

VAPOR-PHASE REACTION AND ITS ROLE IN CELLULOSE GASIFICATION

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Chapter 1

Introduction

1.1 Energy and Environmental Issues and Biomass Utilization

Global population has increased from 5.8 to 7.3 billion during the last two decades and is predicted to grow further to 8.7 billion in the next 20 years ("U.S. Census Bureau," 2016). With the population growth, the world primary energy demand is projected to grow by no less than 39% in the next 28 years to reach 17 billion tons of oil equivalent per year (British petroleum, 2012). Although the renewable energies will be rapidly introduced recently, the dependency ratio of energy on fossil fuels is projected to be still as high as 85% in 2030 (petroleum, 2012). In spite of the predicted high fossil fuel dependency, the amounts of fossil fuels (resources) is limited on the earth. Thus, fossil fuels are not sufficient to meet the future energy demand. The resulting price increase is also concerned because this greatly affects the world economy.

Excessive utilization of fossil fuels also causes the global environmental issues. Utilization of fossil fuels, which are the carbon-based materials stored in the earth, leads to the increase in the concentration of the atmospheric CO₂, the greatest contributor of green-house effect gas leading to global warming (IPCC, 2013). Sulfur and nitrogen included in fossil fuels cause acid rain issues through converting into SO_x and NO_x during their combustion (Ando et al., 1996), which significantly damage the forest and other ecosystems. So, these drawbacks also make the utilization of fossil fuels difficult, and hence alternative energy resources are strongly desired for future sustainable society.

Biomass is a candidate of the alternative resource to fossil fuels, since it is a renewable and carbon-neutral resource. Approximately 1.8 billion tons (dry ton) of

biomass resources are accumulated on the earth and one tenth of the amount is annually renewed continuously (Whittaker, 1979; Saka, 2001). This annual production in energy corresponds to as large as 6 times of the total energy demand in the world.

It should be noted that most of the biomass resources (>90%) exist in the forest ecosystems, and hence the contribution of woody part is quite large for the biomass resources on the earth. Because cellulose, hemicellulose and lignin are the major wood constituents, forest biomass is chemically treated as a mixture of these polymers. These biomass resources are called as lignocellulosics. Agricultural wastes such as rice straw and corn stover are also included in lignocellulosics. In this dissertation, cellulose gasification is focused.

There is an issue relating to the utilization of edible biomass resources for fuels production. For example, bio-ethanol production from sugar cane and corn directly compete with the food supply to people, which results in the increase in food price. Contrary to this, lignocellulosics are non-edible resources, and hence no direct competition with food is expected. For these reasons, lignocellulosics are quite important biomass resources to utilize efficiently.

Traditional use of wood as fuel wood is conducted mainly in the developing countries and contributes significantly (~10%) to the world annual energy supply. On the other hand, utilization of wood as energy resources in developed countries is not effectively conducted, although large amounts of waste biomass exist in these countries. To increase the utilization of biomass energy in the developed countries, conversion technologies play key roles, since solid biomass resources with high moisture content, low density, and low heating value are not the suitable energy resources for modernized society (Tillman, 1978). For these reasons, liquid fuels such as bio-ethanol and bio-diesel for transportation and electricity produced in biomass power stations are the options for the developed countries. Accordingly, it is important to establish the conversion technologies of wood biomass.

1.2 Biomass Gasification as a Key Technology for Bio-fuels and Bio-chemicals Production

Gasification converts solid biomass resources into gas which includes CO, H₂, CH₄, and smaller amounts of other hydrocarbon gases such as ethylene and acetylene. Biomass gasification is normally conducted at high temperatures > 800 °C to maximize the gas formation. Accordingly, these temperatures are much higher than those utilized for other thermochemical conversion technologies including fast pyrolysis, carbonization and torrefaction. The other characteristic feature of gasification is use of gasifying agents such as air (O₂) and steam, which promotes the gasification of solid carbonized intermediates (char).

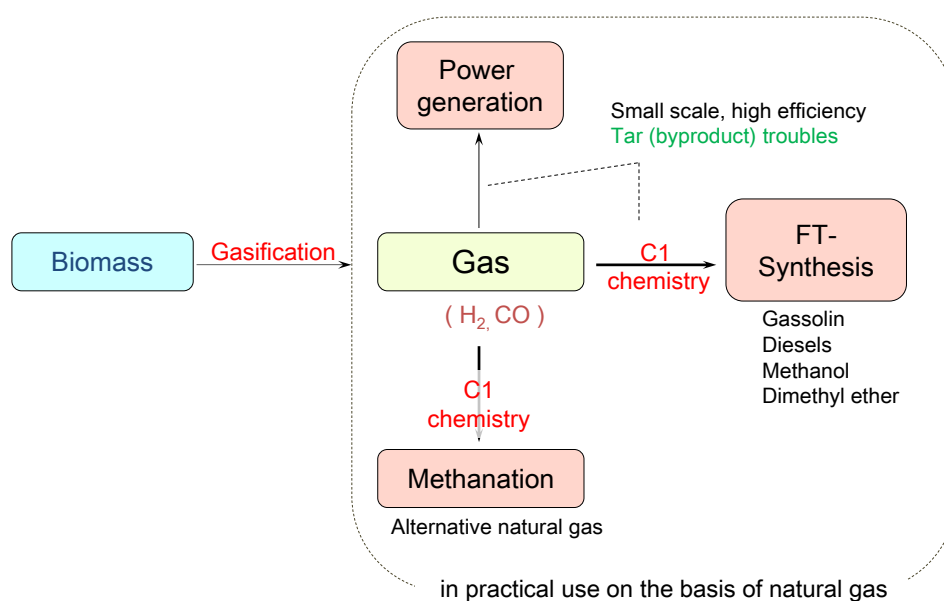
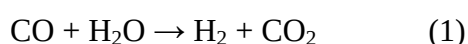


Figure 1-1. Application directions of the producer gas obtained by biomass gasification.

Possible application directions of biomass gasification are summarized in Figure 1-1. The producer gas could be directly utilized for gas engine or gas turbine to

generate electricity (power generation). Alternatively, various types of gas and liquid fuels and chemicals could be produced via CO and H₂ in the producer gas through various catalytic conversion methods including Fischer-Tropsch (FT) synthesis and methanation. A mixture of CO and H₂ is denoted as “Syngas” or “Synthesis gas”, which can be produced also from fossil resources, i.e., coal, natural gas and even petroleum. To maximize the syngas production from biomass, steam gasification is a good option, because steam converts CO into H₂ via the water gas shift reaction (equation 1).



From the next section, FT synthesis, methanation, and power generation are briefly introduced along with their situations. Gasification is expected to be a hub process for future chemical platform (Hayashi et al., 2014), since FT synthesis produces petroleum, which can directly substitute the today’s fossil petroleum infrastructures. It is also noted that all of the utilization methods described in Figure 1-1 have been commercialized based on natural gas and coal.

1.2.1 Fischer-Tropsch (FT) synthesis

The FT synthesis was invented by Fischer and Tropsch in 1923 in Germany, originally for the production of liquid fuel (synthetic petroleum) from coal. Because this process can convert solid and gaseous carbon-based resources into liquid, these processes based on biomass, coal, and natural gas are called as BTL (biomass to liquid), CTL (coal to liquid), and GTL (gas to liquid) technologies, respectively.

These technologies have a long history for commercialization. During the World War II, many CTL plants were constructed in Germany, and then moved to South Africa, where large volumes of synthetic petroleum have been produced up to now based on natural gas and coal (Kaneko, 2006). In 1993, similar GTL plant was constructed in Malaysia by Shell MDS Malaysia Sdn. Bhd. (Shell-Global, 2016).

Chevron Nigeria Limited (Chevron, 2016) is also planning to install additional CTL and GTL plants in Nigeria to produce clean diesel and gasoline, since sulfur can be removed during the syngas production stage.

Metal catalysts including Fe and Co are utilized for FT synthesis, where CO is converted into hydrocarbons with the continuous reduction by H₂. Thus, biomass can be converted into hydrocarbons (synthetic petroleum), and hence, various petroleum derived fuels (gas, gasoline, diesel and heavy oil) can be produced from biomass along with the petroleum based chemicals. Accordingly, the present infrastructures based on petroleum could be used directly for the BTL products.

There are many installations of BTL plants at the pilot levels in many countries including European countries, USA, and Japan, but no commercialized plants have been established yet. Choren in Germany is an example of the world's largest BTL plant for the production of diesel fuels from wood biomass, using Carbo-V® system for wood gasification. The 18 million liter of diesel (SunDiesel®) was expected to be produced annually from 65 thousand tone of wood biomass at the cost of 1 euro per liter. However, the project has been interrupted in 2012 due to the termination of governmental subsidies. Thirteen pilot gasification plants in EU for commercial purpose were picked up (Balan et al., 2013). Among them, 4 projects have been interrupted and 3 projects are still in just planning stage even today for similar reasons to the Choren's case.

1.2.2 Methanation

Methane production via syngas is an option of the utilization of the producer gas from biomass. Because methane is the major constituent of natural gas that is supplied by gas companies, this process is greatly attracted by gas companies for increasing the security of the natural gas supply. Nickel based catalysts are utilized for the conversion of syngas to methane.

In 2015, an electric company in Sweden opened the world's largest pilot plant

which produces methane through methanation via the syngas obtained from biomass gasification (GoBiGas project). They intended to supply the product methane to Swedish natural gas grid and to expand the productivity from 20 to 80MW after 7 years of pilot operation.

1.2.3 Power generation

Biomass power plants presently utilize a combustion-steam turbine process to generate electricity. This is a well-established system, but the low electricity efficiency normally less than 20% is a drawback of this system. This is mainly due to the small plant size that is inevitable for biomass power plant due to the difficulty in accumulating the large amount of biomass with low energy density. The present high electricity efficiency (~50%) of the power plants based on fossil fuels can be accomplished by the high temperature/pressure steam which can be supplied only by the large size plant made of expensive materials. Thus, combustion-steam turbine system is greatly dependent on the plant size and not suitable for biomass power generation.

Producer gas expands the choice of power generation systems. Utilization of the producer gas for gas engine and gas turbine systems are the potential way with much improved efficiency even for the small systems. For the gas turbine system, combined process is also possible, which generate additional electricity by steam turbine with the steam generated by the high-temperature exhaust gas from the gas turbine system. This increases the electricity efficiency more.

1.3 Tar Problem and Mitigation Technologies

1.3.1 Tar problem

Tar is the volatile products which give condensable materials by cooling during the gas production from gasifier. There are several types of tar, some of which

cause coking on the pipeline wall from the gasifier. Polycyclic aromatic hydrocarbons (PAHs) such as naphthalene and other higher molecular weight compounds are also known to cause “tar troubles” by condensing on the pipeline wall (Milne and Evans, 1998; Bridgwater, 2003; Lopamudra Devi et al., 2003). These processes cause the clogging of pipeline from gasifier, and when tar is condensed on the engine for power generation, the engine is damaged. Tar also causes deactivation of FT and methanation catalysts through coking on its surface (Paethanom et al., 2012). Accordingly, tar problems are the critical issues to solve in order to establish the reliable biomass gasification processes, and many attempts have been tried to mitigate the tar problems.

1.3.2 Mitigation technology

Technologies for mitigating tar problems are categorized into gasifier design, tar cracking, and mechanical/physical treatments. Combinations of those treatments are also adopted. Alternatively, installation of these tar elimination processes increases the cost of biomass gasification.

1.3.2.1 Gasifier design

Gasifier design is known to affect the tar content of the producer gas. The gasifier type is divided into two types, i.e., fixed-bed and fluidized bed gasifiers. In the fluidized bed gasifier, biomass is heated with the heating media such as sand fluidizing with the injection of air or steam as gasifying agents, which results in a very effective heat conduction from the media to biomass.

In the fixed bed gasifier, biomass is fed from the top of the gasifier, and drying, pyrolysis forming volatiles and char, volatiles gasification, char gasification, and char combustion take place sequentially in this order during moving from the upper to the lower side of the gasifier. This type is further categorized into up-draft (counter-current) and down-draft (co-current) gasifiers depending on the direction for recovering the

product gas. For the up-draft type gasifier, gas is recovered from the top of the gasifier, and hence, the sensible heat of the gas is efficiently utilized for pyrolysis and drying processes, which increases the thermal efficiency of the system. However, relatively large amount of tar is produced from the up-draft type gasifier. Accordingly, tar removal is inevitable for utilization of the producer gas for any applications.

On the other hand, the down-draft type produces gas from the bottom of the gasifier. This promotes the secondary degradation of the volatile intermediates and significantly reduces the tar content of the producer gas. The major drawback of this type is the difficulty in the scale-up of the system (limited to approximately 500 kg/h) (Hosoya, 2008). The tar levels of the fluidized-bed type gasifier are normally between up-draft and down-draft type gasifiers.

Consequently, choice of the gasifier type significantly affects the quality of the product gas.

1.3.2.2 Tar cracking

Tar cracking, which is the method to decompose tar and its derived coke in and after the gasifier, is categorized into three methods, i.e., catalytic cracking, thermal cracking, and oxidation by O_2 and H_2O (gasifier agents).

As for the catalytic cracking, a number of catalysts have been proposed and include natural materials such as dolomite and olivine and synthetic catalysts including $NiAl_2O_3$. Application of these catalysts is not very successful because of the insufficient activity for the reduction of tar content (Hayashi et al., 2006) along with the catalyst deactivation and poisoning (Sehested, 2006; Yung et al., 2009). Thus, additional reactivation stage is necessary, which leads to the increase in the gasification cost.

Direct cracking without the addition of any catalysts at high temperatures with gasification agents (O_2 and H_2O) have been applied to reduce the tar content. Kinoshita et al. (Kinoshita et al., 1994) reported that tar yield during gasification decreased with the increasing gasifier temperature (in the range of 800–850 °C and 1050–1300 °C).

Thus, high temperature gasification is normally effective for tar reduction, whereas thermal efficiency of the gasification system decreases. Use of excess amount of O₂ (air) that is equivalent to the level of complete oxidation is also reported to be effective (Kinoshita et al., 1994; Hernández et al., 2013). Alternatively, Hernández pointed out the enhancement of the formation of PAHs by these methods with the reduction of the contents of phenolic compounds. The PAHs are the tar components that are difficult to decompose (Hernández et al., 2013). In addition, additional use of O₂ promotes the oxidation of the gaseous products into CO₂, which reduces the heating value of the product gas, although hydro (H₂O)-reformed gas retains higher heating value (Higman and Burgt, 2008). The drawback of hydro-reformation is the additional use of heat to compensate the endothermic reactions of the conversion from tar to hydrogen, which reduces the thermal efficiency of the system.

1.3.2.3 Mechanical/physical treatments

Mechanical/physical treatments are categorized into two types (dry and wet treatments) as summarized in Table 1-1 (Anis and Zainal, 2011). Dry gas cleaning is usually applied before gas cooling, and the operating temperatures are normally very high (>500°C) with some exception, while wet gas cleaning is usually conducted after the gas cooling at lower operating temperatures around 20–60 °C.

For dry gas cleaning, the installation of cyclone and rotating particle separators (RPS) are the easy way, while the tar removal efficiency is not sufficient. On the other hand, fabric or ceramic filters and filters packed with activated carbon or sand reduce tar content more efficiently, but the installation of these devices is costly. For example, ceramic filter is reported to remove about 75–97.9% of the tar from the producer gas (de Jong et al., 2003). Nevertheless, ceramic filters have not been introduced for demonstration plants due to the cost and complexity in their installation in gasifier. Cleaning of the used filter is not easy, since tar accumulation on the surface cause eventual clogging on them.

Activated carbon and char can be used as a cheap adsorbent for tar (Hasler and Nussbaumer, 1999), although these are also reacted with gasifying agents such as O₂ or H₂O during gasification.

Table 1-1 Classification of mechanical/physical gas cleaning systems (Anis et al. 2011)

Basic type	Equipment
Dry	Cyclone, rotating particle separators (RPS), electrostatic precipitators (ESP), bag filters, baffle filters, ceramic filters, fabric/tube filters, sand bed filters, adsorbers, etc.
Wet	Spray towers, packed column scrubber (wash tower), impingement scrubbers, venture scrubbers, wet electrostatic precipitations, OLGA, wet cyclones, etc.

Electrostatic precipitation (ESP) is a filtration system using electrostatic effects. It has a bigger gap for gaseous stream to pass through, and hence the clogging would be avoided in ESP. However, the electricity consumption is rather greater to accomplish the higher precipitation (removal) efficiency.

Wet gas cleaning systems include spray towers, packed column scrubber (wash tower), impingement scrubbers, venture scrubbers, wet electrostatic precipitations, OLGA, wet cyclones, and so on. These methods have been widely applied for the pilot gasification plant (Anis and Zainal, 2011). ESP, packed system of water scrubber, and wet cyclone are reported to achieved 50-90%, 40-70%, or 40-90% removal of tar, respectively (Hasler and Nussbaumer, 1999; H. Boerrigter, 2004; Lettner F, 2007). However, these processes have a drawback of large volume of waste water producing from the systems. Clogging inside the scrubbing system is also reported as a problem, due to the condensation of insoluble oily products and salts (Lettner F, 2007; Lee et al., 2008).

To overcome the waste water problem, oil is utilized for the scrubbing media

instead of water. Figure 1-2 shows the system flow of GoBiGas pilot plant as described above. In this process, rapeseed oil methyl ester (RME, a kind of biodiesel) is utilized for scrubbing the gaseous products to remove tar, and the resulting mixture is injected to the combustion reactor and utilized for generation of the process heat.

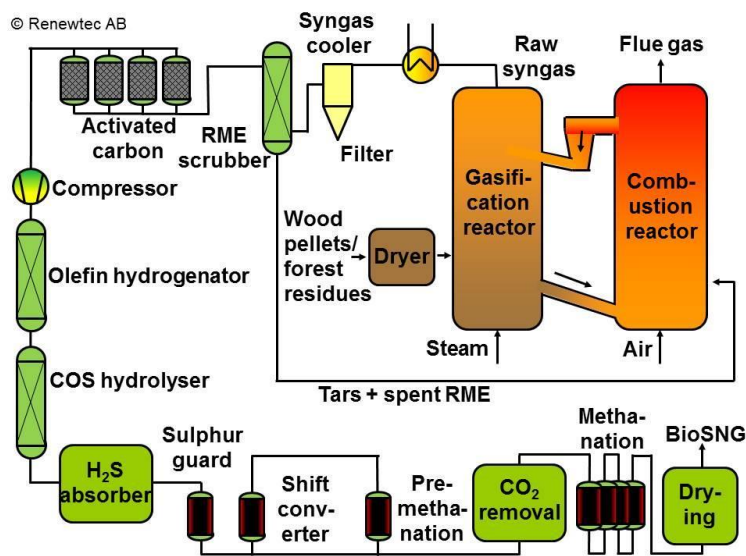


Figure 1-2. Schematic figures of GoBiGas pilot plant.
RME: rapeseed methyl ester, SNG: synthetic natural gas

Consequently, many attempts have been conducted to mitigate the tar problems, whereas no sufficient systems have been established yet. Nevertheless, no attempts have been conducted to inhibit the tar problems by altering the gasification reactions. Better understanding of the chemistry involved in gasification would provide insights into the development of tar-free clean gasification systems. For these reasons, gasification mechanisms (molecular mechanisms) of cellulose, which is the major component of lignocellulosic biomass, are briefly summarized in the next section, since this dissertation particularly focuses on the secondary reactions of cellulose gasification.

