supplied to the outer part of the tube from the pyrolyzer to quench the pyrolysis reactions. The gas wash bottle held a dimethylsulfoxide ( $\text{DMSO}-d_6$ ) solution (2.0 mL) containing an oximation reagent ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ , 20 mg) to recover volatile products.

### Pyrolysis

In preparation for the pyrolysis trials, a sample (15 mg) in a ceramic boat was inserted into the middle of the primary pyrolysis zone. A nitrogen flow ( $400 \text{ mL min}^{-1}$ ) was supplied for 30 min before each pyrolysis reaction to sweep out the air inside the reactor. The secondary reaction zone was preheated at a designated temperature (400, 500, 600, or 900 °C). After preheating the primary pyrolysis zone at 150 °C for 30 min, the temperature was raised up to 500 °C at  $70 \text{ °C min}^{-1}$  and then held at 500 °C for 2 min. Then, the quartz glass tube in the primary pyrolysis zone was cooled by opening the furnace cover and subsequently applying an air flow. The nitrogen flow was maintained for the additional 2 min to sweep any residual products into the gas wash bottle and gas bag.

The residence time for the secondary reactions of the volatile intermediates was defined as the period over which the volatiles were present in the region of the reactor with temperatures within  $\pm 25 \text{ °C}$  of the set

value. The internal temperature profiles of the primary pyrolysis and secondary reaction zones were obtained for each set temperature through direct measurement during preliminary control trials conducted without the addition of the sample. A constant nitrogen flow of  $400 \text{ mL min}^{-1}$  was supplied during each experimental trial under inert conditions, while a constant nitrogen flow of  $250 \text{ mL min}^{-1}$  and air flow  $150 \text{ mL min}^{-1}$  for  $\text{O}_2/\text{N}_2$  conditions. The residence time changed depending on the temperature of the secondary reaction zone, which was 1.4, 1.2, 1.1, and 0.8 s at 400, 500, 600, and 900 °C, respectively. These are close to the residence times estimated for actual biomass gasification. The pressure inside the reactor was measured and was equal to the atmospheric pressure.

### Product analysis

The condensates on the interior wall of the reactor tube and in the line between the reactor and the gas wash bottle were removed by rinsing with the solution in the gas wash bottle ( $\text{DMSO}-d_6$ , 2.0 mL) containing an oximation reagent ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ), where the aldehydes and ketones were converted into the corresponding less volatile aldoximes and ketoximes (both *cis* and *trans* isomers). The resulting solution was analyzed directly by means of  $^1\text{H}$  NMR spectroscopy using a Bruker AC-400 (400 MHz) spectrometer following the addition of 2-furancarboxylic acid as an internal standard. The products and any unreacted sample were quantified from the peak areas of the NMR spectroscopy signals compared with those of the internal standard.

Noncondensable gases were analyzed using a micro GC instrument (Varian CP-4900) under the following chromatographic conditions: channel (1) column: MS5 A (10 m); carrier gas: Ar; column temperature: 100 °C; column pressure: 170 kPa; detector: thermal conductivity detector (TCD); retention times (s):  $\text{H}_2$  (26.4),  $\text{N}_2$  (45.7),  $\text{O}_2$  (35.4),  $\text{CH}_4$  (60.6), and  $\text{CO}$  (86.9); channel(2) column: PoraPLOT Q (10 m); carrier gas: He; column temperature: 80 °C:

column pressure: 190 kPa; detector: TCD; retention times (s): CO<sub>2</sub> (19.9), C<sub>2</sub>H<sub>4</sub> (23.5), C<sub>2</sub>H<sub>6</sub> (26.3), C<sub>3</sub>H<sub>6</sub> (57.4), and C<sub>3</sub>H<sub>8</sub> (63.2). Hydrocarbon gases with more than 3 carbons, except for propylene and propane, were identified by their GC/MS data measured on a Shimadzu GCMS-QP2010 and quantified by GC using a Shimadzu GC-14B instrument under the following conditions: column: RESTEC, Rt@alumina BOND/N<sub>2</sub>SO<sub>4</sub> (30 m, 0.53 mm Ø), carrier gas: He, column temperature: 60 °C (0–2 min), 40–200 °C (2–16 min, 10 °C min<sup>-1</sup>), 200 °C (16–20 min); detector: flame ionization detector; retention time (min): propadiene (4.2), acetylene (4.3), 1-butene (5.7), 1-butene (5.8), butane (6.1), butane (6.2), 1,3-butadiene (7.5), and methyl acetylene (7.6).

## RESULTS AND DISCUSSION

The <sup>1</sup>H-NMR spectra obtained from the pyrolysis/gasification of cellulose-derived volatiles at 400, 500, 600 and 900 °C under N<sub>2</sub> or 7% O<sub>2</sub>/N<sub>2</sub> flow are shown in Figure 2. The volatile products were formed from the cellulose pyrolysis occurring in the primary

pyrolysis zone during the heating process from 150 to 500 °C at a rate of 70 °C/min, because cellulose is reported to degrade effectively in the temperature range between 350 (slow heating condition) and 450 °C (fast heating condition) [18]. The results obtained at the second-stage temperature of 400 °C represent the primary pyrolysis of cellulose. Most of the signals in the spectra were assigned to the aldehydes/ketones as their oxime derivatives and the signals of LG and 1,6-anhydro-β-D-glucofuranose (AGF). The identification of these products is described in detail in a previous paper on the pyrolysis of gaseous LG [10]. In addition, the signals of benzene and methanol were observed in the spectra obtained under N<sub>2</sub> and 7% O<sub>2</sub>/N<sub>2</sub> flow, respectively, both of which are not produced from gaseous LG.