1.4 Gasification Mechanism of Cellulose

1.4.1 Two-stage process

Wood gasification reactions are believed to proceed in two stages, i.e., primary pyrolysis and secondary reactions stages, as illustrated in Figure 1-3. In the primary pyrolysis stage, cellulosic biomass is converted into volatile intermediates and primary char, both of which further decompose into gaseous products along with tar and coke as by-products. Gasifying agents such as O_2 and H_2O may contribute to the reactions in the latter stage, particularly for char gasification (Milne and Evans, 1998; Rapagnà et al., 1998; Bridgwater, 2003).

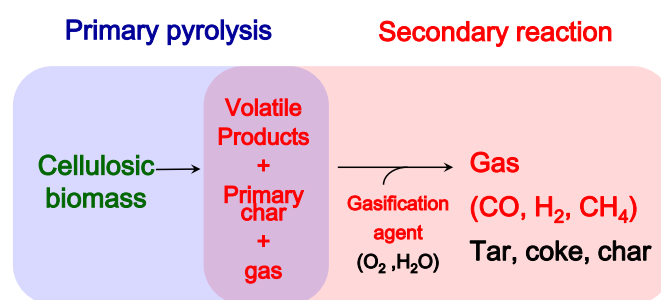


Figure 1-3. Two-stage process for gasification of cellulosic biomass.

1.4.2 Levoglucosan as a primary pyrolysis product

Thermogravimetric analysis (TGA) is frequently used for studying the temperature range for the pyrolytic degradation of wood and its constituent polymers, i.e., cellulose (45–55%), hemicellulose (20–25%) and lignin (20–30%) [value range in parenthesis: content in lignocellulosic biomass, (Masuda et al., 1989)]. The major weight-loss of wood is observed in the temperature range of 200–400 °C, where most of the primary pyrolysis reactions take place (Ramiah, 1970). Therefore, even in gasification conducted at higher temperatures, primary pyrolysis reactions are expected

to proceed when the temperature is raised up to this temperature range.

The weight-loss temperature in TGA varies depending on the constituent polymers. Weight-loss of lignin starts at as low as 200°C and observed in a wide range of temperature between 200–800°C with the major weight-loss arising from the primary pyrolysis reactions observed around 300-400°C. On the other hand, weight-loss of polysaccharide fractions (cellulose and hemicellulose) occur in much narrower temperature range with the derivative of TG (DTG) peaks around 300 and 350°C, respectively, to form relatively small amounts of char as residues (~10 % for cellulose), and the weight-loss at the higher temperatures is quite small. These observations suggest that the volatile intermediates play much more important roles in gasification of the polysaccharide fractions than solid char. The greater thermal stability of cellulose than hemicellulose is believed to originate from the crystalline nature of cellulose.

The volatiles from the pyrolysis of cellulose have been investigated with the various analytical methods such as gas chromatography (GC) – mass spectrometry (MS) and nuclear magnetic resonance (NMR) spectrometry and identified to include anhydrosugars [1,6-anhydro-β-D-glucopyranose (levoglucosan, LG) and 1,6-anhydro-β-D-glucofuranose (AGF, the franose isomer of LG), dehydration products such as furfural, and fragmentation products including glycolaldehyde, hydroxyacetone, and acetic acid.

Among the pyrolysis products from cellulose, LG is known to form in substantial yields; Bradbury et al. (1979) and Kwon et al. (2007) reported to obtain LG in 58% and 70% yields, respectively, from the vacuum pyrolysis of cellulose (Figure 1-4). Accordingly, LG has been considered to be a key intermediate during cellulose pyrolysis/ gasification. This is also supported by the experimental results that LG and cellulose gave similar pyrolysis products (Greenwood et al., 1961; Glassner and Pierce, 1965; Byrne et al., 1966; Wodley, 1971). This is a reason why the secondary reactions of LG are particularly emphasized in this dissertation.

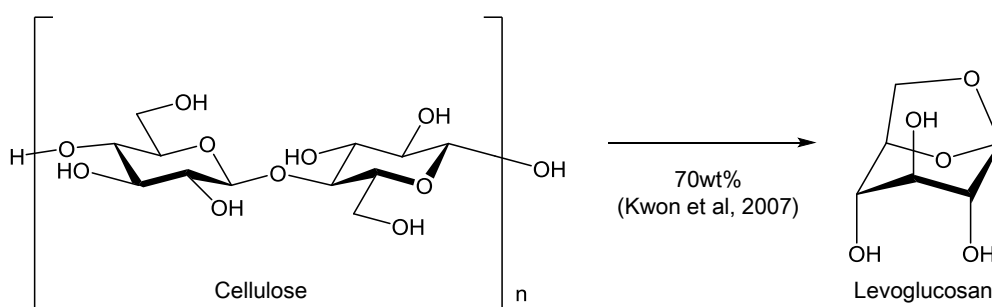


Figure 1-4. Levoglucosan formation as the major primary product during cellulose pyrolysis.

1.4.3 Secondary reactions

Secondary reactions are expected to occur in different phases. Volatile intermediates suffer from the gas-phase secondary reactions prior to condensing on the wall of gasifier and pipeline with lower temperatures, where the intermediates are further decompose in the liquid phase. For char intermediates, solid- and liquid-phase secondary reactions would proceed. The reactivities have been suggested to vary greatly depending on the phase of secondary reaction and the chemical composition (cellulose, hemicellulose, and lignin). Hosoya et al. (2007) reported that cellulose-derived volatile intermediates were quite reactive for gasification than cellulose char and lignin-derived products (volatiles and char) in ampoules at 600°C. Thus, cellulose-derived volatiles are quite important intermediates for gasification.

Secondary reactions at the gasification temperatures >600°C have been studied very limitedly, whereas those of liquid-phase LG at relatively low pyrolysis temperatures (<400°C) have been studied extensively. Thermal polymerization through transglycosylation is a well-known reaction of LG and other simple glycosides, starting at temperatures as low as 240°C (Pictet, 1918; da Silva Carvalho et al., 1959; Wolfrom et al., 1959; Shafizadeh et al., 1971; Shafizadeh et al., 1972; Shafizadeh and Fu, 1973; Ponder and Richards, 1990; Kawamoto et al., 2003). This polymerization reaction is

also claimed to determine the char yield from cellulose pyrolysis (Kawamoto et al., 2003).

It should be noted that the onset temperature of LG polymerization (240°C) is much lower than the formation temperature of LG from cellulose pyrolysis (~350°C). These apparently conflicting results have been explained by the influences of the reaction phase. Hosoya et al. (2008b) found that cellulose-derived volatile intermediates produced significant amounts of tar and coke only after the condensing on the reactor wall with low temperatures during pyrolysis (gasification) of cellulose at 800°C. Combined with the results of the subsequent studies, where the relative contributions of the gas- and liquid-phase reactions of LG was altered gradually, they concluded that the gaseous LG tend to give gaseous products selectively, while the molten (liquid) LG gives polymerization products and coke along with other low molecular-weight (MW) condensable products such as furfural and 5-hydroxymethyl furfural (5-HMF), as summarized in Figure 1-5.

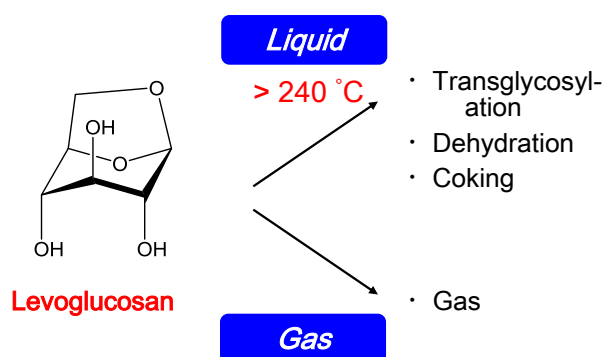


Figure 1-5. Different reactivities of LG as expected in the gas and liquid phases (Hosoya et al., 2008a).

Levoglucosan is also known to be stabilized in some aprotic solvents including aromatic substances and polyethers. For example, LG is stabilized in aromatic substances up to 350°C even after heating for 15 min (Hosoya et al., 2006). Based on

these results, “hydrogen bond theory” has been proposed (Matsuoka et al., 2012; Kawamoto et al., 2013; Kawamoto et al., 2014), in which proton donation through intermolecular hydrogen bonding acts as an acid catalyst to promote transglycosylation and dehydration reactions prevailing in the liquid-phase pyrolysis of LG and other glycosides. Activity as a base-catalyst can also be postulated for the promotion of the fragmentation reactions giving aldehydes and ketones such as glycolaldehyde. In aromatic substance or polyether, these catalytic activities can be suppressed by the complexation to LG and glycosides through $\text{--OH}/\pi$ and --OH/ether O type of hydrogen bonds formation, respectively.

Based on these lines of information, the gas-phase secondary reactions of cellulose-derived volatile intermediates are expected to be different from those of the liquid-phase reactions. However, this has not been confirmed due to the difficulty in the investigation of the pyrolysis of only gaseous LG and other glycosides, since these substances tend to polymerize prior to the evaporation.

1.5 Summary of This Dissertation

Molecular mechanisms of cellulose gasification, particularly on the reactions relating to tar/coke formation, would provide insights into the development of tar-free clean gasification processes. However, the information on the vapor-phase reactions during cellulose gasification at high temperatures ($>600^{\circ}\text{C}$) is very limited. Under these circumstances, this dissertation mainly deals with the vapor-phase secondary reactions of LG and other related compounds to understand the molecular mechanisms involved in cellulose gasification.

In *Chapter 1*, the background of this dissertation is briefly summarized, which includes the prospects and issues of gasification-based biomass utilization technologies and the molecular mechanisms of cellulose gasification as accumulated until recently.

In *Chapter 2*, eight major volatile intermediates (including LG) produced from the primary pyrolysis stage of cellulose are compared in ampoule reactors under

nitrogen or oxygen/nitrogen at 600°C in terms of the relationships between the chemical structure of volatile and gas composition and the coke-forming reactivity in the gas and molten phases. These results would be useful to understand the coke formation behaviors in cellulose gasification, which leads to the tar trouble in biomass gasification.

To investigate only the vapor-phase reactions of LG, an experimental set up is developed in *Chapter 3*, which enables the evaporation of LG prior to the molten-phase reactions occurring. This chapter deals with the vapor-phase reactions of LG in the temperature range of 500-900°C, in contrasted with the liquid-phase reactions leading to coke formation. Interestingly, gaseous LG is reported to be stable up to 500°C in this chapter. *Chapter 4* also utilizes this experimental set up to study the molecular mechanisms for the pyrolysis of gaseous LG, its degradation products along with simple polyalcohols.

Chapter 4-Section 4.1 deals with the vapor-phase reactions of glyceraldehyde (a C3 aldose) and 1,3-dihydroxyacetone (a C3 ketose) as models of LG-degradation intermediates, because LG is suggested to give fragmentation products with carbonyl (C=O) group selectively as the intermediates to the noncondensable gases in *Chapter 3*. Bimolecular concerted mechanisms that effectively reduce the activation energies of some heterolysis reactions are also proposed in *Section 4.1* by combination of the theoretical calculations with Gaussian 09 software with the experimental data.

In *Chapter 4-Section 4.2*, vapor-phase reactions of simple polyalcohols as the simplest model compounds of LG are described with the aid of theoretical calculations. The experimental results also indicate that the ratio of oxygenated gas (CO and CO₂)/hydrocarbon gas (methane, ethylene, acetylene and so on) is directly related to the progression level of dehydration reactions.

In *Chapter 4-Section 4.3*, the vapor-phase thermal stability is compared between LG and methyl glucosides, models free of bicyclic ring system of LG. LG is reported to be much more stable than methyl glucosides against transglycosylation and fragmentation reactions due to the steric hindrance arising from the bicyclic ring system

in this chapter. Methyl glucosides are reported to form LG quite selectively in the gas phase in the pyrolysis temperature ranging between 200-300°C probably through concerted heterolysis mechanisms in this chapter.

Kinetics of thermal degradation of gaseous LG is discussed in *Chapter 4-Section 4.4* along with the theoretical calculations. As a result, some concerted heterolysis reactions are postulated for the relatively-low-temperature (~500°C) reactions of LG, whereas radical chain reactions are suggested to play more important roles particularly at the higher temperatures. Steric effects of the bicyclic ring of LG are reported to affect the reactivity quite significantly.

In *Chapter 5*, cellulose gasification is studied with the similar experimental set up and compared with the data obtained for the gaseous LG. With the clarification of the vapor-phase secondary reactions of LG, cellulose gasification mechanisms and roles of vapor-phase reactions of LG are clearly presented.

Finally, concluding remarks of these investigations are summarized in *Chapter 6* along with the future prospects of these studies.

Chapter 2

Gas and Coke/soot-forming Reactivities of Cellulose-derived Tar Components

2.1 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 ($\text{CO} + \text{H}_2$) by 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 (L. Devi et al., 2003; Wang et al., 2004; Devi et al., 2005; Kumar et al., 2009), water or oil scrubbing (Paethanom et al., 2012), and other physicochemical procedures. However, only a few studies have focused on the formation and elimination of coke/soot (Coll et al., 2001; Zhang et al., 2010). 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 (Hosoya et al., 2008b; Zhang et al., 2010). Hosoya et al. (2007) 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. (2009a) 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. (2011a) 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. (2009) 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 (Lipska and Wodley, 1969; Tsuchiya and Sumi, 1970; Piskorz et al., 1986; Hosoya et al., 2007; Asmadi et al., 2011a; Norinaga et al., 2013). These include water, anhydrosugars, aldehydes, ketones, acids, furans, and alcohols. The pyrolysis reactivities of simple compounds such as acetic acid (Bamford and Dewar, 1949; Blake and Jackson, 1968; Nguyen et al., 1995; Leplat and Vandooren, 2012) and formic acid

(Nelson and Engelder, 1925; Saito, Kakumoto, Kuroda, et al., 1984; Tokmakov et al., 1997; Akiya and Savage, 1998; Wang et al., 2000) have been well studied in relation to the combustion mechanisms of hydrocarbons as fuels. Shin et al. (2001) studied the secondary reactions of levoglucosan, 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 (Kawamoto et al., 2003; Hosoya et al., 2008a; Kawamoto et al., 2008; Kawamoto et al., 2009; Bai, Johnston, Sadula, et al., 2013) 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 (Hosoya et al., 2006; Kawamoto et al., 2013) as well as in the gas phase (Hosoya et al., 2008a). 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 N₂ 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 O₂ addition, which is believed to act as an accelerating agent for gasification, on gas and coke/soot formation are also discussed.

2.2 Materials and Methods

2.2.1 Materials

Levoglucozan (**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 (Scifinder. Chemical Abstracts Service: Columbus)] 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) after melting of **2**.

2.2.2 Pyrolysis and product analysis

Pyrex glass ampoule reactors (internal diameter: 8.0 mm, length: 80 mm, wall thickness: 1.0 mm) (Figure 2-1) 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.

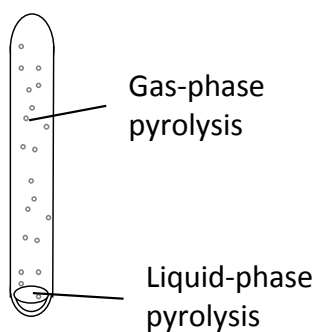


Figure 2-1. Liquid- and gas-phase pyrolysis reactions in closed ampoule reactor.

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 molar 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. (2011b), 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 gas-collecting apparatus before opening the ampoule. Details of the gas-collection method using this apparatus are given in the literature (Hosoya et al., 2008b). After collection of the gaseous products, the residues inside the ampoule reactor were extracted twice with MeOH (1.0 mL) to obtain the MeOH-soluble (tar) and MeOH-insoluble (coke and soot) products. In this paper, black carbonaceous solid substances deposited on the reactor wall or at the bottom were defined as coke, and tiny black particles as soot. The amounts were not quantified in this study. The MeOH-soluble products were not characterized further.

The composition of the noncondensable gases was determined by micro gas chromatography, using a Varian CP-4900 instrument, under the following chromatographic conditions: channel (1) column: MS5A 10 m; carrier gas: argon; column temperature: 100 °C; column pressure: 170 kPa; detector: thermal conductivity detector (TCD); retention times (s): H₂ (26.4), N₂ (45.7), O₂ (35.4), CH₄ (60.6), and CO (86.9); channel (2) column: PoraPLOT Q 10 m; carrier gas: helium; column temperature: 80 °C; column pressure: 190 kPa; detector: TCD; retention time (s): CO₂ (19.9), C₂H₄ (23.5), C₂H₆ (26.3), C₃H₆ (57.4), and C₃H₈ (63.2).

2.3 Results and Discussion

2.3.1 Coke- and soot-forming reactivities

Photographs of the ampoule reactors after pyrolysis of compounds **1–8** at 500 and 600 °C in N₂ (A) and O₂/N₂ (B) for 10 min followed by tar extraction are shown in Figure 2-2, along with photographs of the MeOH-soluble tar fractions. In N₂, no soot was observed for any of the compounds used in this study. Only furfural and 5-HMF pyrolyzed in O₂/N₂ gave significant amounts of soot. These influences of O₂ addition (Figure 2B) will be discussed later. The MeOH-soluble fractions were almost colorless, except in the cases of furans **4** and **5**, which gave yellow solutions. Extensive conversion of the tar products soluble in MeOH may occur at these high pyrolysis

temperatures.

In N₂ (Figure 2-2A), the coke-formation reactivities in the liquid- and gas-phase reactions were found to differ depending on the chemical structure of the cellulose primary volatile products **1–8**. Primary coke was clearly observed for levoglucosan (**1**), glycolaldehyde (**2**), furfural (**4**), and 5-HMF (**5**) at the bottom of the reactor at both temperatures. These coke materials were formed through liquid-phase reactions before volatilization of these compounds. The other compounds did not produce any detectable coke at the bottom of the reactor. These compounds evaporated before the liquid-phase coking reactions occurred.

Additionally, furfural (**4**) and 5-HMF (**5**) produced another type of coke material (secondary coke) all over the reactor wall at 550 (not shown) and 600 °C. Acetic acid (**6**) also produced a similar type of coke at 600 °C, although the amount looked much smaller than those from the furanic compounds. This type of coke material was formed through gas-phase reactions after volatilization of compounds **4–6** and their decomposition products.

Hosoya et al. (2008a) reported that levoglucosan did not form any coke materials in gas-phase pyrolysis, although it readily gave coke in liquid-phase reactions. The present results support these previous findings. As a molecular mechanism to explain this phenomenon, Matsuoka et al. (Matsuoka et al., 2012) and Kawamoto et al. (Kawamoto et al., 2013) proposed that proton donation through intermolecular hydrogen-bonding catalyzes char/coke-forming dehydration reactions and transglycosylation reactions of reducing and non-reducing sugars, respectively. Such weak acid catalysis would prevail in the liquid-phase pyrolysis of levoglucosan and glycolaldehyde in their molten states, where the formation of intermolecular hydrogen bonds is possible. Such intermolecular hydrogen-bonding is not important in gas-phase pyrolysis.

Although the coke-formation behaviors of furfural and 5-HMF have not been well discussed yet, these results were similar to those reported for lignin-derived volatile products (Asmadi et al., 2011a). The chemical structural feature that these

compounds often have in common is aromaticity, and aromaticity may be related to the characteristic gas-phase coking reactions. A formation mechanism for solid carbonized products from reducing sugars under hydrothermal conditions has been proposed, based on the time-course changes in solid-state NMR spectra (Camillo Falco et al., 2011). This mechanism includes the polymerization of furanic intermediates, followed by rearrangement of the furan rings to benzene rings. In the case of gas-phase coking, the formation of propargyl radicals, which are known to be potential coke precursors, has been reported in high-temperature pyrolysis of unsubstituted furan (Vasiliou et al., 2009). Such mechanisms may be involved in coke formation from furfural and 5-HMF, although further study is necessary to confirm the molecular mechanisms.

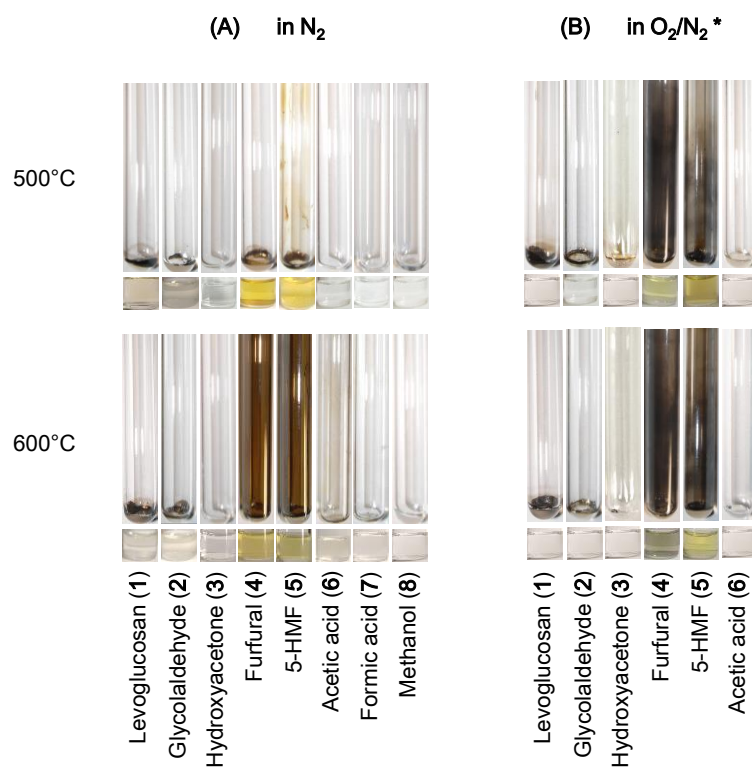


Figure 2-2. Photographs of ampoule reactors along with MeOH-soluble portions obtained after pyrolysis of compounds **1–8** in N_2 or O_2/N_2 and subsequent extraction with MeOH. *Amount of O_2 : 0.3 molar equiv. with respect to stoichiometric amount of O_2 required for complete oxidation to CO_2 and H_2O .

These results give us some insights into coke formation during the gasification

and pyrolysis of cellulosic biomass. Levoglucosan, glycolaldehyde, furfural, and 5-HMF were found to be converted to coke materials by cooling these gases to temperatures lower than their dew points, leading to coking on the wall of the pipeline from the gasifier or pyrolyzer. Levoglucosan and 5-HMF, with higher boiling points of 385 °C (Shoji et al, 2014) and 291.5 ± 30.0 °C (Scifinder. Chemical Abstracts Service: Columbus), respectively, are especially important, because they are expected to condense on the wall at higher temperatures. In contrast, furfural, 5-HMF, and acetic acid would tend to be converted to coke materials on the gasifier or pyrolyzer reactor wall through gas-phase reactions. It should be also noted that most of the compounds except for furans did not produce secondary coke, which arises from the limited reactivities of these compounds for refractory tar formation. No heavy and refractory tar materials were detected from these compounds.

2.3.2 Gas-forming reactivities

The carbon-based yields of total gaseous products, i.e., CO, CH₄, CO₂, C₂H₄, C₂H₆, C₃H₆, and C₃H₈, formed from compounds **1–8** during pyrolysis at 500, 550, and 600 °C for 10 min under N₂ and O₂/N₂ are shown in Figure 2-3. In this section, only the gas-formation reactivity under N₂ is discussed; the influence of O₂ addition is discussed later.

The effects of pyrolysis temperature on the gas-forming reactivities of compounds **1–8** differed depending on their chemical structures. The gas yields from compounds **1–6** increased with increasing pyrolysis temperature, whereas those of formic acid (**7**) and MeOH (**8**) were constant, at around 60% and almost 0%, respectively, in the temperature range 500–600 °C.

At 500 °C, formic acid (**7**) gave the highest gas yield (56.8%), followed by glycolaldehyde (**2**) (33.7%) and levoglucosan (**1**) (25.9%). These compounds would therefore be important intermediates for gas formation at such a low pyrolysis temperature. The gas yields from the other compounds, i.e., hydroxyacetone (**3**), furans

4 and **5**, and MeOH (**8**) were low, ranging from 1.0% to 10.9%.

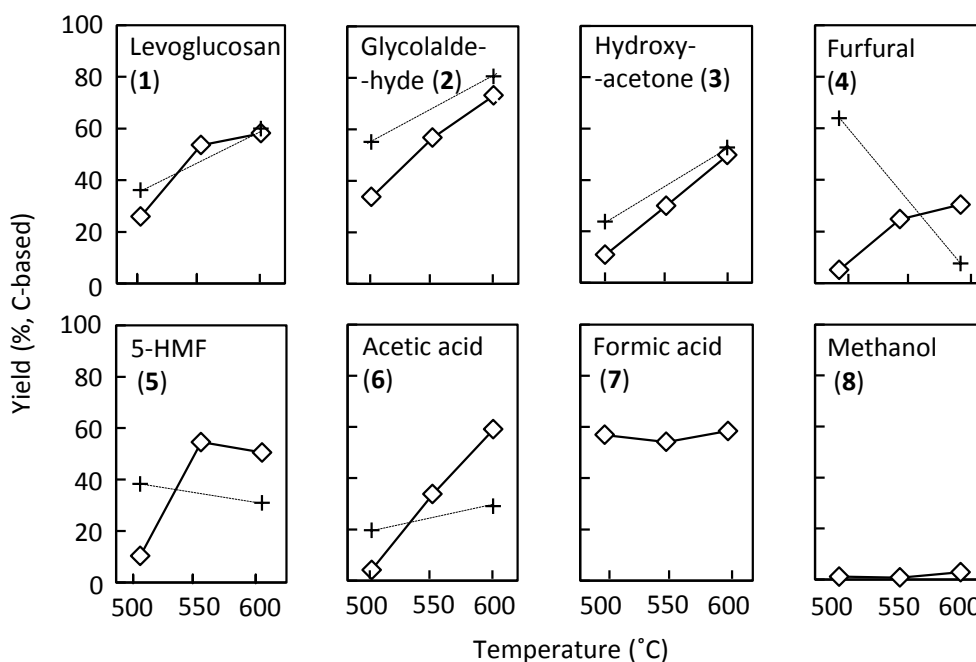


Figure 2-3. Yields (% , carbon based) of gaseous products from pyrolysis of compounds **1–8** in N₂ or O₂/N₂ at 500, 550, and 600 °C. Starting compound (6.0 mg) ◇: in N₂, +: in O₂/N₂. Amount of O₂: 0.3 molar equivalent with respect to stoichiometric amount of O₂ required for complete oxidation to CO₂ and H₂O.

As the pyrolysis temperature increased to 550 and 600 °C, the gas yields from glycolaldehyde (**2**), hydroxyacetone (**3**), and acetic acid (**6**) increased linearly up to 73.1%, 49.7%, and 59.0%, respectively, at 600 °C, whereas those from levoglucosan (**1**), and furans **4** and **5** tended to level off in the temperature range 550–600 °C. The latter group of compounds gave substantial amounts of coke, as shown in Figure 2-2, and such coke by-production would be responsible for the leveling off of the gas yields. These enhanced gas formation reactivities in the temperature range 550–600 °C are consistent with the earlier observations of the gas formation reactivity evaluated for the pyrolysis vapor from cellulose with a two-stage pyrolysis reactor (Antal, 1983).

Interestingly, the gas yield (50.5%) from 5-HMF (**5**) at 600 °C, which leveled

off in the temperature range 550–600 °C, was almost double that (30.4%) from furfural (**4**). The ratio of these values, ≈ 1.7 , correlates well with the ratio (≈ 1.7) of the carbon contents (33% and 20%, respectively) of the substituent groups in the furanic compounds. These observations suggest that the side chains of the furanic compounds are important sites for the gas-forming reactions. The furan ring, with an aromatic character, would be stable under pyrolysis conditions in N₂.

The gas-formation reactivity of formic acid has been well described in the literature (Nelson and Engelder, 1925; Saito, Kakumoto, Kuroda, et al., 1984; Tokmakov et al., 1997; Akiya and Savage, 1998; Wang et al., 2000). For example, Nelson et al. (1925) reported that formic acid decomposed completely to gaseous products at 450 °C during slow pyrolysis in a Pyrex tube. The pyrolytic decomposition mechanisms of formic acids have also been well discussed, and include unimolecular and bimolecular reactions with activation energies of 62.1–81.6 kcal/mol (Saito et al., 1984) and 26.7–30.7 kcal/mol (Wang et al., 2000), respectively. The relatively high gas-formation reactivity of formic acid, even at the lowest temperature of 500 °C, observed in this study indicates that this decomposition proceeds by the bimolecular mechanism.

Unimolecular and bimolecular reactions for the pyrolysis of acetic acid have also been proposed. The activation energies for these reactions were reported to be 61.9–67.5 kcal/mol (Bamford and Dewar, 1949; Nguyen et al., 1995) and 34.2 kcal/mol (Blake and Jackson, 1968), respectively. The relatively low gas-formation reactivity of acetic acid at 500 °C suggests that the decomposition mechanism is different from that of formic acid, although only the H in formic acid is replaced by a methyl group in acetic acid. The aldehydic character of formic acid may play an important role in the gas-forming reactions at 500 °C. To explain these reactivity differences, Blake et al. (Blake and Jackson, 1968) suggested that acetic acid decomposes at 500 °C by a unimolecular reaction mechanism, but by mixed unimolecular and bimolecular reaction mechanisms at temperatures above 500 °C.

Compounds **2–8** are known to be formed during the thermal decomposition of

levoglucosan, therefore these compounds are expected to be present as intermediates in gas formation from levoglucosan. This could be why the observed gas-formation reactivity of levoglucosan was the average of those of compounds **2–8**.

2.3.3 Gas composition and formation mechanism under N₂

The volumes of CO, H₂, CH₄, and CO₂, which are the major gaseous products from compounds **1–8** at 500 and 600 °C, are shown in Figure 2-4. Their compositions (mol%), including the C₂–C₃ gases (C₂H₄, C₂H₆, C₃H₆, and C₃H₈), are summarized in Figure 2-5. The gaseous products formed from compounds **1–8** varied depending on their chemical structures and the pyrolysis temperature.

At 500 °C, among compounds **1–8**, formic acid (**7**) was the predominant source of H₂ and CO₂. Many studies (Simmons and Gentry, 1986; Li et al., 2001; Hosoya et al., 2008b) have reported relatively high concentrations of CO₂ during the early stage of cellulose pyrolysis. The present results suggest that the decomposition of formic acid as a cellulose pyrolysis intermediate is responsible for these observations.

With increasing pyrolysis temperature to 600 °C, the CO yields from levoglucosan (**1**), glycolaldehyde (**2**), hydroxyacetone (**3**), and furans **4** and **5** increased substantially. The amounts of CO from carboxylic acids **6** and **7** were comparatively low, and MeOH (**8**) gave only a very small amount of CO, even at 600 °C. H₂ formation from glycolaldehyde (**2**) increased significantly at 600 °C, and it is suggested that **2** will become a very important source of H₂, along with formic acid (**7**). Although the gas-formation reactivity of MeOH (**8**) was very low, even at 600 °C, a comparatively large amount of H₂ was formed from this compound. The amounts of CH₄ formed from compounds **1–6** also increased significantly at 600 °C. Consequently, the molar fractions of H₂ and CH₄ at 600 °C tended to increase with increasing pyrolysis temperature from 500 to 600 °C (Figure 2-5).

Most of the compounds used in this study, especially levoglucosan (**1**) and glycolaldehyde (**2**), produced a certain amounts of CO, but acetic acid (**6**) and MeOH

(8) did not. This is consistent with the well-known observation that CO is the major gaseous product from cellulose and other carbohydrate biomasses. CH₄ formation was very limited at 500 °C. In contrast, the effects of temperature on the formation of CO₂ were relatively small, and the molar fractions of CO₂ decreased at 600 °C, except in the case of acetic acid (6). Even at 600 °C, the major source of CO₂ was carboxylic acids. Acetic acid, which was very stable at 500 °C, became reactive at 600 °C, forming CO₂. The amount of CO formed from formic acid (7) increased, and the amounts of CO₂ and H₂ decreased.

The gas compositions obtained from compounds 1–8 were reasonably explained based on their functional groups, as shown in Figure 2-6. Compounds 2–7 contain one carbonyl group. The figures in parentheses in the following discussion show the molar fractions (%) obtained from compounds 2–7 at 600 °C (Figure 2-5). An aldehyde group attached to a hydroxymethyl moiety (glycolaldehyde, 2) produces CO (49.7) and H₂ (37.4). When the hydroxymethyl moiety is replaced by a furan ring, the formation of H₂ becomes less important (CO 72.7 from furfural and 68.1 from 5-HMF). A methyl moiety attached to a carbonyl group tends to produce CH₄ (29.0 from hydroxyacetone and 35.6 from acetic acid). A carboxyl group (carbonyl + OH) gives CO₂ preferentially (27.6 from acetic acid and 22.4 from formic acid). These structure–gas composition relationships also suggest that the gaseous products formed at 600 °C are not in equilibrium states, even after a relatively long pyrolysis time of 10 min; for example, glycolaldehyde and acetic acid have the same formula, i.e., C₂H₄O₂, but the compositions of the gaseous products obtained from these compounds were totally different.

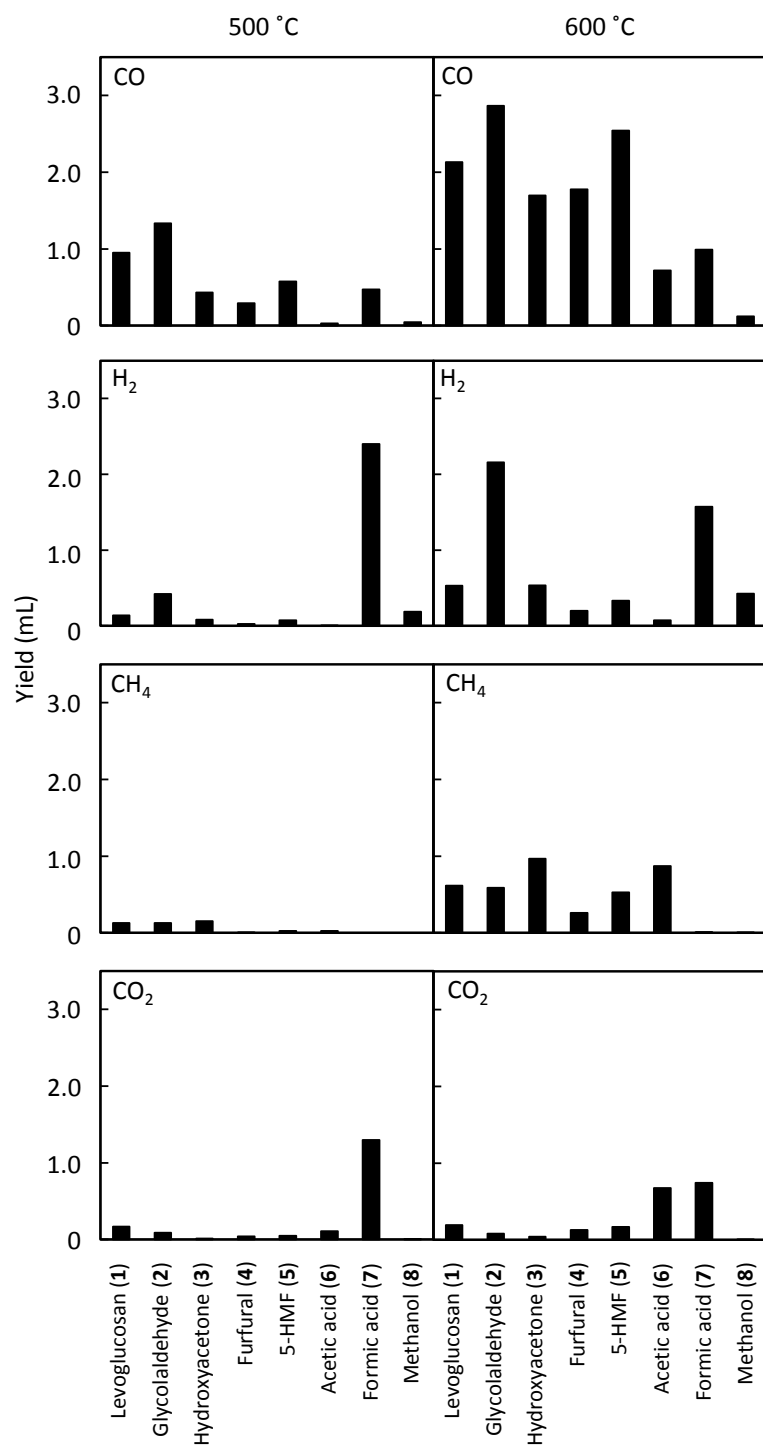


Figure 2-4. Yields of CO, H₂, CH₄, and CO₂ from compounds 1–8 in N₂ at 500 and 600 °C. Starting compound: 6.0 mg.