The yields of the products from cellulose and LG pyrolyses determined from the NMR and gas analyses are summarized in Figure 3. The pyrolysis of LG created solid carbonized product (char) in the primary pyrolysis zone, which indicates that liquid-phase pyrolysis reactions (polymerization and dehydration) com-

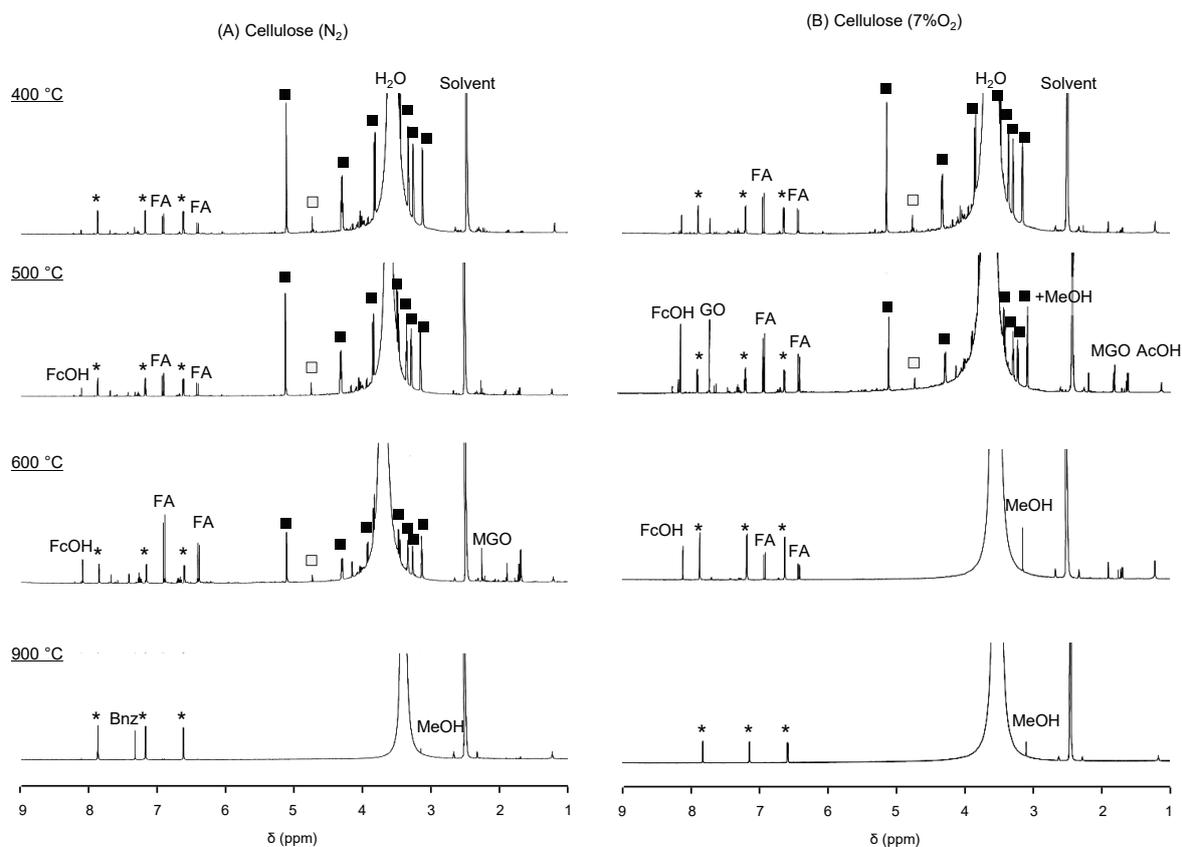


Figure 2. <sup>1</sup>H-NMR spectra of the condensable products recovered in the gas-wash bottle (DMSO-*d*<sub>6</sub>) including the oximation reagents during the pyrolysis of cellulose at the second-stage temperatures of 400, 500, 600, 900 °C under N<sub>2</sub>, 7% O<sub>2</sub>/N<sub>2</sub> flow (primary pyrolyzer: 500 °C); ■: levoglucosan, □: 1,6-anhydro-β-D-glucofuranose, \*: internal standard (2-furancarboxylic acid), FA: formaldehyde, FcOH: formic acid, GO: glyoxal, MeOH: methanol, MGO: methylglyoxal, AcOH: acetic acid, Bzn: benzene.

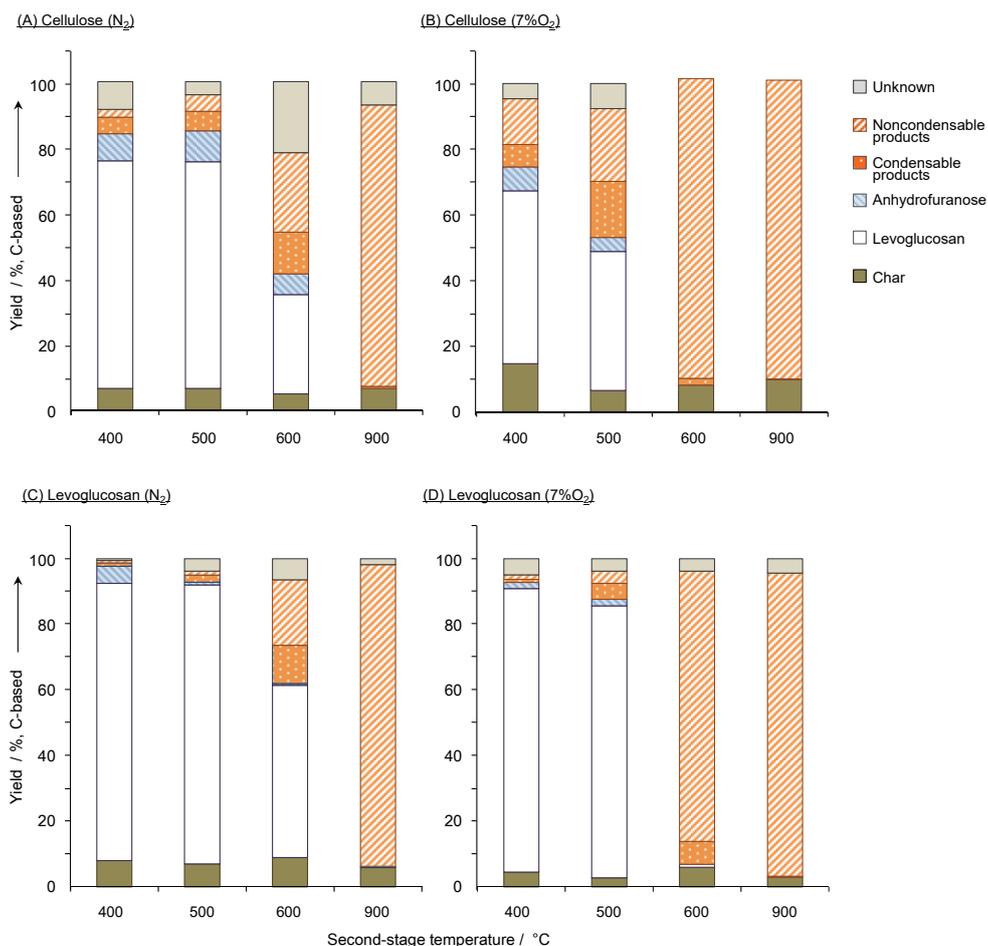


Figure 3. Product compositions from the pyrolyses of cellulose (A, B), levoglucosan (C, D) at the second-stage temperatures of 400, 500, 600, 900 °C under N<sub>2</sub>, 7% O<sub>2</sub>/N<sub>2</sub> flow (primary pyrolyzer: 500 °C).

pete with the direct evaporation of LG at its boiling point of 385 °C [18]. Thus, the liquid-phase reactions can be included in the present pyrolysis of LG. The yields of the condensable volatile products as plotted against the second-stage temperature and previous data of the pyrolysis of gaseous LG [10] are shown in Figure 4.

### Primary pyrolysis

Primary pyrolysis reactions of cellulose can be discussed with the results at the second-stage temperature of 400 °C. The LG yield from cellulose was high as 69.3% (C-based) under N<sub>2</sub>, which confirms LG as the major volatile intermediate during cellulose gasification. This situation did not change under 7% O<sub>2</sub>/N<sub>2</sub> flow (LG yield: 52.6%, C-based). Thus, LG remains an important intermediate even in the presence of oxygen. The small influence of oxygen is explained by the extensive volatile formation during the primary pyrolysis stage, which inhibits the attack of oxygen to cellulose, as indicated in the literature [19,20].

The pyrolysis of LG exhibited similar results at 400 °C to those of cellulose. Some LG in the primary pyrolysis zone may polymerize into polysaccharides before evaporation; hence, volatile formation behaviors can be similar to those of polysaccharide pyrolysis. The most striking difference from the pyrolysis of gaseous LG is the formation of AGF and aromatic substances, furans (furfural and 5-HMF) and benzene (Figure 4). Because the formation of these compounds is completely inhibited in the pyrolysis of gaseous LG [10], these products may form in the liquid-phase pyrolysis of LG. Although the literature [4,8] reported the other benzene derivatives such as toluene, naphthalene and phenol, the NMR and GC-MS analyses in the present study using standard compounds refuted the formation of these products.

Furans and AGF have five-membered rings; therefore, the ring-inversion from pyranose (6-membered ring) is necessary for their formation. Because the reducing sugar, which can adopt the chain structure, makes this conversion probable, the role of the