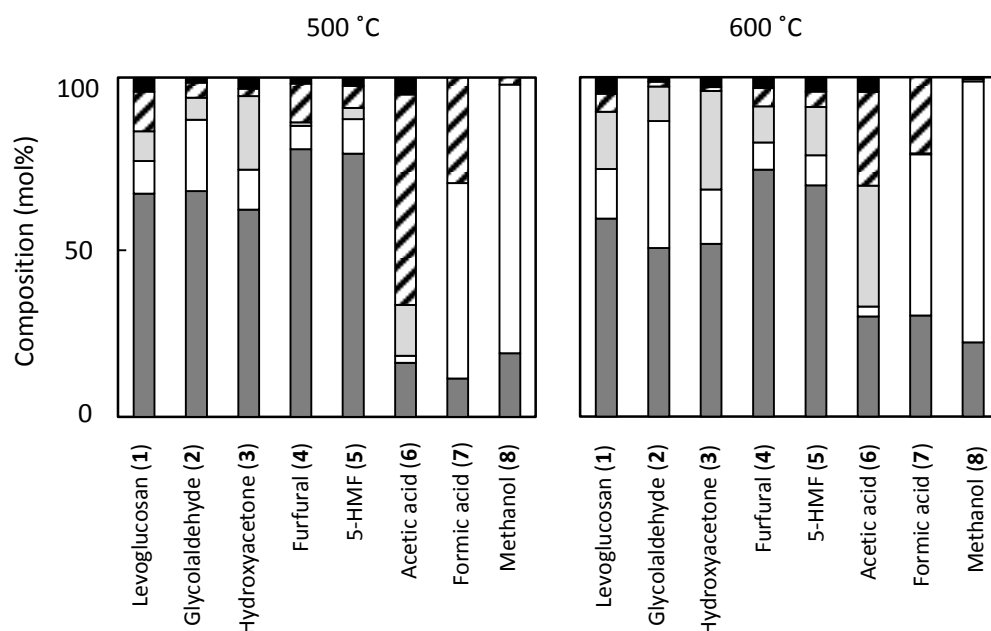


Figure 2-5. Compositions of gaseous products obtained from pyrolysis of compounds **1–8**. ■: CO; □: H₂; ▤: CH₄; ▨: CO₂; and ■: C₂–C₃ gas.

The gas formations observed for the pyrolysis of compounds **1–8** can be reasonably explained by the proposed mechanisms, which include initial homolytic cleavage of the weakest bonds to form radical species, followed by fragmentation through α - and β -scission reactions. The proposed decomposition mechanisms for glycolaldehyde (**2**), hydroxyacetone (**3**), acetic acid (**6**), and furfural (**4**) are illustrated in Figure 2-7. The values shown at the chemical bonds are the bond-dissociation energies (BDEs), which were calculated using Gaussian09/DFT-B3LYP (Frisch et al., 2009). The 6-31+G (d,p) basis set and 6-311+G (d,p) basis set were used for geometry optimization and single-point energy calculations, respectively. Similar radical based decomposition mechanisms are proposed for some simple model compounds such as glycerol (Stein et al., 1983) and 1,3-dioxolane (Cutler et al., 1987).

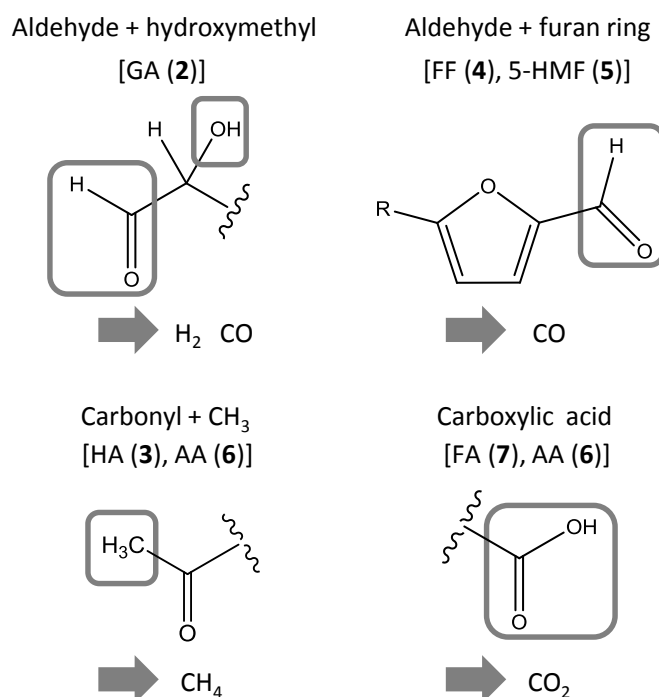


Figure 2-6. Relationships among functional groups and gaseous products formed preferentially during pyrolysis of compounds 2–7 in N_2 at 500 and 600 °C.

The bonds with the lowest BDEs for glycolaldehyde (2), hydroxyacetone (3), and acetic acid (6) were the C–CO bonds; these were calculated to be 72.4, 71.9, and 85.9 kcal/mol, respectively. The homolytic cleavage of this bond in glycolaldehyde (2) gives two radical species, i.e., formyl and hydroxymethyl radicals. The formyl radical subsequently decomposes to CO and an H radical through α -scission. The hydroxymethyl radical produces formaldehyde and an H radical through β -scission. Formaldehyde is known to decompose to CO and H_2 (Klein et al., 1956). The H radicals formed in these processes lead to the formation of H_2 through radical coupling reactions. These reactions explain the preferential formation of CO and H_2 from glycolaldehyde (2).

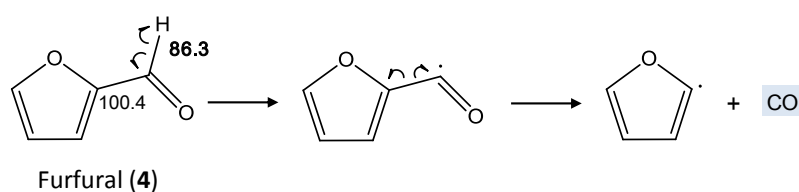
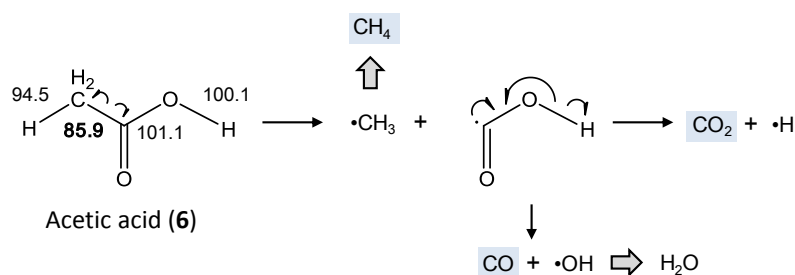
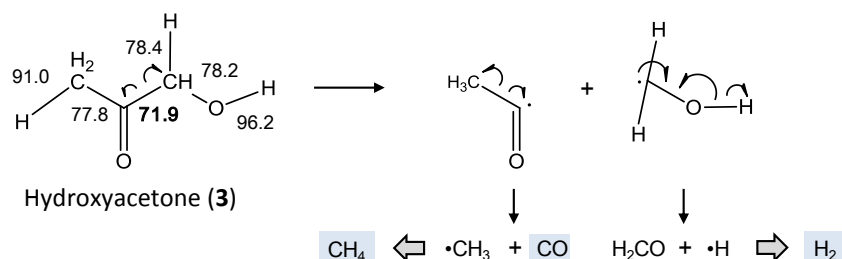
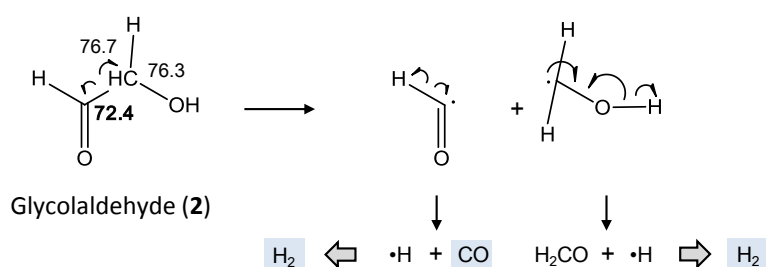


Figure 2-7. Proposed decomposition mechanisms of glycolaldehyde, hydroxyacetone, acetic acid, and furfural, based on homolysis of weakest bonds followed by α - and β -scissions of resulting radical intermediates. The values indicated at the chemical bonds are the bond-dissociation energies, which were calculated using Gaussian09/DFT-B3LYP (Frisch et al., 2009). The 6-31+G (d,p) basis set was used for geometry optimization, and 6-311+G (d,p) was used for single-point energy calculations.

Similar C–CO bond cleavage in hydroxyacetone (**3**) gives an acetyl radical instead of a formyl radical. The acetyl radical forms a methyl radical and CO through a similar α -scission. The methyl radical is converted to CH₄ by H abstraction. A trade-off is therefore observed, and H₂ and CH₄ formation in the pyrolysis of glycolaldehyde (**2**) and hydroxyacetone (**3**) (Figure 2-5) are explained by this mechanism.

The calculated BDE (85.9 kcal mol⁻¹) for the C–CO bond of acetic acid, compared with those of glycolaldehyde (72.4 kcal mol⁻¹) and hydroxyacetone (71.9 kcal/mol), could explain the lower gas-forming reactivity of acetic acid. After homolysis of the C–CO bond of acetic acid, a methyl radical, which is further converted to CH₄ by H abstraction, is formed along with a carboxyl radical. The carboxyl radical decomposes to CO₂ and an H radical through β -scission, or to CO and a hydroxyl radical through α -scission. These mechanisms well explain the formation of CO and CO₂ from acetic acid.

For furfural (**4**), the bond with the lowest BDE was the H–CO bond (86.3 kcal/mol) rather than the C–CO bond (100.4 kcal/mol). The latter bond is very strong because the furan radical formed through homolytic cleavage of this bond is very unstable. The relatively high BDE of the H–CO bond is therefore the reason for the relatively low gas-forming reactivity of furfural (**4**). Homolysis of this bond, followed by α -scission, gives CO and a furan radical. This is also consistent with the preferential formation of CO from furfural. The furan radical is stabilized by radical-coupling reactions. As a result of the stability of the aromatic furan ring, the gas-forming reactivity of the furan ring is very limited under N₂.

2.3.4 Influence of O₂ on coke/soot- and gas-forming reactivities

The effects of the addition of O₂ to the pyrolysis media on coke/soot- and gas-forming reactivities are shown in Figures 2-2 and 2-3, respectively. The influence on each gaseous component formed from compounds **1–6** is also shown in Figure 2-8 as

the volume difference (mL), which was calculated by subtracting the volume of each gaseous product produced under N₂ from that produced under O₂/N₂. A positive value indicates enhanced formation of the component in the presence of O₂ and a negative value indicates decreased formation.

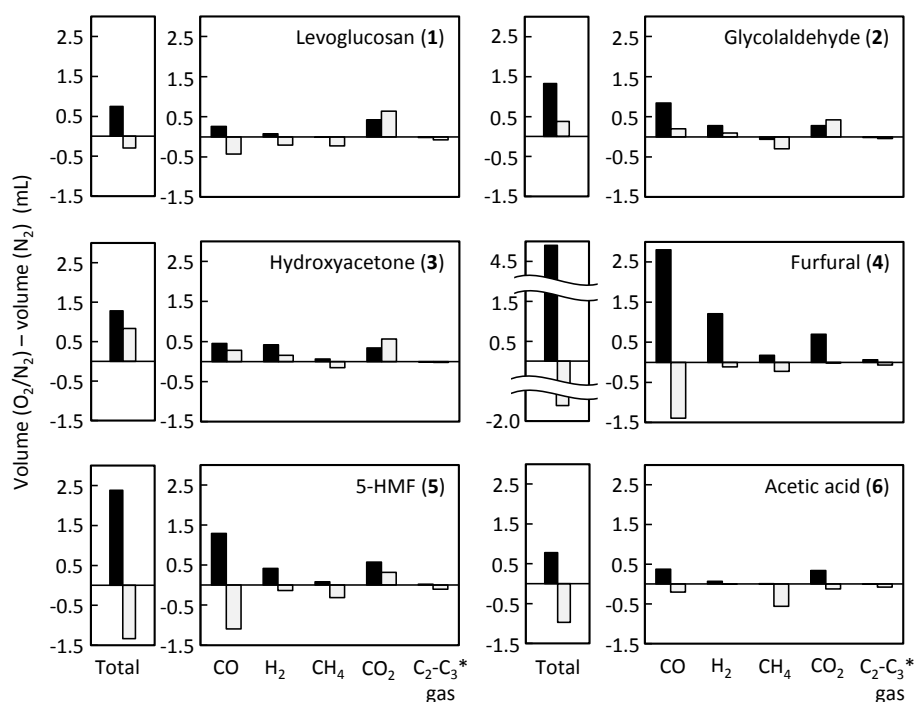


Figure 2-8. Influences of addition of O₂ to pyrolysis media on yields of gaseous products from compounds **1–6** at 500 and 600 °C. ■ : 500 °C; □: 600 °C; *C₂–C₃ gas: ethylene, ethane, propylene, and propane.

The addition of O₂ significantly altered the coke/soot-forming reactivities of furanic compounds **4** and **5**, as shown in Figure 2-2. Although no coke was observed on the upper side of the reactor wall from compounds **4** and **5** under N₂ at 500 °C, coke/soot formed in the presence of O₂. The nature of the coke/soot materials also changed in the presence of O₂. The coke observed under N₂ covered the reactor wall, whereas black powder-like materials (soot) were obtained in the presence of O₂. O₂ therefore enhanced soot formation from furfural (**4**) and 5-HMF (**5**), even at the lower

temperature of 500 °C. Coke formation from hydroxyacetone at the bottom of the reactor was also enhanced in the presence of O₂, although no such coke was observed under N₂. This indicates that O₂ also influenced the liquid-phase reactions of **3**.

In contrast, coke formation from acetic acid (**6**) decreased in the presence of O₂ at 600 °C. O₂ therefore affected the pyrolysis reactions of furanic compounds and acetic acid differently; further studies will be necessary to clarify the details of these effects.

For the gas-forming reactivities observed in Figure 2-3, the influences of O₂ addition varied depending on the pyrolysis temperature. At a lower temperature of 500 °C, the yields of gaseous products from compounds **1–6** generally increased by 10.2–58.9% (based on the starting compound) in the presence of O₂. In contrast, at a higher temperature of 600 °C, these positive effects of O₂ became smaller (only 1.8–7.3%) for levoglucosan (**1**), glycolaldehyde (**2**), and hydroxyacetone (**3**), and the gas yields from furanic compounds **4** and **5** and acetic acid (**6**) decreased by 22.8%, 19.7%, and 30.0% (based on the starting compound), respectively. It is surprising that gas formation from furfural (**4**) was almost completely inhibited at 600 °C, even in the presence of O₂. O₂ was therefore found to affect the gas yields from these compounds differently, depending on the pyrolysis temperature, i.e., 500 and 600 °C. It should also be noted that O₂ does not always enhance gas formation from the intermediates of cellulose pyrolysis.

The influences on the gas compositions from compounds **4–6** (Figure 2-8) were also very different depending on the pyrolysis temperature, i.e., 500 or 600 °C. These influences could not be explained merely by oxidation of the gaseous components by O₂. O₂ addition substantially enhanced the formation of CO from furanic compounds **4** and **5** at 500 °C, but the CO formations were suppressed at 600 °C. The volumes of CO₂, which is the final product of complete oxidation of the gaseous products, did not increase much at either temperature, especially at 600 °C. Similar trends in the influence of O₂ on the total gas yield were observed for acetic acid pyrolysis. The volumes of CO and CO₂ from acetic acid increased at 500 °C in the presence of O₂, whereas the volumes of most of the gaseous products, including CO₂, decreased at 600 °C. These

results are surprising; they suggest that O₂ is not simply a gasifying agent, but has very complex effects on the pyrolysis reactions of furanic compounds and acetic acid. The influences of O₂ on the coke/soot- and gas-forming reactivities of compounds **1–6** are summarized in Table 2-1.

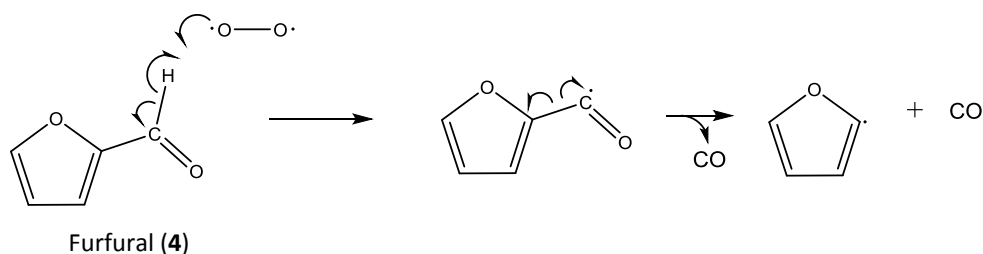
Such influences of O₂ can be explained by modifying the thermal decomposition mechanisms proposed for reactions under N₂ (Figure 2-7). An example of the proposed acceleration mechanism involving O₂ for the pyrolytic decomposition of furfural at 500 °C is shown in Scheme 2-1. The biradical character of O₂ plays an important role in this mechanism. O₂ abstracts H from the aldehydic C–H bond of furfural to form a carbonyl radical, which is the same product as is obtained through homolytic cleavage of H–CO under N₂ (Figure 2-7). Accordingly, such H abstraction by O₂ would reduce the gas-formation temperature. Similar activation mechanisms are also probable for levoglucosan (**1**), glycolaldehyde (**2**), hydroxyacetone (**3**), and acetic acid (**6**).