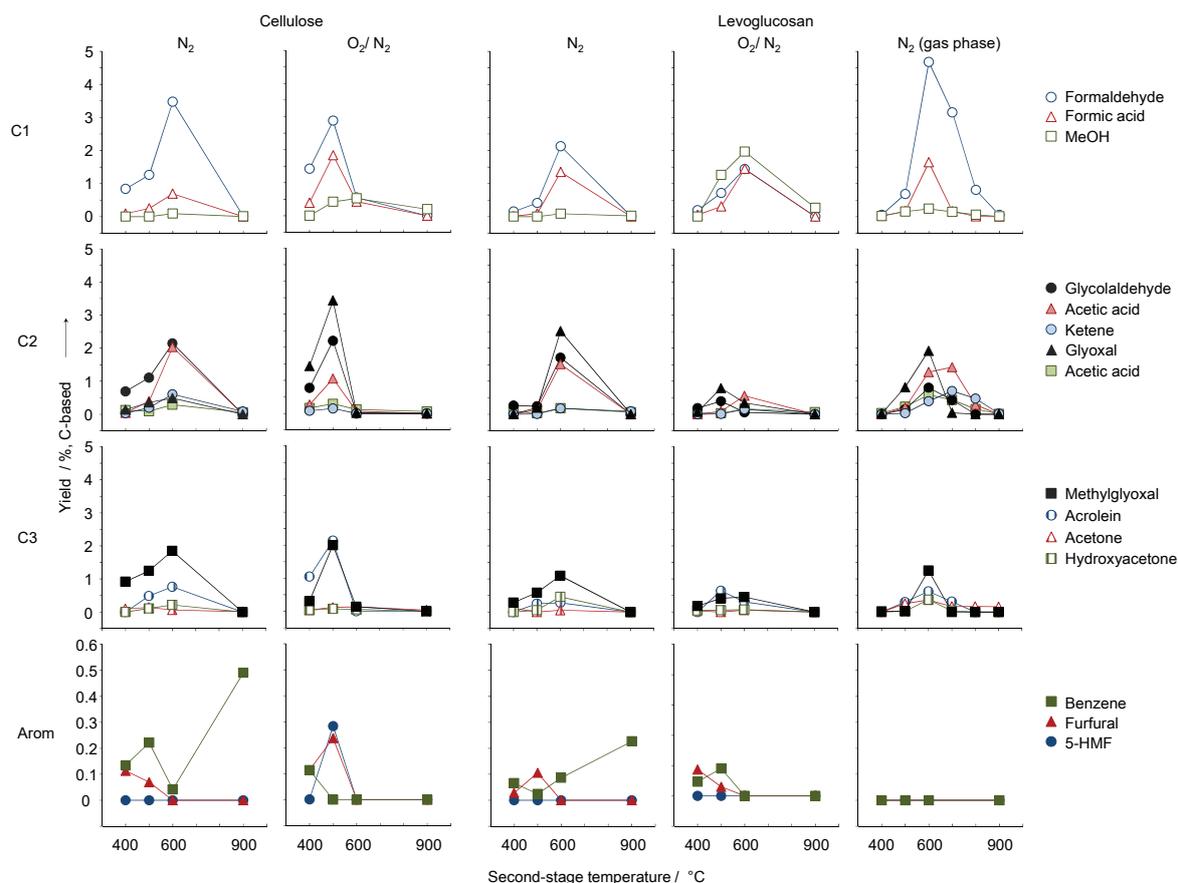


Figure 4. Change in the composition of the condensable products from cellulose, levoglucosan by increasing the second-stage temperature from 400 to 900 °C under N<sub>2</sub>, 7% O<sub>2</sub>/N<sub>2</sub> flow (primary pyrolyzer: 500 °C), along with previous results using gaseous levoglucosan [10].

reducing sugar moiety has been indicated for the formation of furans and AGF [21,22]. This proposal is supported by the experimental results, because the yields of furans and ANF decrease in the order of glucose > cellobiose > cellulose [21]. AGF can form via the glucose chain structure through re-cyclization into the furanose isomer. This conversion occurs in the liquid phase, because any conversion from LG to AGF is observed in the gas-phase conversion of LG [10]. Recent literature [23,24] supports the inclusion of the reducing sugars such as glucose during cellulose pyrolysis and reports hydrolysis reactions proceeding during cellulose pyrolysis under normal pressure conditions.

The role of furans as intermediates for the conversion of cellulose to char has been reported by Pastorova *et al.* [25], using pyrolysis-GC analyses of pre-heated cellulose samples, where the products depend on the pretreatment temperature: anhydrosugars (< 250 °C) → furans → benzenes (> 350 °C). The conversion, furans → benzenes, was extensively studied for the hydrothermal carbonization of reducing

sugars using solid-state NMR [26-28]. These findings indicate that the benzene obtained at 400 °C forms via furans (furfural and 5-HMF) produced from the liquid-phase primary pyrolysis of LG and cellulose. Although heterolytic dehydrations of simple polyalcohols proceed at high temperatures > 500-600 °C in the gas phase [16], the dehydration of glyceraldehyde (an aldose) can occur at 400 °C through highly reactive dehydrations via the cyclic transition states of enol intermediates [17]. A similar dehydration mechanism has been proposed for the glucose dehydration into 5-HMF and furfural via 3-deoxyglucosone [29,30].

#### Gas-phase secondary reactions

The pyrolysis products changed by increasing the second-stage temperature (Figures 3 and 4), which indicates the conversion of the volatile intermediates into the noncondensable gases. The contribution of the gas formation from the char intermediates is minor because the temperature of the primary pyrolyzer (500 °C) is insufficient for the gasification of char and the heating period of char fraction is only 2 min after reaching 500 °C. The changes in

the compositions of the noncondensable gases are summarized in Figures 5 and 6.

Under  $N_2$  flow, the conversion from the volatiles to gases started at 600 °C and completed at 900 °C for both cellulose and LG. CO was the major gas component along with the smaller amounts of  $H_2$ ,  $CO_2$ , unsaturated hydrocarbons (ethylene and acetylene) and methane (Figure 5). These results are concordant with those of the pyrolysis of gaseous LG in a previous study [10]. This indicates that the influences of the products from the liquid-phase pyrolysis on the LG reactivity are minor. Furthermore, the behaviors during the pyrolysis of cellulose and LG were similar to those of the gaseous LG, although the influences of the oxygen were more significant as discussed below.

Fifteen volatile intermediates were detected as condensable products (Figure 4), which include C3 (hydroxyacetone, acetone, acrolein and methylgly-

oxal), C2 [glycolaldehyde, glyoxal, acetaldehyde, acetic acid (AcOH) and ketene] and C1 (formaldehyde, formic acid and methanol (MeOH)) compounds along with the aromatics [5-HMF, furfural and benzene]. Most of these intermediates disappeared at 900 °C, except for benzene, AcOH, ketene and MeOH (0.7 and 0.4%, C-based, in total for cellulose and LG pyrolyses, respectively). Among them, benzene was predominant (74.6 and 55.4% for cellulose and LG pyrolyses, respectively). These compounds, particularly benzene, can be important final tar components of  $N_2$  cellulose pyrolysis.

Some unsaturated C4 hydrocarbons were identified as noncondensable gases, including 1,3-butadiene, 1-butene, *cis/trans*-2-butene and isobutene (Figure 6). These compounds were determined in the present study from the pyrolysis of gaseous LG. These compounds have been discussed using the secondary reactions of furanic compounds [31,32],

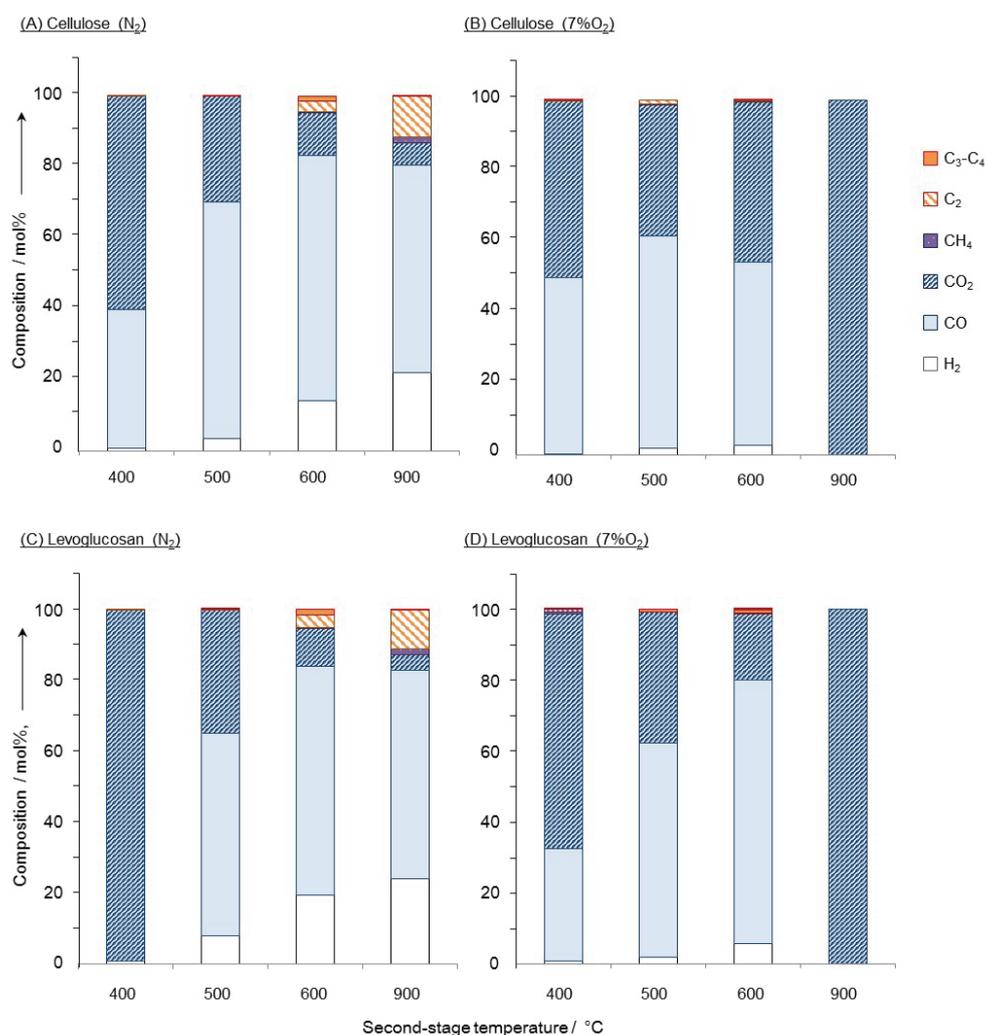


Figure 5. Compositions of the noncondensable gases from the pyrolyses of cellulose (A, B), levoglucosan (C, D) at the second-stage temperatures of 400, 500, 600, 900 °C under  $N_2$ , 7%  $O_2/N_2$  flow (primary pyrolyzer: 500 °C).