Table 2-1. Summary of influences of addition of O₂ on coke-, soot-, and gas-formation behaviors of compounds **1–6** at 500 and 600 °C (LG: levoglucosan, GA: glycolaldehyde, HA: hydroxyacetone, FF: furfural, 5-HMF: 5-hydroxymethylfurfural, AA: acetic acid; +: increase > 0.2 mL, ++: increase > 0.8 mL, +++: increase > 2.0 mL, -: decrease > 0.2mL, --: decrease > 0.8 mL)

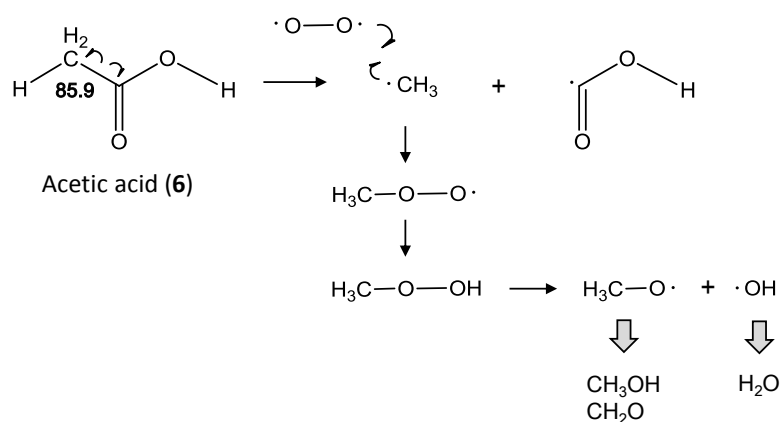
	LG (1)	GA (2)	HA (3)	FF (4)	5-HMF (5)	AA (6)
500 °C						
Coke / soot				++	++	-
Gas						
CO	+	++	+	+++	++	+
H ₂		+	+	++	+	
CH ₄						
CO ₂	+	+	+	+	+	+

600 °C						
Coke / soot				+	+	
Gas						
CO	-		+	--	--	-
H ₂	-					
CH ₄	-	-		-	-	-
CO ₂	+	+	+		+	

The mechanism of acceleration by O₂ in soot formation from furanic compounds is more complex; reactions of O₂ with furfural or furan radicals are considered to be involved.



Scheme 2-1. Proposed mechanism for acceleration by O₂ of pyrolytic decomposition of furfural at 500 °C through H abstraction.



Scheme 2-2. Proposed mechanism for inhibition by O₂ of gas formation from acetic acid at 600 °C, involving homolytic cleavage of C–CO bond of acetic acid followed by radical-coupling reactions with O₂.

A rational molecular-based explanation of the inhibitory effects of O₂ on gas formation from furanic compounds and acetic acid observed at 600 °C is also difficult to

identify at present. One explanation is the inhibition of gas formation from acetic acid, based on the timing of the reaction with O₂ (Scheme 2-2), although further study is necessary to finalize the mechanism. The C–C bond of acetic acid may cleave spontaneously at 600 °C before reacting with O₂, because acetic acid is already reactive at 600 °C, even without O₂. Accordingly, O₂ would react with the resulting radical species such as methyl radicals. This leads to the formation of methyl hydroperoxide, which further decomposes to MeOH and water via homolytic cleavage of the weak O–O bond. These reactions may reduce gas formation, because MeOH was quite stable in the gas-forming reaction at 600 °C (Figure 2-3).

2.4 Summary

The gas- and coke/soot-forming reactivities of eight cellulose pyrolysis intermediates under N₂ or O₂/N₂ in the temperature range 500–600 °C in ampoule reactors were clarified.

1. Levoglucosan, glycolaldehyde, furfural, and 5-HMF produced coke materials in their molten states (primary coke), which indicates that these volatile intermediates are possible precursors for coke formation after condensation on the wall of the pipeline from the pyrolyzer/gasifier.
2. Furfural and 5-HMF also produced another type of coke material over the entire reactor wall (secondary coke). This was considered to be formed via gas-phase reactions. Acetic acid also produced this type of coke to a lesser extent.
3. The gas-forming reactivity varied depending on the chemical structures of the compounds. The reactivities were in the order formic acid > glycolaldehyde and levoglucosan > hydroxyacetone, 5-HMF, furfural, and acetic acid > MeOH. These reactivities were found to be inversely correlated with the BDEs of the weakest bonds in these compounds.

4. The product gas composition also varied depending on the chemical structures of the compounds. The roles of these pyrolysis intermediates in the formation of CO, CH₄, CO₂, C₂–C₃ gases, and H₂ from cellulose pyrolysis were as expected. The formation of these gaseous products was reasonably explained by the proposed reaction mechanisms, which involved homolytic cleavage of the weakest bond to form radical species, followed by their subsequent fragmentation via α - and β -scission reactions.
5. O₂ addition generally enhanced gas formation at the lower temperature, 500 °C. This was explained by initiation of radical chain reactions through H abstraction by biradical O₂.
6. The influences of O₂ on the gas-forming reactions of furfural, 5-HMF, and acetic acid at 600 °C were not explained by this activation mechanism. Unexpectedly, the gas yields from these compounds decreased in the presence of O₂. Based on these results, it was suggested that O₂ does not always enhance gas formation from the intermediates of cellulose pyrolysis.
7. The addition of O₂ enhanced soot formation from furfural and 5-HMF across the temperature range 500–600 °C.

Chapter 3

Vapor-phase Reactions of Levoglucosan as an Intermediate of Cellulose Gasification

3.1 Introduction

Gasification is a promising technology for the conversion of biomass resources into biofuels and biochemicals. The gases generated by this process can be utilized for power generation and the production of synthetic petroleum and chemicals through FT synthesis. Issues related to tar formation, however, represent a challenge that must be solved to allow the establishment of reliable systems. This is required as tar causes clogging of the gasifier outlet and can damage engines and turbines used for power generation by condensing and coking on walls. Coking by tar materials also deactivates FT catalysts. An improved understanding of the chemistry involved in biomass gasification would, therefore, assist in the upgrade of existing gasification processes to produce cleaner gases.

Biomass gasification proceeds as a two-stage process that consists of a primary pyrolysis step to form volatiles and solid char materials and the secondary reactions of these primary products (Antal, 1983; Evans and Milne, 1987; Boroson et al., 1989; Rath and Staudinger, 2001; Morf et al., 2002; Norinaga et al., 2013). Coking, which forms solid carbonaceous residues represents a secondary reaction of the volatile materials.

Hosoya et al. (2007) have studied the coking behavior of cellulose, which is a major component of wood and other lignocellulosic biomass resources, in Pyrex glass tubes under nitrogen at 800 °C. Coking was observed primarily following the condensation of volatile intermediates on the reactor walls at lower temperatures. Thus,

coking reactions were determined to occur after the cooling of the gaseous volatile intermediates during cellulose gasification, which led to the clogging of the pipeline from the gasifier. Later, Fukutome et al. (2014) compared the coking behaviors of various cellulose-derived volatile intermediates in a Pyrex glass ampoule under nitrogen at 600 °C. Levoglucosan (LG), glycolaldehyde, furfural, and 5-HMF were found to form coke in the molten state before vaporization. Thus, these intermediates were believed to contribute to the coking process after condensation. These findings led to a hypothesis: the gas-phase secondary reactions of cellulose-derived volatile intermediates such as LG and glycolaldehyde do not generate tar and coke during gasification, rather it is molten-phase reactions that produce coke.

LG is the primary intermediate product of cellulose pyrolysis (Glassner and Pierce, 1965; Bradbury et al., 1979; Shafizadeh et al., 1979; Radlein et al., 1987; Radlein et al., 1991). Kwon et al. (2007) and Shafizadeh et al. (1979) have reported LG yields as high as 70.1 and 58% from the pyrolysis of cellulose under vacuum in the temperature range from 400 to 430 °C. Many researchers (Greenwood et al., 1961; Glassner and Pierce, 1965; Byrne et al., 1966; Wodley, 1971) have concluded that the chemical compositions of the pyrolysis products are similar for both LG and cellulose. Thus, the pyrolysis reactions of LG have been studied extensively to better understand cellulose pyrolysis. (Pictet, 1918; da Silva Carvalho et al., 1959; Wolfrom et al., 1959; Glassner and Pierce, 1965; Shafizadeh et al., 1971; Wodley, 1971; Shafizad.F and Lai, 1972; Shafizad.F and Fu, 1973; Ponder and Richards, 1990; Shin et al., 2001; Kawamoto et al., 2003; Hosoya et al., 2006; Hosoya et al., 2008a; Zhang et al., 2012; Kawamoto et al., 2013). In the molten state, the condensation of LG through transglycosylation reactions has its onset at approximately 230-250 °C (Pictet, 1918; da Silva Carvalho et al., 1959; Wolfrom et al., 1959; Shafizad.F and Fu, 1973; Ponder and Richards, 1990; Kawamoto et al., 2003), a range that is much lower than the boiling point of LG [385 °C (Shoji et al., 2014)] and the formation temperatures of LG from cellulose [>300–350 °C (Shafizadeh, 1982)]. Based on these results, the relative evaporation/condensation efficiency of LG has been suggested as the main factor that

determines the selectivity for volatiles/char in cellulose pyrolysis (Kawamoto et al., 2003; Bai, Johnston, and Brown, 2013). However, only a few studies [(Shin et al., 2001; Hosoya et al., 2008a) have focused on the gas-phase reactions of LG.

The vapor-phase secondary reactions of the volatile products from wood (Evans and Milne, 1987; Boroson et al., 1989; Rath and Staudinger, 2001; Morf et al., 2002) and cellulose (Antal, 1983; Evans and Milne, 1987; Norinaga et al., 2013) have been studied using two-stage experimental setups that consist of primary and secondary pyrolysis reactors. Evans and Milne (1987) reported variations in the product compositions obtained from the vapor-phase secondary reactions of the volatile products of wood and its constituent polymers by direct analysis with a molecular-beam mass spectrometer. Using a similar system, Shin et al. (2001) reported the vapor-phase conversion of LG and other cellulose-derived primary products in the temperature range of 500–700 °C. However, their work does not, strictly speaking, deal with the gas-phase reactions of LG, because the polymerization and other molten-phase reactions of LG occur at temperatures above 230–250 °C, and so take place before complete vaporization. Therefore, products from the molten-phase reactions of LG may be included in the gas-phase secondary reactions stage. Hosoya et al. (Hosoya et al., 2008a) compared the reactivities of molten- and gas-phase LG by using a dual space ampoule reactor at 400 °C, and found that gaseous LG produced CO and CO₂ selectively, in contrast with the formation of coke and other low-molecular-weight products in the molten state. These results encouraged us to further investigate the gas-phase reactions of LG to address the above hypothesis.

In this chapter, we report the gas-phase secondary reactions of LG studied by using a flow-type two-stage tubular reactor that includes an evaporator. The data are compared with those obtained for the molten-phase pyrolysis of LG to characterize the gas-phase reactions. Finally, the associated molecular mechanisms of cellulose gasification are discussed with a focus on the tar and coke formation that arises from the different reactivities in the gas and molten phases.

3.2 Materials and Methods

3.2.1 Two-stage tubular reactor

The two-stage tubular reactor (Figure 3-1) used in this study consisted of two electric cylindrical furnaces (internal diameter: 35 mm, length: 160 mm, Asahi Rika Seisakusho Co., Ltd.), that served as the evaporator and pyrolyzer. Each furnace included a quartz glass tube (internal diameter: 15 mm, wall thickness: 1.5 mm), and these were connected to one another. The tube used in the evaporator had two fringes set 30 mm apart to allow the application of LG to the desired area. The right end of the evaporator was attached to a nitrogen cylinder via a mass flow controller (Horiba SEC-400MK3), and the other end, which comes from the pyrolyzer, was connected to a gas wash bottle via a glass wool filter and then to a gas bag. Air flow was supplied to the outer part of the tube that comes from the pyrolyzer to quench the pyrolysis reactions. A DMSO- d_6 solution (2.0 mL) that contained an oximation reagent ($\text{NH}_2\text{OH} \cdot \text{HCl}$; 20 mg) was placed in the gas wash bottle to recover the volatile products.

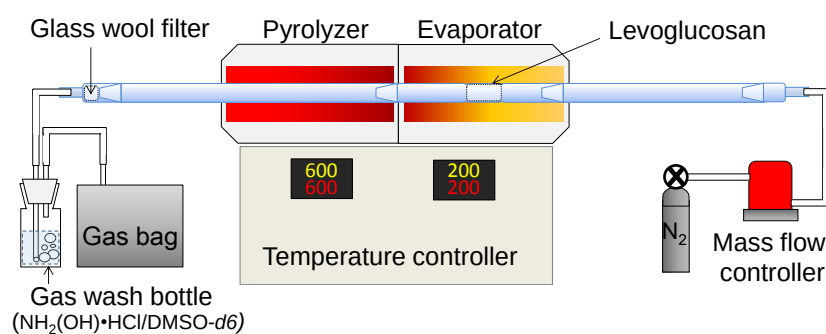


Figure 3-1. Flow-type two-stage tubular reactor consisting of a levoglucosan evaporator connected to a pyrolyzer and product recovery units.

3.2.2 Gas-phase pyrolysis

A solution of LG (15 mg, Carbosynth Ltd., Berkshire, UK) in methanol (0.20 mL) was applied to the area separated by the fringes in the evaporator tube, after which the methanol was evaporated under a nitrogen flow and the tube was completely dried in a desiccator under vacuum. A nitrogen flow (400 mL min^{-1}) was supplied for 30 min before each pyrolysis trial to sweep out the air inside the reactor. The pyrolyzer was preheated at the designated temperature (between 400 and 900 °C), the evaporator was heated to 120 °C over 5 min, and this temperature was maintained for an additional 5 min. The evaporator was subsequently heated to 200 °C at 16 °C min^{-1} . When the temperature reached approximately 185 °C, the LG melted and began to vaporize. After holding the evaporator at 200 °C for 5 min, heating was stopped and the tube reactor was cooled by opening the furnace covers and applying an air flow. The nitrogen flow was maintained for an additional 2 min to sweep any residuals products into the gas wash bottle and gas bag.

The residence time of the pyrolyzer was defined as the period in which the gaseous substances were present in the region of the pyrolyzer with temperatures within the set value $\pm 25 \text{ °C}$. The internal temperature profiles of the pyrolyzer and evaporator were obtained for each set temperature by direct measurement during preliminary control trials conducted without the addition of LG. A constant nitrogen flow of 400 mL min^{-1} was supplied during each experimental trial, and the residence time changed depending on the temperature of the pyrolyzer. The residence times at 400, 500, 600, 700, 800, and 900 °C were determined to be 1.4, 1.2, 1.1, 1.0, 0.87, and 0.80 s. The pressure inside the reactor was measured and was found to equal atmospheric pressure.

3.2.3 Molten-phase pyrolysis

LG was placed at the bottom of a Pyrex glass tube reactor (internal diameter: 8.0 mm, thickness: 1.0 mm, length: 300 mm). The air inside the reactor was replaced

with N₂ by using an aspirator connected through a three-way tap, and the reactor was inserted into a muffle furnace preheated at 350 °C through a small hole of the top of the furnace. After heating for 5 min, the reactor was taken out and immediately cooled with flowing air (30 s) and then in cold water (30 s).

3.2.4 Product analysis

The condensates on the reactor tube wall and the line between the reactor and the gas wash bottle were rinsed off with DMSO-*d*₆ (2.0 mL) to obtain the high-bp fractions. Low-bp fractions were obtained from the gas wash bottle as DMSO-*d*₆ solutions. These solutions were analyzed directly by ¹H NMR spectroscopy by using a Bruker AC-400 (400 MHz) spectrometer with the addition of 2-furoic acid as an internal standard. Quantification of the products along with the recovered LG was performed based on the peak areas of the NMR signals compared with those of the internal standard.

The noncondensable gases other than acetylene were determined by micro-GC by using a Varian CP-4900 instrument under the following chromatographic conditions: channel (1) column: MS5A 10 m; carrier gas: Ar; column temperature: 100 °C; column pressure: 170 kPa; detector: TCD; retention times (s): H₂ (26.4), N₂ (45.7), O₂ (35.4), CH₄ (60.6), and CO (86.9); channel (2) column: PoraPLOT Q 10 m; carrier gas: He; column temperature: 80 °C; column pressure: 190 kPa; detector: TCD; retention time (s): CO₂ (19.9), C₂H₄ (23.5), C₂H₆ (26.3), C₃H₆ (57.4), and C₃H₈ (63.2). The quantification of acetylene was conducted by GC by using a Shimadzu GC-14B instrument under the following chromatographic conditions: column: RESTEC, Rt@-Alumina BOND/N₂SO₄ (30 m, 0.53 min⁻¹), carrier gas: He, column temperature: 60 °C (0-2 min), 40-200 °C (2-16 min, 10 °Cmin⁻¹), 200 °C (16-20 min); detector: flame ionization detector; retention time of acetylene: 4.3 min.

3.3 Results and Discussion

The two-stage tubular reactor is illustrated in Figure 3-1. In this device, a quantity of LG inserted in the quartz glass tube of the evaporator was heated under a nitrogen flow of 400 mL min^{-1} . The temperature of the evaporator was controlled carefully in the vicinity of $200 \text{ }^{\circ}\text{C}$, a temperature between the LG melting point ($185 \text{ }^{\circ}\text{C}$) and the onset temperature (approximately $250 \text{ }^{\circ}\text{C}$) at which the condensation and other molten-phase reactions of LG occur. In this system, the LG was vaporized completely without decomposition and then fed into the pyrolyzer. This was confirmed by the analysis of the recovered substances using gel permeation chromatography (GPC; column: Asahipac GS-220HQ) without heating at the pyrolyzer.

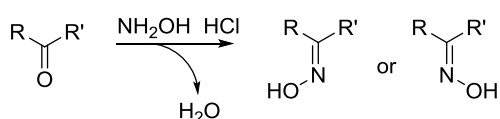
The gaseous LG was heated in the temperature range of $400\text{--}900 \text{ }^{\circ}\text{C}$ within the pyrolyzer, and the resulting pyrolyzates were recovered as condensable and noncondensable substances. Unreacted LG and the condensable products were obtained from two regions: on the walls of the cooling line that leads from the pyrolyzer and in a DMSO- d_6 solution that contained an oximation reagent ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in a gas wash bottle. These are referred to as the high- and low-bp fractions, respectively. Some products with relatively low boiling points did not condense on the walls of the cooling line and were instead captured in the gas wash bottle, in which aldehydes/ ketones and ketene were effectively converted into the corresponding less volatile aldoximes/ketoximes (cis/trans isomers) and N-acetylhydroxyamine, respectively (Scheme 3-1). The noncondensable gases were collected in a gas bag.