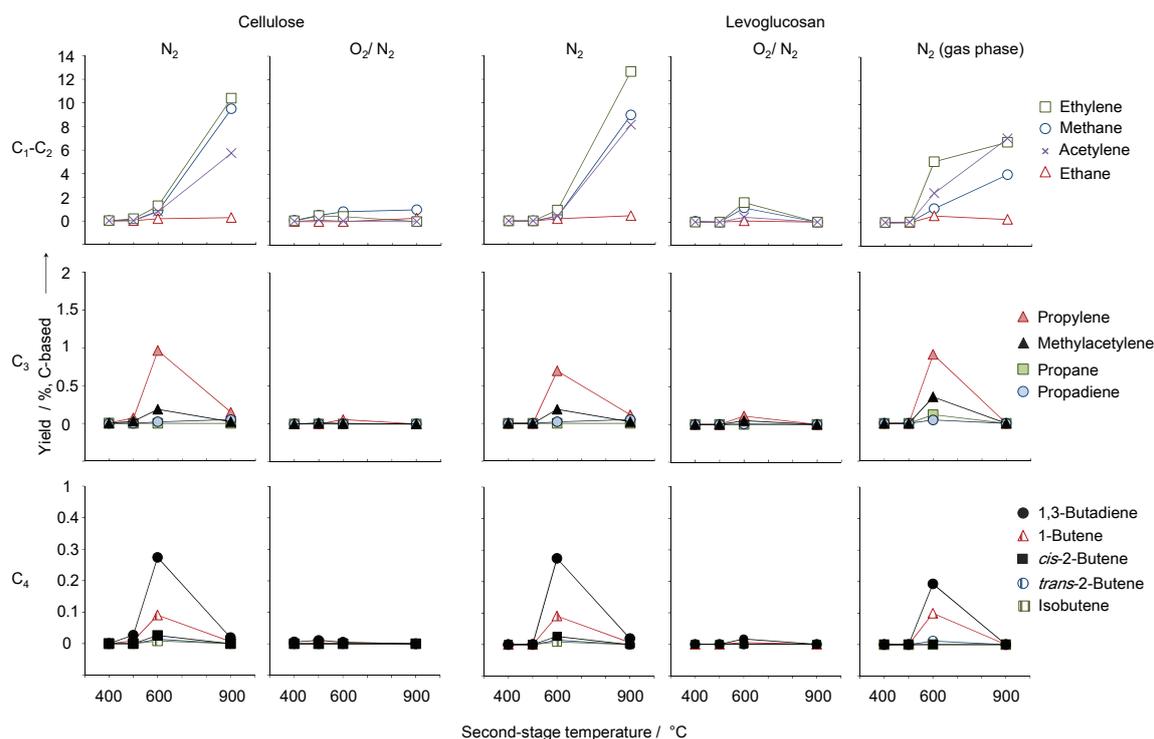


Figure 6. Change in the composition of the noncondensable gases from cellulose, levoglucosan by increasing the second-stage temperature from 400 to 900 °C under  $N_2$ , 7%  $O_2/N_2$  flow (primary pyrolyzer: 500 °C), along with previous results using gaseous levoglucosan [10].

which showed benzene and its derivatives subsequently. A large amount of 1,3-butadiene was detected along with methyl acetylene and other minor products (benzene, AcOH, formaldehyde, formic acid and MeOH) from the gas-phase pyrolysis of furfural at temperatures of 60 °C for the primary pyrolyzer (evaporator) and 900 °C for the second-stage pyrolyzer. However, the benzene yield was only 5% (C-based). Furthermore, furans and benzene were not produced from gaseous LG [10], although 1,3-butadiene and 1-butene were observed. These results indicate that the benzene formation via these C4 compounds is not important in the gas phase. The other formation mechanisms including the volatiles from the liquid-phase pyrolysis may be involved for the pyrolyses of cellulose and LG, because the benzene yields increased between 600 and 900 °C (Figure 4).

The oxygen in the  $N_2$  flow changed these gas-phase conversions. The influence was minor for the pyrolysis of LG at 400 and 500 °C, but greater for that of cellulose (Figure 3). At 600 °C, both cellulose and LG were almost completely gasified. Therefore, oxygen accelerates the fragmentation of LG and other volatile intermediates into gaseous products. Synergistic effects of  $O_2$  and volatiles from cellulose can enhance the acceleration effects, even at tempera-

tures such as 400–500 °C, although the details of these effects are unknown presently.

The oxygen in the flow altered the compositions of the tar/gas fractions. Although benzene remained even at 900 °C under  $N_2$  flow (Figures 2 and 4), the inclusion of  $O_2$  completely decomposed benzene, but increased the MeOH yields at 900 °C. Therefore, the final tar composition at 900 °C changed to MeOH (0.2% (cellulose) and 0.02% (LG), C-based) along with smaller amounts of AcOH and acetone.

For the gaseous components (Figures 5 and 6), the contents of unsaturated hydrocarbons from cellulose and LG pyrolyses decreased dramatically in the presence of oxygen from 15.3 to 2.8% and from 16.8 to 0.6% (C-based on noncondensable gas), respectively, at 600 °C, where gasification completed. The methane yields also decreased, but less effectively. At 900 °C,  $CO_2$  became predominant by complete oxidation.

These influences of  $O_2$  can be discussed with a biradical mechanism. A previous study [15] suggested that the radical chain mechanisms are important for the gas-phase fragmentation of LG. Therefore, the addition of radical species such as  $O_2$  (biradical) accelerates fragmentation reactions. Radicals add to the unsaturated  $C=C$  and  $C\equiv C$  to form oxygenated structures [33], which converts the unsaturated hydro-

carbons including benzene into oxygenated gases. The radical coupling of  $\bullet\text{CH}_3$  with oxygen (biradical) forms MeOH *via* the peroxide intermediate, which reduces the methane yield.

### Molecular mechanisms of cellulose gasification

Building on the literature information, the molecular mechanisms of cellulose gasification are proposed as illustrated in Figure 7, which included solid/liquid- and gas-phase conversions.

Cellulose has a heterogeneous layered structure [34–36], containing cellulose microfibrils (crystallites) aggregating into larger components, and reducing end groups. Therefore, the cellulose pyrolysis proceeds heterogeneously. From the X-ray analysis during the pyrolysis [37], cellulose crystallites degrade from a direction orthogonal to the fiber axis, whereas the molecules inside the crystallites are stable. Roles of the quite reactive reducing ends, which exist at the one crystallite end, have been suggested to accelerate cellulose pyrolysis, because hydrolysis forms additional reducing ends [38].

Large amounts of LG and AGF are produced by the transglycosylation reactions and evaporated into the gas phase. AGF may be formed *via* the reducing sugars. However, dehydration and fragmentation reactions proceed for the reducing sugars, which generate furans, benzene, fragments, water and other

products into the gas phase. All the intermediates degrade in the gas phase, but the remaining reactive tar components have been reported to convert into coke after condensing on the wall [39]. LG, glycolaldehyde, furfural and 5-HMF have been suggested to contribute to these coking reactions [40].

The results of the present investigations provide the information for the gas-phase conversions as summarized in the following conclusions.

### CONCLUSIONS

1) LG (max. 69.3%, C-based) is the major volatile intermediate from the primary pyrolysis of cellulose.

2) The volatile intermediates, including LG, are stable at 400 and 500 °C under  $\text{N}_2$  flow, whereas they became reactive at 600 °C for fragmentation and completely gasify at 900 °C.

3) Most gas/tar formations from the cellulose-derived volatiles are explained by the fragmentation reactions of gaseous LG, except for some minor reactions originating from the molten-phase primary pyrolysis, which produces benzene and furans along with AGF.

4) Oxygen accelerates the fragmentation of the volatile intermediates, and cellulose was completely gasified at 600 °C with reducing benzene and hydro-

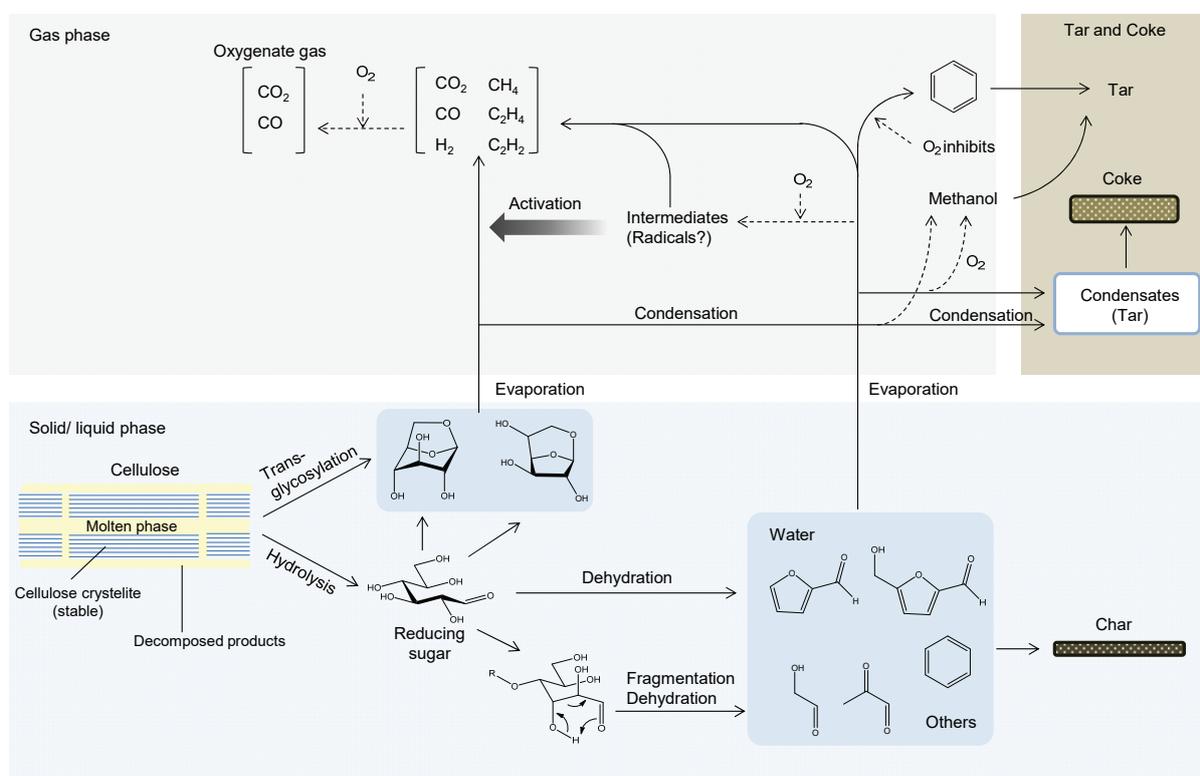


Figure 7. Proposed gasification mechanisms of cellulose.

carbon gas productions. A biradical mechanism involving oxygen explains these results, because this promotes radical chain reactions and adds to the multiple bonds of benzene and unsaturated hydrocarbon gases.

5) The greater acceleration effects of oxygen for cellulose than LG indicate synergetic effects of oxygen and cellulose-derived volatiles.

6) The final tar compositions depend on the pyrolysis environment: benzene and smaller amounts of ketene and acetic acid under N<sub>2</sub>, and methanol and smaller amounts of acetic acid and acetone under 7% O<sub>2</sub>/N<sub>2</sub>.