The C-based yields (%) of the condensable and noncondensable products from the pyrolysis of gaseous LG at residence times from 0.8 to 1.4 s and at temperatures between 400 and $900 \text{ }^{\circ}\text{C}$ are shown in Figure 3-2. Although the molten LG has been pyrolyzed at temperatures as low as $250 \text{ }^{\circ}\text{C}$, (Kawamoto et al., 2013) the pyrolytic decomposition of the gaseous LG started at $500 \text{ }^{\circ}\text{C}$ and became more pronounced in the temperature range of 600 to $700 \text{ }^{\circ}\text{C}$. By increasing the temperature to $900 \text{ }^{\circ}\text{C}$, the LG was almost completely converted into noncondensable gases. Evans and Milne (1987)

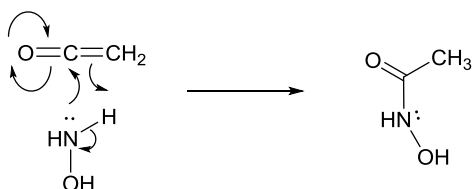
have also reported such unexpected stability for gaseous LG.

The condensable products formed in relatively high yields at the mid-range temperatures of 600 and 700 °C, in which the yields amounted to 13.7 and 8.1% (C-based), respectively. Only very small amounts of condensable products [0.2% (C-based)] were detected at 900 °C. Thus, the condensable products were evidently relatively stable intermediates in the conversion from LG to noncondensable gases.

Oximation of aldehyde and ketone



Acetylation of hydroxyamine with ketene



Scheme 3-1. The derivatization of aldehydes, ketones and ketene with hydroxylammonium chloride as an oximation reagent in the gas wash bottle.

The mass balance was lower than 100% at 600 °C, at which the yields of condensable products are relatively high. Underestimation of some condensable products with relatively low boiling points would be a reason, as discussed later, because of the evaporation from the gas wash bottle under bubbling conditions with a nitrogen flow.

No coke or colored substances were detected anywhere in the experimental setup during these trials. All the condensates found in the cooling line from the pyrolyzer at each temperature were completely recovered as colorless solutions by extraction with DMSO-*d*₆.

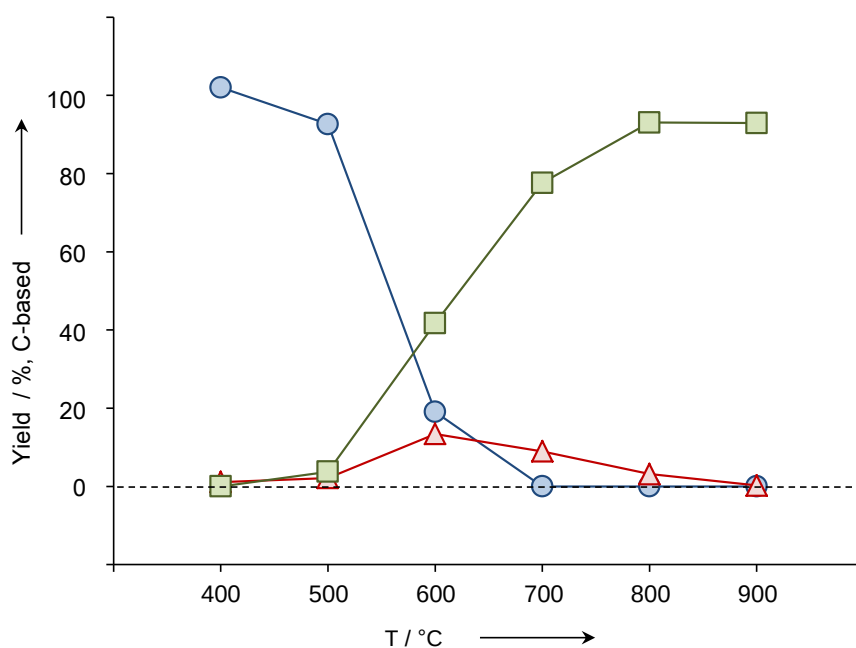


Figure 3-2. Recoveries (% , C-based) of levoglucosan (LG) and yields (% , C-based) of the condensable products and non-condensable gases during the pyrolysis of gaseous LG at 400 to 900 °C with residence times of 0.8 to 1.4 s under a N₂ flow of 400 mL min⁻¹. Legend: ●, recovery of LG; ▲, condensable products; ■, non-condensable gases.

3.3.1 Levoglucosan formation during cellulose gasification

In *Chapter 5*, cellulose in the evaporator of the two-stage tubular reactor (Figure 3-1) was pyrolyzed at 500 °C, and the evolved primary pyrolysis vapor was heated in the pyrolyzer. With this system, the yield of LG was measured first without heating the volatiles at the pyrolyzer. As a result, the LG yield from cellulose pyrolysis was high as 69.3 % (C-based), which confirms that LG is the major volatile intermediate during cellulose gasification in the present tubular reactor system. This situation did not change under 7 % O₂/N₂ flow (LG yield: 52.6 %, C-based). Thus, we continued to study vapor-phase degradation of LG to understand the roles of vapor-phase reactions during cellulose gasification.

3.3.2 Condensable products

The identities of the condensable products were determined from their ^1H NMR spectra by comparison with spectra of reference compounds. Examples of the spectra of the high- and low-bp fractions obtained from the pyrolysis of gaseous LG at 600 °C (residence time 1.1 s) are shown in Figure 3-3a and b, respectively. An enlarged spectrum of the low-bp fraction with the identification of the signals is presented in Figure 3-4a along with the spectrum obtained from the pyrolysis of molten LG under nitrogen at 350 °C over 5 min for comparison.

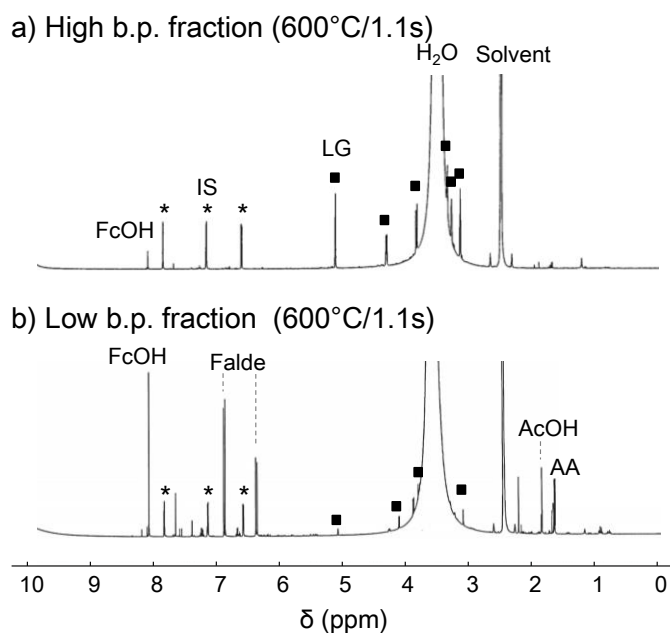
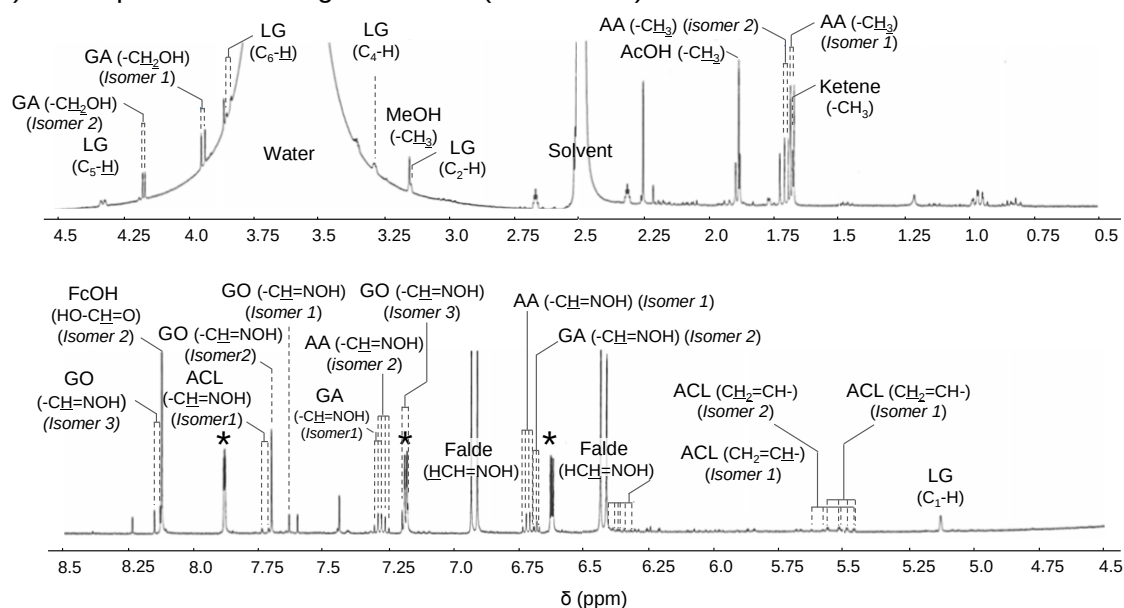


Figure 3-3. ^1H NMR spectra of a) high and b) low bp condensable fractions obtained from the pyrolysis of gaseous levoglucosan at 600 °C with a residence time of 1.1 s under a N_2 flow of 400 mL min^{-1} . Legend: FcOH, formic acid; Falde, formaldehyde; LG, levoglucosan; AcOH, acetic acid; AA, acetaldehyde; ■, signals assigned to LG.

a) Low b.p. fraction from gaseous LG (600°C/1.1s)



b) Tar fraction from pyrolysis of molten LG (350°C/5min)

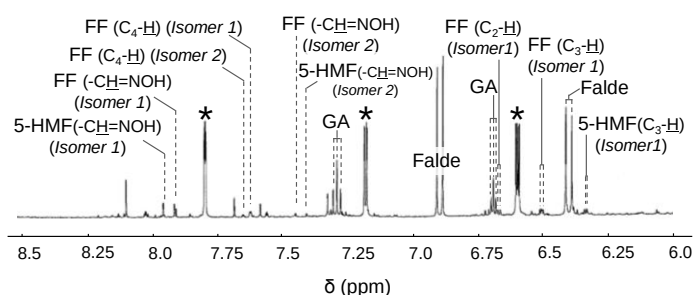


Figure 3-4. Signal assignments for the ^1H NMR spectrum of (a) the low boiling point fraction obtained from the pyrolysis of gaseous levoglucosan (LG) at 600 °C with a residence time of 1.1 s under a N_2 flow of 400 mL min^{-1} and (b) the pyrolysis products from molten LG at 350 °C over 5 min. Legend: AA, acetaldehyde; ACL, acrolein; ACT, acetone; AcOH, acetic acid; Falde, formaldehyde; FcOH, formic acid; FF, furfural; 5-HMF, 5-hydroxymethylfurfural; GA, glycolaldehyde; GO, glyoxal; HA, hydroxyacetone; MeGO, methyl glyoxal; MeGO (mono), methyl glyoxal mono oximated.; * signals assigned to 2-furoic acid (internal standard).

No high-molecular-mass refractory tars were detected, although some reports (Evans and Milne, 1987; Norinaga et al., 2013) indicate the formation of such compounds during the gas-phase secondary reactions of cellulose pyrolysis. The high-bp fractions obtained at all temperatures applied in this study were completely soluble in water and did not include any products with higher molecular masses than LG, as determined by GPC analysis. Peaks in the NMR spectrum (Figure 3-3a) were also assigned to LG and lower-molecularmass products, such as formic acid, all of which were also observed in the low-bp fraction. No polymerization products of LG were detected even after condensation on the walls of the cooling line. This is attributed to the nitrogen flow applied in these experiments, which was able to transport the LG to surfaces with temperatures lower than the LG polymerization temperature of 250 °C.

As indicated from the assignments of the NMR signals in Figure 3-4a, the low-bp fractions were found to include C1–C3 fragmentation products, such as aldehydes (formaldehyde, acetaldehyde, glycolaldehyde, glyoxal, methylglyoxal, and acrolein), ketones (hydroxyacetone and acetone), acids (formic acid and acetic acid), alcohol (methanol), and ketene. The yields (% C-based) of the condensable products are shown in Figure 3-5 as a function of the temperature of the pyrolyzer. Methanol, formaldehyde (oxime), and acetone (oxime) etc., which have relatively low boiling points, tended to evaporate from the gas wash bottle, and this may have led to the underestimation of the yields of these products in this system. Products with more than four carbon atoms (C4) were not detected at all. The C3 products methylglyoxal, acrolein, hydroxyacetone, and acetone were identified, although their yields were relatively low compared with those of the C1 and C2 products. Thus, C1 and C2 aldehydes/ acids accounted for the majority of the condensable products.

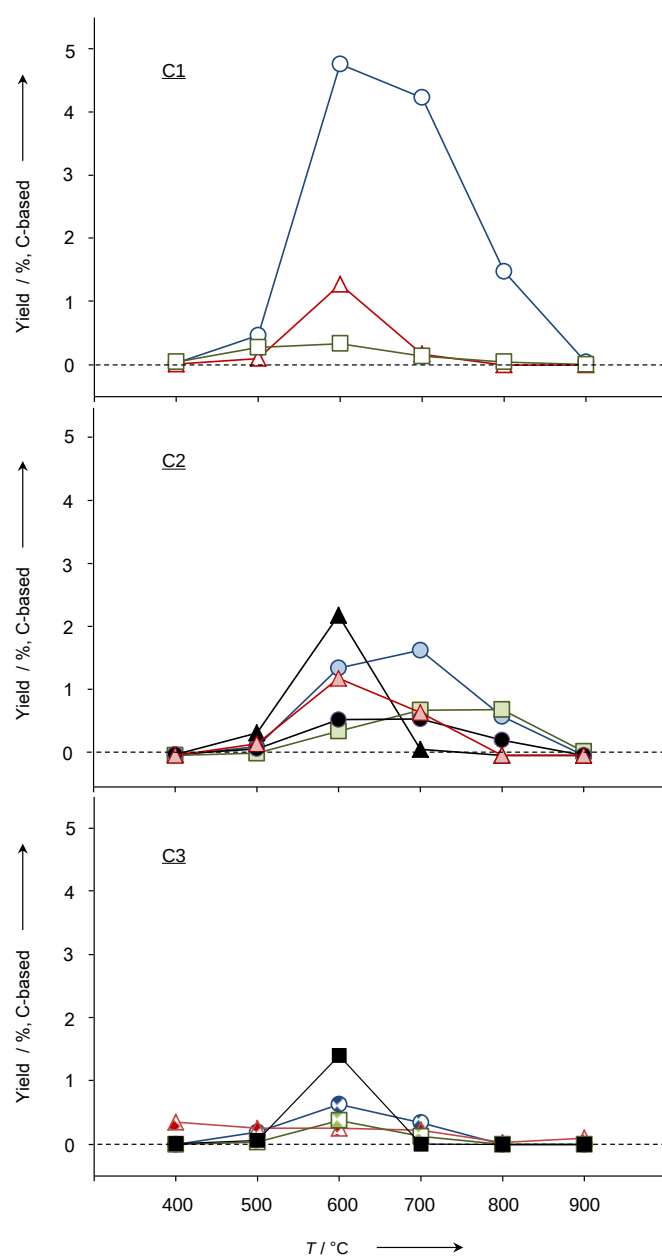


Figure 3-5. Yields (% , C-based) of the condensable products obtained from the pyrolysis of gaseous levoglucosan at 400 to 900 °C with residence times of 0.8–1.4 s under a N₂ flow of 400 mL min⁻¹. Legend: ○, formaldehyde; △, formic acid; □, methanol; ▲, glyoxal; ●, acetaldehyde; △, glycolaldehyde; ■, ketene; ●, acetic acid; ○, acrolein; △, acetone; ■, hydroxyacetone; ■, methylglyoxal.

The compositions of the condensable products varied depending on the temperature of the pyrolyzer. The yields of formic acid, glyoxal, and methylglyoxal reached their maximum values at 600 °C and then decreased sharply at 700 °C. This pronounced temperature dependence likely arises from the lability of these products at 700 °C. Formic acid is known to decompose into CO₂, H₂, CO, and H₂O as low as 250 °C, (Nelson and Engelder, 1925; Saito, Kakumoto, Kuroda, et al., 1984; Tokmakov et al., 1997; Akiya and Savage, 1998; Wang et al., 2000; Fukutome et al., 2014) whereas glyoxal is reported to decompose into formaldehyde and CO at 450 °C (Steacie et al., 1935; Saito, Kakumoto, and Murakami, 1984). Accordingly, the formation of formic acid, glyoxal, and methylglyoxal from gaseous LG are likely to be the rate-determining steps for the conversion of LG into noncondensable gases at temperatures higher than 700 °C.

In contrast, acetaldehyde and ketene exhibited peak yields at higher temperatures of 700 and 800 °C, respectively. As LG disappeared completely at 700 °C, these products appear to have been formed through secondary reactions of the intermediates generated by gaseous LG. Ketene is reported to form from acetic acid (Bamford and Dewar, 1949; Blake and Jackson, 1968) during pyrolysis, and this is supported by the trends of the yields of acetic acid and ketene in Figure 3-5. Although details of these reaction pathways are not known, Asmadi et al. (2010) have reported that the formation of acetaldehyde from wood samples was delayed during pyrolysis at 600 °C.

A kind of dehydration reaction, which leads to the formation of furfural, 5-HMF, and coke, is known to proceed during the pyrolysis of molten LG. Several signals assigned to furfural and 5-HMF were clearly observed in the NMR spectrum that results from the pyrolysis of molten LG (Figure 3-4b) along with the formation of coke and polymerization products. Interestingly, no signals assigned to furans were observed in the spectra that resulted from gaseous LG (Figures 3-3 and 3-4a).

Accordingly, by maintaining the LG strictly in the gas phase, the fragmentation reactions were promoted selectively rather than the polymerization (transglycosylation)

and dehydration reactions. These results suggest that the transglycosylation and dehydration reactions are characteristic of the molten-phase pyrolysis of LG and other carbohydrates. Molecular mechanisms associated with the molten- and gas-phase pyrolysis reactions are discussed later in terms of the hydrogen bonding formed in the molten state.

Table 3-1. Proportions (mol %) of non-condensable gases obtained from the pyrolysis of gaseous levoglucosan at 500 to 900 °C with residence times of 0.80 to 1.2 s under a N₂ flow of 400 mL min⁻¹

	Pyrolysis temperature (°C)				
	500	600	700	800	900
H ₂	5.3	17.0	20.5	21.8	25.1
Oxygenated gas	90.3	70.3	66.1	54.5	65.4
CO	63.8	64.1	59.5	56.9	56.9
CO ₂	26.5	6.2	6.6	7.6	8.5
Hydrocarbon gas	4.3	12.6	13.4	13.6	9.6
CH ₄	2.4	2.6	3.7	4.1	3.5
C ₂ H ₆	0.0	0.6	1.2	1.2	0.1
C ₃ H ₈	0.0	0.1	0.0	0.0	0.0
C ₂ H ₄	1.0	5.8	5.9	5.7	2.9
C ₃ H ₆	0.0	0.7	0.4	0.1	0.0
C ₃ H ₄	0.9	2.8	2.2	2.5	3.1

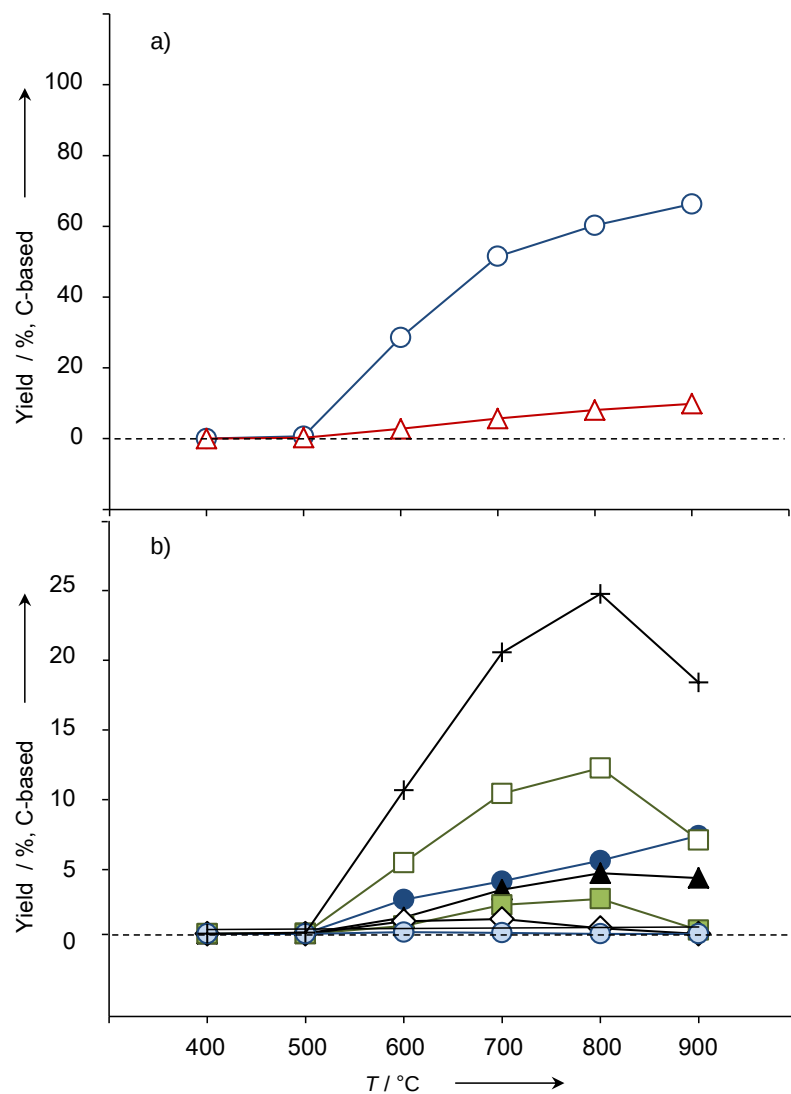


Figure 3-6. Yields (% C-based) of (a) oxygenated and (b) hydrocarbon gases obtained from the pyrolysis of gaseous levoglucosan at 400 to 900 °C with residence times of 0.8 to 1.4 s under a N₂ flow of 400 mL min⁻¹. Legend: ○, CO; △, CO₂; +, hydrocarbon gases (total); □, C₂H₄; ●, C₂H₂; ▲, CH₄; ■, C₂H₆; ◇, C₃H₆; ●, C₃H₈.

The results of the present study also provide insights into the pyrolytic formation of several products from LG and cellulose. Hydroxyacetone, which is a typical product of the pyrolysis of molten LG, (Shafizad.F and Lai, 1972; Hosoya et al., 2008a) was generated in only minimal quantities from the gaseous LG, and hence this compound is formed selectively in the molten-phase reactions of LG. Some researchers (Piskorz et al., 1986; Richards, 1987) have proposed the competitive formation of glycolaldehyde and LG during the primary pyrolysis stage of cellulose.

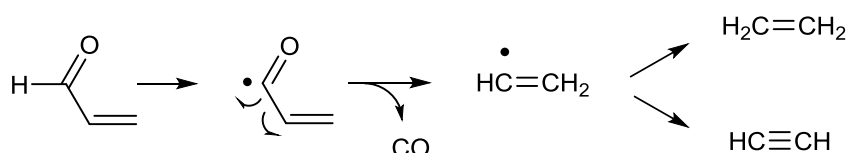
However, the present study observed the formation of glycolaldehyde from the gas-phase pyrolysis of LG clearly, which indicates that at least a secondary reaction pathway exists for the formation of glycolaldehyde from cellulose. The major components of the noncondensable gases were determined to be CO, H₂, CO₂, ethylene, acetylene, and methane and ethane, propane, and propylene were minor components.

Yields (C-based%) and compositions (mol%) of these gases as a function of the temperature of the pyrolyzer are shown in Figure 3-6 and Table 3-1, respectively. These gases may be categorized as oxygenated or hydrocarbon gases and H₂. The hydrocarbon gas concentrations were normally low, in the range of 2.7–14.3 mol %, which reached a maximum at 800 °C, whereas the oxygenated gases and H₂ accounted for 65.5–92.5 and 4.8–21.1 mol%, respectively.

The production of the noncondensable gases started at 500 °C, which was also observed in the case of the condensable products, although the yield at that point was only 2.7 %. The oxygenated gases (CO and CO₂) were predominant (92.5 mol%) at 500 °C. The proportion of these oxygenated compounds, however, decreased to 73.7 mol% at 600 °C as the concentrations of products other than CO₂ were increased significantly on raising the temperature from 500 to 600 °C. This observation is consistent with literature reports (Simmons and Gentry, 1986; Bilbao et al., 1995; Li et al., 2001; Hosoya et al., 2008b; Shen et al., 2010) that CO₂ is formed preferentially at relatively low pyrolysis temperatures. In the temperature range of 600–800 °C, the gas compositions did not change greatly, even though the gas yield increased significantly. These results indicate that similar gas formation mechanisms are involved in this

temperature range. At 900 °C, the hydrocarbon gas content decreased, which will be discussed later.

Saturated hydrocarbon gases with more than three carbon atoms were almost negligible at all temperatures in this study. Methane (0.4–5.1 mol%) and ethane (0–1.1 mol%) were found, but the effect of the pyrolysis temperature was different in both cases. Methane was usually observed as the major saturated hydrocarbon gas even at the lowest temperature of 500 °C, whereas ethane started to form at 600 °C (0.6 mol%) and its proportion increased to 1.1 mol% at 700 and 800 °C with a sharp decrease to 0.1 mol% at 900 °C.



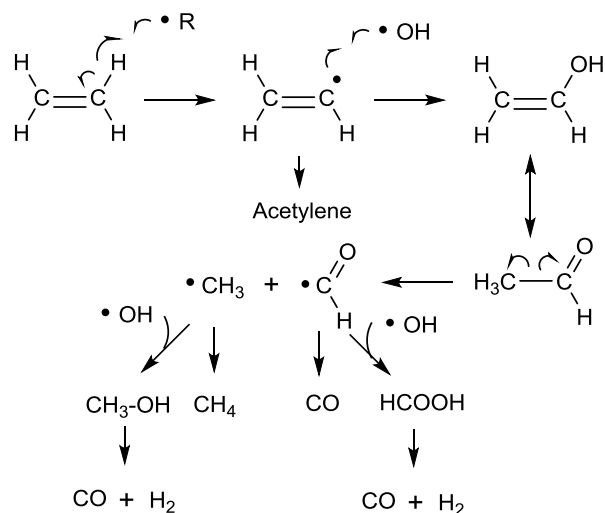
Scheme 3-2. Pathways for the formation of ethylene and acetylene from acrolein.

These results could be explained if we suppose that methane forms over the course of the fragmentation reactions of gaseous LG via the methyl radical. The formation of methane from acetic acid is a well-known reaction in pyrolysis (Bamford and Dewar, 1949; Blake and Jackson, 1968; Mackie and Doolan, 1984; Leplat and Vandooren, 2012). Conversely, the formation of ethane would involve a pathway that includes hydrogen addition to ethylene with the coupling of two methyl radicals, and ethylene was produced even at the lowest temperature of 500 °C. The α -scission reaction of the acrolein radical forms the vinyl radical, which is further converted into ethylene (Stein et al., 1983) and acetylene by hydrogen abstraction and β -scission reactions, respectively (Scheme 3-2). The hydrogen radical concentration would be

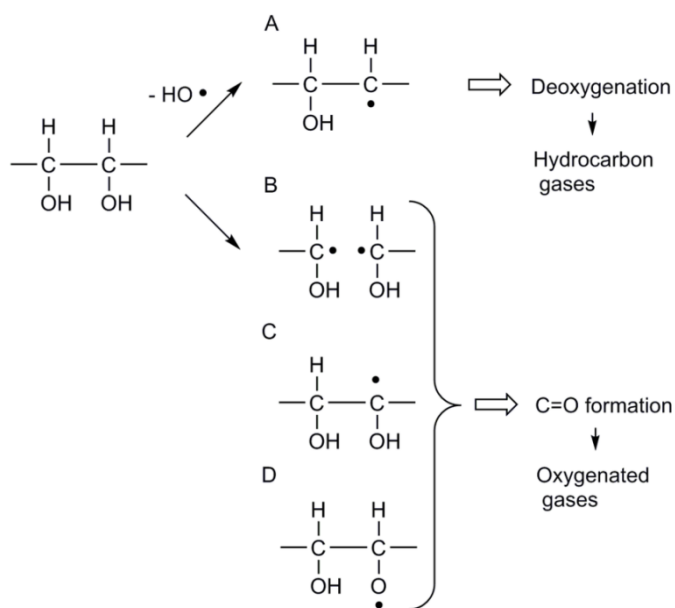
increased if the temperature is increased from 500 to 600 °C, as indicated by the trend of the yield of H₂, and this could enhance the formation of ethane. The sharp decrease in the ethane concentration at 900 °C results from the instability of the C–C bond if subjected to homolysis to generate methane via the resulting methyl radicals. Methane, which has only strong C–H bonds, is more stable than ethane.

Unsaturated hydrocarbons, the C=C and C–H bonds of which are resistant to homolysis and hydrogen abstraction reactions, respectively, represented the remaining hydrocarbon gases (ethylene: 1.4–5.8 mol%, acetylene: 0.9–2.9 mol%). The ethylene and acetylene yields attained their maximum values at 700 °C (5.8%, C-based) and 900 °C (2.9 %, C-based), respectively. Similar levels of ethylene have also been reported to form during the fast pyrolysis of cellulose at 850 °C with a short residence time of 0.3 s (Graham et al., 1984).

If the temperature was increased from 800 to 900 °C the ethylene content decreased from 5.1 to 3.5 mol%. Together with the decrease in the ethane content, this contributed to the decrease in the hydrocarbon gas content from 13.9 (800 °C) to 10.5 mol% (900 °C). Alternatively, the levels of oxygenated gases, H₂, and acetylene increased in this temperature range. Accordingly, ethylene was evidently converted into these gases at 900 °C. This is also supported by the O-based yields of the products, which increased from 92.6% at 800 °C to approximately 100% at 900 °C. This change would involve the oxidation of ethylene (Scheme 3-3). At the higher temperature, the hydrogen abstraction reaction of C–H bonds occurs to only a minor degree, and vinyl hydrogen atoms would be abstracted by radical species to form vinyl radicals, which possibly lead to the formation of more labile oxygenated intermediates by coupling with oxygen-centered radicals such as COH. These reactions promote the formation of oxygenated gases and H₂. Acetylene is also formed from these vinyl radical intermediates.

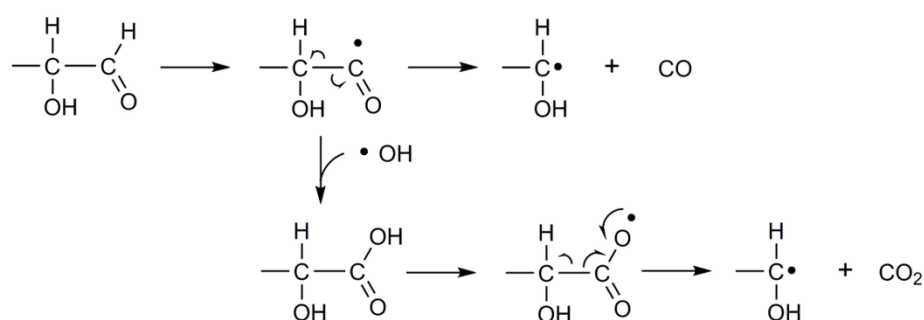


Scheme 3-3. Possible reactions during the conversion of ethylene to acetylene, oxygenated gases and hydrogen at 900 °C.



Scheme 3-4. Formation of intermediate radicals through the homolysis and abstraction of hydrogen atoms responsible for selectivity between hydrocarbon and oxygenated gases from gaseous levoglucosan.

Details of the decomposition mechanisms of gaseous LG is presented in *Chapter 4* but we suggest here that homolysis along with several radical chain reactions can explain the fragmentation reactions that eventually result in the formation of the noncondensable gases. With this mechanism in mind, the preferential formation of oxygenated gases over hydrocarbon gases can be understood based on the initial reactions presented in Scheme 3-4.



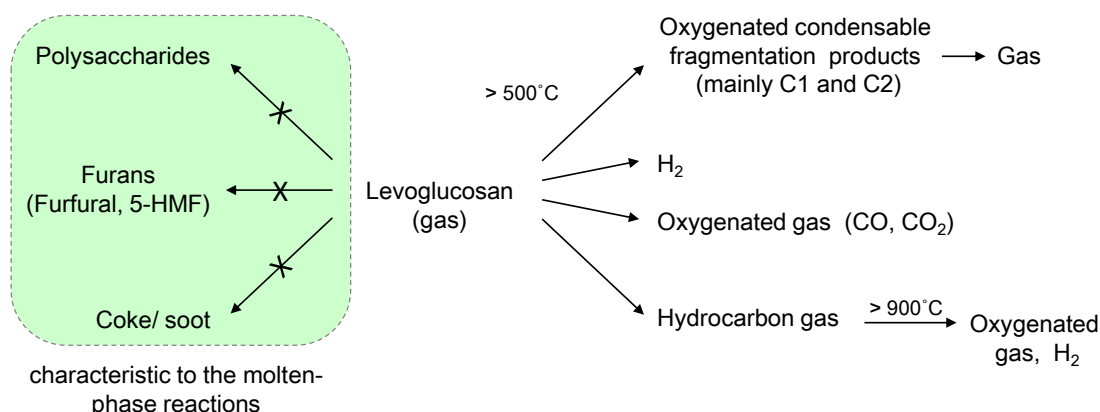
Scheme 3-5. Possible pathways from aldehydes to CO and CO₂.

The production of hydrocarbon gases from LG requires a deoxygenation step. Direct homolysis of the C–O bonds forms radical A, which subsequently generates an olefinic structure by the elimination of the OH group through a β -scission reaction. However, the bond dissociation energies of C–OH bonds are normally higher than those of the corresponding C–C bonds, and hence the formation of radical B is preferred during the homolysis process. Additionally, radicals C and D can form by the hydrogen abstraction reactions of the C–H and O–H moieties, respectively. Radicals B, C, and D result in the formation of aldehydes and ketones that are further converted into CO and CO₂. The aldehydes in particular are expected to be converted into CO and CO₂ via the aldehyde radicals shown in Scheme 3-5.

3.3.3 Molecular mechanisms that govern the gas- and molten phase reactions

Gaseous LG generated only fragmentation products and, eventually, noncondensable gases at temperatures above 500 °C (Scheme 3-6). Interestingly, the dehydration reactions that lead to the formation of furans and coke/soot were not observed during the gas-phase pyrolysis of LG, and hence these reactions are believed to be unique to the molten-phase pyrolysis, along with the transglycosylation reactions. As the carbonaceous products consist primarily of benzene-ring compounds, coke and soot formation can be considered as a kind of aromatization process to form benzene rings. An interesting proposal has been made for the formation mechanism of carbonaceous products based on benzene rings (Pastorova et al., 1994; Zhang et al., 2002; Titirici et al., 2008; Baccile et al., 2009; C. Falco et al., 2011) that includes the polymerization of furan precursors followed by rearrangement from furan to benzene rings. This indicates that the furan formation and the coke/soot formation shown in Scheme 3-6 are closely related to each other in terms of the aromatization reactions that form furan and benzene rings through dehydration reactions.

The resistance of gaseous LG to pyrolytic decomposition up to 500 °C indicates strongly that the activation mechanisms only occur during molten-phase pyrolysis as the molten-phase reactions of LG normally occur at 250 °C. Kawamoto and coworkers have proposed a hydrogen bond theory, for the activation mechanisms of molten-state carbohydrates, which include LG, based on the unexpected stability observed in proton acceptor solvents such as aromatics (Hosoya et al., 2006; Kawamoto et al., 2014) and polyethers (Matsuoka et al., 2012; Kawamoto et al., 2013; Kawamoto et al., 2014). In this theory, intermolecular hydrogen bonding between carbohydrate molecules mimics the actions of acid and base catalysts at elevated temperatures. With this form of acid catalysis, dehydration and transglycosylation reactions can proceed at lower temperatures in molten carbohydrates. The stability of gaseous LG is explained by this theory as the occurrence of such activation mechanisms through intermolecular hydrogen bonding is not expected in the case of gaseous LG.



Scheme 3-6. Summary of the pyrolytic conversion of gaseous levoglucosan.

3.3.4 Roles of gas- and liquid-phase reactions in cellulose gasification

The nature of the gas-phase reactivity of LG provides insight into the gasification mechanism of cellulose in terms of the effects of phase transition (Figure 3-7). Cellulose gasification occurs in a sequential three-stage process that involves a primary molten-phase pyrolysis stage followed by gas- and molten-phase secondary reactions.

Depolymerization and other pyrolysis reactions occur in the molten phase formed at the surface of cellulose crystallites in the temperature range of 300–450 °C (Boutin et al., 1998; Boutin et al., 2002; Matsuoka et al., 2014; Shoji et al., 2014). Some of the resulting low-molecular-weight products, which include LG, evaporate into the gas phase, whereas the others are repolymerized and eventually converted into carbonaceous material (char) through dehydration reactions. The coke-forming behavior of cellulose is discussed below based on the reactivity of LG as the major volatile product and changes brought about by the phase transition from the gas to molten phase.