## REFERENCES

- [1] F. Shafizadeh, R.H. Furneaux, T.G. Cochran, J.P. Scholl, Y. Sakai, *J. Appl. Polym. Sci.* **23** (1979) 3525-3539
- [2] G.J. Kwon, D.Y. Kim, S. Kimura, S. Kuga, *J. Anal. Appl. Pyrolysis* **80** (2007) 1-5
- [3] M.J. Antal, *Ind. Eng. Chem. Prod. Res. Dev.* **22** (1983) 366-375
- [4] R.J. Evans, T.A. Milne, *Energy Fuels* **1** (1987) 123-137
- [5] E.J. Shin, M.R. Nimlos, R.J. Evans, *Fuel* **80** (2001) 1697-1709
- [6] S. Li, J. Lyons-Hart, J. Banyasz, K. Shafer, *Fuel* **80** (2001) 1809-1817
- [7] P. Morf, P. Hasler, T. Nussbaumer, *Fuel* **81** (2002) 843-853
- [8] K. Norinaga, T. Shoji, S. Kudo, J. Hayashi, *Fuel* **103** (2013) 141-150
- [9] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **83** (2008) 64-70
- [10] A. Fukutome, H. Kawamoto, S. Saka, *ChemSusChem* **8** (2015) 2240-2249
- [11] H. Kawamoto, T. Hosoya, Y. Ueno, T. Shoji, S. Saka, *J. Anal. Appl. Pyrolysis* **109** (2014) 41-46
- [12] S. Matsuoka, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **93** (2012) 24-32
- [13] H. Kawamoto, Y. Ueno, S. Saka, *J. Anal. Appl. Pyrolysis* **103** (2013) 287-292
- [14] T. Hosoya, Y. Nakao, H. Sato, H. Kawamoto, S. Sakaki, *J. Org. Chem.* **74** (2009) 6891-6894
- [15] A. Fukutome, H. Kawamoto, S. Saka, submitted
- [16] A. Fukutome, H. Kawamoto, S. Saka, in preparation
- [17] A. Fukutome, H. Kawamoto, S. Saka, *ChemSusChem* **9** (2016) 703-712
- [18] T. Shoji, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **109** (2014) 185-195
- [19] F. Shafizadeh, A.G.W. Bradbury, *J. Appl. Polym. Sci.* **23** (1979) 1431-1442
- [20] D. Shen, J. Ye, R. Xiao, H. Zhang, *Carbohydr. Polym.* **98** (2013) 514-521
- [21] D. Gardiner, *J. Chem. Soc., C: Organic* (1966) 1473-1476
- [22] K. Kato, *Agr. Biol. Chem.* **31** (1967) 657-663
- [23] Y. Yu, D. Liu, H. Wu, *Energy Fuels* **26** (2012) 7331-7339
- [24] S. Matsuoka, H. Kawamoto, S. Saka, *Carbohydr. Res.* **346** (2011) 272-279
- [25] I. Pastorova, R.E. Botto, P.W. Arisz, J.J. Boon, *Carbohydr. Res.* **262** (1994) 27-47
- [26] M.-M. Titirici, M. Antonietti, N. Baccile, *Green Chem.* **10** (2008) 1204
- [27] N. Baccile, G. Laurent, F. Babonneau, F. Fayon, M.M. Titirici, M. Antonietti, *J. Phys. Chem., C* **113** (2009) 9644-9654
- [28] C. Falco, F. Perez Caballero, F. Babonneau, C. Gervais, G. Laurent, M.M. Titirici, N. Baccile, *Langmuir* **27** (2011) 14460-14471
- [29] R.J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de Vries, *Chem. Rev. (Washington, DC, U. S.)* **113** (2013) 1499-1597
- [30] C. Perez Locas, V.A. Yaylayan, *J. Agric. Food Chem.* **56** (2008) 6717-6723
- [31] A. Lifshitz, C. Tamburu, R. Shashua, *J. Phys. Chem., A* **102** (1998) 10655-10670
- [32] K. Norinaga, H. Yang, R. Tanaka, S. Appari, K. Iwanaga, Y. Takashima, S. Kudo, T. Shoji, J. Hayashi, *Biomass Bioenergy* **69** (2014) 144-154
- [33] A.F. Parsons, *An Introduction to Free radical Chemistry*, Blackwell Science Ltd, London, 2000, p. 65
- [34] L. Salmén, *C. R. Biol.* **327** (2004) 873-880
- [35] L. Salmén, I. Burgert, *Holzforschung* **63** (2009) 121-129
- [36] N. Terashima, K. Kitano, M. Kojima, M. Yoshida, H. Yamamoto, U. Westermark, *J. Wood Sci.* **55** (2009) 409-416
- [37] G.A. Zickler, W. Wagermaier, S.S. Funari, M. Burghammer, O. Paris, *J. Anal. Appl. Pyrolysis* **80** (2007) 134-140
- [38] S. Matsuoka, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **106** (2014) 138-146
- [39] T. Hosoya, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **78** (2007) 328-336
- [40] A. Fukutome, H. Kawamoto, S. Saka, *J. Anal. Appl. Pyrolysis* **108** (2014) 98-108.

ASUKA FUKUTOME  
HARUO KAWAMOTO  
SHIRO SAKA

Graduate School of Energy Science,  
Kyoto University, Yoshida-honmachi,  
Sakyo-ku, Kyoto, Japan

NAUČNI RAD

## MOLEKULSKI MEHANIZMI KONVERZIJE INTERMEDIJERA U GASNOJ FAZI TOKOM GASIFIKACIJE CELULOZE U ATMOSFERI AZOTA I SMEŠE KISEONIK/AZOT

*Konverzija isparljivih intermedijera celuloze (Avicel PH-101) u gasnoj fazi je proučavana pomoću dvo-faznog eksperimentalnog postupka i poređena sa konverzijom levoglukoza (1,6-anhidro- $\beta$ -D-glukopiranoza). U atmosferi  $N_2$  ili 7%  $O_2/N_2$ , isparenja proizvedena u zoni pirolize (500 °C) su razgrađena u sekundarnoj reakcionoj zoni na 400, 500, 600 ili 900 °C (vreme zadržavanja: 0,8-1,4 s). Na 400 °C u atmosferi  $N_2$ , ostvarena je konverzija levoglukoza od 69,3% (računato na C) kao i konverzija 1,6-anhidro- $\beta$ -D-glukofuranoze od 8,3% (računato na C), što ukazuje da su ovi anhidrošećeri glavni isparljivi intermedijari pirolize celuloze. Levoglukosan i druge isparljive supstance su počeli da se razgrađuju na 600 °C, a potpuna gasifikacija celuloze je na 900 °C. Nastajanje gasa i katrana je objašnjeno ranije publikovanim reakcijama levoglukoza u gasnoj fazi, osim nekih manjih reakcija pirolize rastopljene faze, koja je proizvodila benzen, furane i 1,6-anhidro- $\beta$ -D-glukofuranoze. Sinergijski efekti  $O_2$  i isparljivih jedinjenja su ubrzali fragmentaciju, pa je gasifikacija celuloza završena na 600 °C, što je smanjilo dobijanje benzola i ugljovodonika. Diskutovani su molekularni mehanizmi uključujući delovanja  $O_2$  kao biradikal. Ovaj rad daje uvid u razvoj gasifikacije bez katrana koja održava visoku efikasnost.*

*Ključne reči: gasifikacije celuloze, isparljiva jedinjenja, piroliza, levoglukoza, reakcije u gasnoj fazi, molekularni mehanizam.*