As shown in the photographic image of the reactor (Figure 3-7) after the pyrolysis of cellulose at 800 °C under nitrogen followed by tar-extraction (Hosoya et al.,

2007), large amounts of coke were formed in the molten-phase secondary reactions. This coke formation is attributed to the change in reactivity caused by the transition from the gas to molten phase, in which the dehydration and transglycosylation reactions become effective even at lower temperatures. In contrast, gaseous LG and decomposition products (primarily C1 and C2 fragmentation products) were gasified cleanly without the formation of tar or coke if the residence time was sufficient to complete the gasification.

Cellulose gasification also produced coke during the gas-phase secondary reactions stage, although to a lesser extent (Figure 3-7). In *Chapter 2* the authors identified furans (furfural and 5-HMF) as the potential precursors of this type of coke formation by studying the coke-forming reactivities of eight major volatile products of cellulose in closed ampoules at 600 °C. However, gaseous furans are reported to be stable up to approximately 800 °C (Grela et al., 1985; Grela and Colussi, 1986). These results suggest that this type of coke is produced by the volatile intermediates formed from the molten-phase reactions of furans during the primary pyrolysis stage of cellulose. These same intermediates are not produced by the gas-phase reactions of LG. For this reason, the gas-phase reactions of LG are also clean in terms of the lack of coking in the gas phase.

In the gasification of lignocellulosic biomass, the reactions of gaseous LG are modified by the coexisting volatile intermediates formed from the other components such as lignin and hemicellulose. Hosoya et al., (2009b) proposed strong interactions between the volatile intermediates from cellulose and lignin by using a dual space ampoule reactor at 600 °C. Accordingly, further studies would be necessary to draw conclusions about the gas-phase reactions in lignocelluloses gasification.

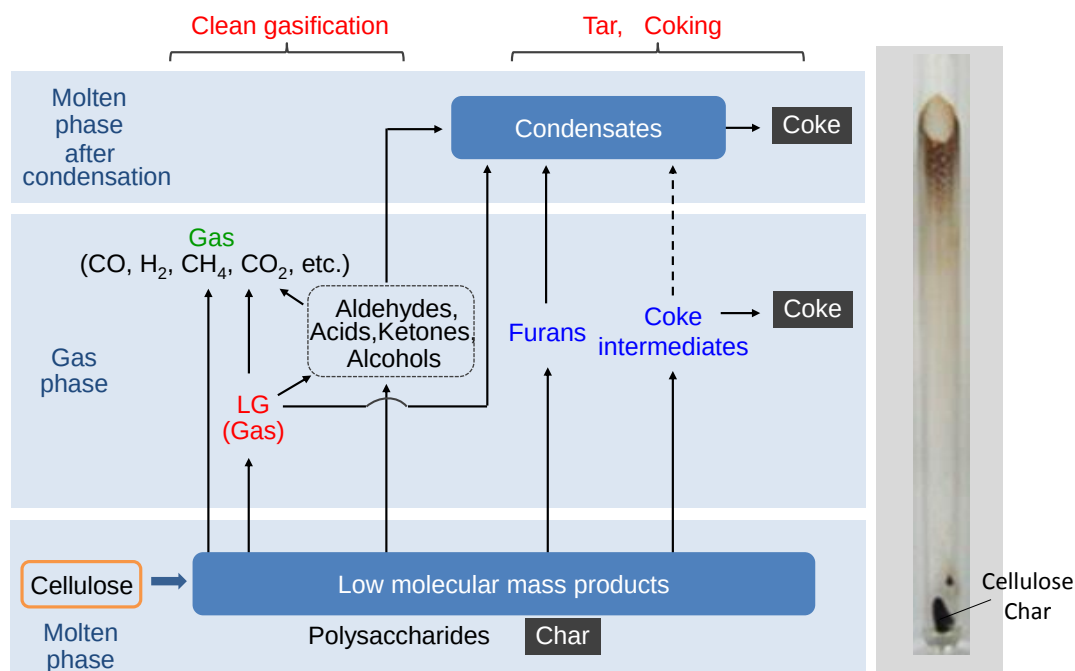


Figure 3-7. Proposed steps in the gas-phase reactions of levoglucosan (LG) along with the tar and coke formation mechanisms in cellulose gasification. Image: coke formation following cellulose pyrolysis in a glass tube with a temperature gradient from 800 °C (bottom) to room temperature (upper end of the tube) (Hosoya et al., 2007).

3.4 Summary

The gas-phase pyrolysis of LG was studied by using a two-stage tubular reactor during the evaporation of LG under a nitrogen flow at 400–900 °C with residence times of 0.8–1.4 s. The following results were obtained.

1. LG in the gas phase was much more stable during pyrolysis than in the molten state.
2. The stability of gaseous LG was explained by the associated lack of intermolecular hydrogen bonding that can mimic the effects of acid and base catalysts.
3. The gas-phase pyrolysis of LG generated fragmentation products selectively at temperatures above 500 °C. No dehydration products (furans and coke) or transglycosylation (polymerization) products were detected under these conditions. Thus, these products are believed to be unique to the pyrolysis of molten LG.
4. The coke-formation behavior of cellulose can be explained reasonably by considering the different reactivities of LG in the gas and molten phases. Substantial coke formation occurred upon cooling of the remaining LG to form the molten phase, in which intermolecular hydrogen bonding becomes effective and serves as an acid catalyst to promote transglycosylation and dehydration reactions even at low temperatures.
5. The gas-phase reactions of LG were found to contribute to tar- and coke-free gasification to produce cleaner gases. Conversely, molten-phase reactions result in tar and coke formation.
6. The precursors that react to form coke in the gas phase appear to originate from the molten phase reactions during cellulose pyrolysis.

Chapter 4

Molecular Mechanisms of Vapor-phase Degradation of Levoglucosan

4.1 Vapor-phase Reactions of Glyceraldehyde and 1,3-Dihydroxyacetone

4.1.1 Introduction

Biomass gasification is considered to be a key future technology for power generation with gas engines (or turbines) as it allows the production of synthetic petroleum and chemicals through the FT process. However, biomass gasification is not yet mature; the generation of tar, which can cause coking and clogging of gasifier piping, remains an important issue, as does the deactivation of the FT catalyst. Additionally, the high temperatures (800–1000 °C) applied during gasification to mitigate tar formation also reduce the energy efficiency of the process. Accordingly, the establishment of tar and coke-free gasification processes that can operate at lower temperatures is a necessary step before the mass commercialization of this process. As such, an understanding of the chemistry involved in biomass pyrolysis and gasification would be very helpful, as the intermediates formed through primary pyrolysis are further converted into gas and tar/coke.

In *Chapter 3*, we studied the pyrolysis behavior of levoglucosan (LG) as the major intermediate during the gasification of cellulosic biomass. Interestingly, the reactivities of this compound differed between gas and molten-phase pyrolysis (Hosoya et al., 2008a). In the molten phase, LG is converted into various polymerization

products along with coke and furans, as dehydration products, at temperatures as low as 250 °C. In contrast, LG is stable up to 500 °C in the gas phase. These different reactivities can be explained reasonably by the hydrogen-bonding theory, in which proton donation through intermolecular hydrogen bonding acts as an acid catalyst to promote the molten-phase reactions. Furthermore, as gaseous LG is converted selectively to noncondensable gases via C1/C2 fragments (primarily aldehydes) without the formation of coke, furans, or polymerization products, the condensation of these products followed by molten-phase reactions is suggested as the cause of coking in the pipeline from the gasifier (*Chapter 2*).

To better understand the associated reaction mechanism, we studied the kinetics of the thermal decomposition of gaseous LG in *Section 4.4*. Nonlinear relationships between $-\ln [\text{LG}]$ and residence time suggested a radical chain mechanism rather than processes with first-order kinetics. On the basis of reports of the radical chain reactions of carbohydrates with COH radicals at ambient temperature, C=O formation through hydrogen abstraction was considered as a possible initiation reaction.

Another point to consider is the product composition. As noted, there was only limited formation of large ($>\text{C}_3$) fragments during the pyrolysis of gaseous LG. The sole C3 products were acrolein, which has a stable C=C bond that resists homolysis, and smaller amounts of methylglyoxal and hydroxyacetone (*Chapter 3*). On the basis of these results, various extremely reactive intermediates, which go undetected, are apparently involved in the decomposition of gaseous LG (*Section 4.4*). These considerations lead to a hypothesis: the formation of C=O groups through hydrogen abstraction is the rate-determining step during the pyrolytic fragmentation of gaseous LG, and the resulting carbonyl intermediates would immediately decompose into C1 and C2 fragments. To examine the validity of this hypothesis, the pyrolytic reactivities of glyceraldehyde and 1,3-dihydroxyacetone (aldose and ketose), simple C3 models of decomposition intermediates with C=O groups from LG pyrolysis, were compared with that of glycerol. Several studies have used glycerol pyrolysis as a model for biomass pyrolysis (Stein et al., 1983; Nimlos et al., 2006; Paine Iii et al., 2007; Geng et al., 2012;

Ye et al., 2012). Stein et al. (1983) described the pyrolysis of gaseous glycerol under an argon/steam flow at 700 °C and explained the formation of acrolein and acetaldehyde by invoking radical chain mechanisms. Several theoretical studies (Nimlos et al., 2006; Geng et al., 2012; Ye et al., 2012) have also addressed the reaction parameters associated with some heterolysis reactions, including cyclic Grob fragmentation and dehydration, although it is still uncertain whether these heterolysis reactions actually occur during glycerol pyrolysis owing to the lack of systematic experimental studies.

In contrast, only a few experimental and theoretical studies of the pyrolysis of glyceraldehyde (Kabyemela et al., 1997; Paine Iii et al., 2008; Matsuoka et al., 2012; Wu et al., 2013; Honma and Inomata, 2014) and 1,3-dihydroxyacetone have been reported (Kabyemela et al., 1997; Paine Iii et al., 2008; Matsuoka et al., 2012). The flash pyrolysis of solid glyceraldehyde and 1,3-dihydroxyacetone dimer (Paine Iii et al., 2008), the pyrolysis of a polyether solution (Matsuoka et al., 2012), and degradation processes in hot-compressed water (Kabyemela et al., 1997; Liang et al., 2015) have all been studied experimentally, and a theoretical investigation was conducted for hot-compressed water (Honma and Inomata, 2014; Liang et al., 2015). Accordingly, the pyrolytic reactivities of gaseous glyceraldehyde and 1,3-dihydroxyacetone have not been compared systematically with that of glycerol.

In the present study, glycerol and glyceraldehyde/1,3-dihydroxyacetone were pyrolyzed in the gas phase at 400, 600, or 800 °C under a N₂ flow at residence times ranging from 0.9 to 1.4 s by using an experimental setup consisting of an evaporator and a pyrolyzer. The effects of C=O groups on the pyrolytic reactivity are discussed on a molecular basis according to the experimental data as well as theoretical calculations conducted at the MP4 (SDQ)/cc-pVTZ level.

4.1.2 Materials and methods

4.1.2.1 Materials

The reagents used for the pyrolysis trials were purchased from the following companies: D, L-glyceraldehyde oligomer and glycerol from Nacalai Tesque, Inc., Kyoto, Japan; 1,3-dihydroxyacetone dimer from Aldrich, Saint Louis, MO, USA. These chemicals were used as received without further purification.

4.1.2.2 Two-stage tubular reactor

The two-stage tubular reactor (Figure 3-1) was used and composed of two cylindrical electric furnaces (internal diameter: 35 mm, length: 160 mm, Asahi Rika Seisakusho Co., Ltd.), which served as the evaporator and pyrolyzer, 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 evaporator was attached to a nitrogen cylinder through a mass flow controller (Horiba SEC-400MK3), and the other end, from the pyrolyzer, was connected to a gas wash bottle through a glasswool 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 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.

4.1.2.3 Pyrolysis

In preparation for the pyrolysis trials, a sample (15 mg) contained in a ceramic boat was inserted into the middle of the evaporator. A nitrogen flow (400 mL min^{-1}) was supplied for 30 min before each pyrolysis reaction was conducted to sweep out the air inside the reactor. The pyrolyzer was preheated at a designated temperature (400, 600, or 800°C), and the evaporator temperature varied depending on the sample. For glycerol, the evaporator was heated to 120°C over 5 min, and this temperature was maintained for an additional 5 min. The evaporator was heated subsequently to 200°C at $16^\circ\text{C min}^{-1}$. The evaporator was held at 200°C for 5 min, heating was ceased, and

the tube reactor was cooled by opening the furnace covers and subsequently applying an air flow. During the evaporation of glyceraldehyde and 1,3-dihydroxyacetone, the evaporator was heated to 100 °C over 4 min and subsequently heated to 140 °C at 2.5 °C min⁻¹. The evaporator was held at 140 °C for 12 min, and heating was stopped. The nitrogen flow was maintained for an additional 2 min to sweep any residuals products into the gas wash bottle and gas bag.

The residence time of the pyrolyzer was defined as the period over which the gaseous substances were present in the region of the pyrolyzer with temperatures within 25 °C of the set value. The internal temperature profiles of the pyrolyzer and evaporator were obtained for each set temperature through direct measurement during preliminary control trials conducted without the addition of a sample. A constant nitrogen flow of 400 mL min⁻¹ was supplied during each experimental trial; hence, the residence time changed depending on the temperature of the pyrolyzer. The residence times at 400, 600, and 800 °C were 1.4, 1.2, and 0.9 s, respectively, which were close to the residence times estimated for actual biomass gasifications. The pressure inside the reactor was measured and was equal to the atmospheric pressure.

4.1.2.4 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 (2.0 mL), which contained an oximation reagent (NH₂OH • HCl), and the aldehydes and ketones were converted to the corresponding less volatile aldoximes or ketoximes (both cis and trans isomers). After each experimental trial, the condensates were washed from the internal wall with the DMSO-*d*₆ solution in the gas wash bottle. The resulting solution was analyzed directly by means of ¹H NMR spectroscopy using a Bruker AC-400 (400 MHz) spectrometer following the addition of 2-furoic 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.

With the exception of acetylene, noncondensable gases were analyzed using a micro GC instrument (Varian CP-4900) under the following chromatographic conditions: channel (1) column: MS5A (10 m); carrier gas: Ar; column temperature: 100 °C; column pressure: 170 kPa; detector: TCD; retention times (s): H₂ (26.4), N₂ (45.7), O₂ (35.4), CH₄ (60.6), and 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): CO₂ (19.9), C₂H₄ (23.5), C₂H₆ (26.3), C₃H₆ (57.4), and C₃H₈ (63.2). The quantification of acetylene was conducted using a Shimadzu GC-14B instrument under the following conditions: column: RESTEC, Rt@alumina BOND/N₂SO₄ (30 m, 0.53 mm O), carrier gas: He, column temperature: 60 °C (0–2 min), 40–200 °C (2–16 min, 10 °C min⁻¹), 200 °C (16–20 min); detector: flame ionization detector; retention time of acetylene: 4.3 min.

4.1.2.5 Computational methods

The calculations were conducted using the Gaussian 09 software package (Frisch et al., 2009). The geometry optimizations for all nonradical reactants, products, and TSs were performed by employing the DFT method (M06-2X) and 6-31+G(d,p) basis set. For radical products, UM06-2X/6-31+G(d,p) was employed. Vibrational frequency calculations used the same methods and basis set. The energies of the optimized geometries were calculated using the MP4(SDQ) method.

The CCSD(T) method for nonradicals and UCCSD(T) for radicals were used for single-point energy calculations to estimate the BDEs. The AUG-cc-pVTZ basis set was used for all energy calculations. The E_a values and BDEs were estimated as the relative energies, including zero-point energies, between the reactants and the TSs or radicals. Frequency analysis showed one imaginary mode for the TS and no imaginary modes for the reactants, products, and precomplexes. In addition, we performed intrinsic reaction coordinate (IRC) calculations to ascertain that the TS connected the reactant and product.

According to the a previous report (Lozynski et al., 1997; Callam et al., 2001; Pecul et al., 2002; Vogt et al., 2009) on conformation stability, the glyceraldehyde conformer with two intermolecular hydrogen bonds and the glycerol conformer with three intermolecular hydrogen bonds are the most stable. Accordingly, these conformers were used as the starting points in the present calculations. However, the conformation of the reactants obtained from the IRC calculations did not always coincide with the most stable conformers. In such cases, the conformer obtained from the IRC process was used for the reactant energy calculations, although the differences in the resulting E_a values were only a few kcal mol⁻¹.

4.1.3 Results and discussion

4.1.3.1 Vapor-formation characterization

Before the pyrolysis trials were conducted, the evaporation and vapor-formation characteristics of these compounds were evaluated with the pyrolyzer at room temperature. Glycerol contained in a ceramic boat was inserted into the evaporator (preheated to 200 °C) and was observed to evaporate completely and to be transported readily into the pyrolyzer in the gas flow. In contrast, only 37.1 wt% of the glyceraldehyde oligomer in the evaporator was converted into vapor at a lower evaporator temperature of 140 °C, and the unreacted oligomer remained in the evaporator. Originally, this lower evaporator temperature was employed because the glyceraldehyde oligomer tends to decompose to form a char at 200 °C. Even at 140 °C, the resulting vapor was a mixture of glyceraldehyde (61 %, C-based) and 1,3-dihydroxyacetone (36 %, C-based) on the basis of the analysis of the composition of the vapor components trapped as their oxime derivatives.

In the evaporator, the glyceraldehyde generated from the oligomer is evidently further reacted to give 1,3-dihydroxyacetone via an enol intermediate (keto–enol tautomerization), and this process could compete with the evaporation of the

glyceraldehyde.

However, the vapor obtained from the 1,3-dihydroxyacetone dimer (23.3 wt% yield) under similar conditions consisted exclusively of 1,3-dihydroxyacetone (97.2 wt%). Therefore, in the present study, the pyrolysis results obtained from a mixture of glyceraldehyde (61%) and 1,3-dihydroxyacetone (36%) [abbreviated to Gald–DHA (61/36)] were compared carefully with those from pure 1,3-dihydroxyacetone to understand the pyrolysis reactions of glyceraldehyde.

4.1.3.2 Reactivity

The experimental recoveries and yields (% C-based) of condensable and incondensable products from gaseous glycerol, Gald–DHA (61/36), and DHA at 400 (1.4), 600 (1.2) and 800 °C (0.9) are summarized in Figure 4-1 [the values in parentheses are residence times (s)]. The recoveries from the Gald–DHA and DHA pyrolysis processes presented herein are based on the amounts of vapor formed in the evaporator. The comparatively large amounts of unidentified products observed during the glycerol pyrolysis result from the difficulty in completely recovering glycerol and other low-molecular-weight alcohols (such as MeOH), because these alcohols are not derivatized by the oximation reagent.

Gaseous glycerol was stable at 400 °C and started to decompose at 600 °C (recovery: 38.7%) whereas 65.7% of the Gald–DHA (61/36) and 82.2% of the DHA decomposed into condensable products even at 400 °C. The recoveries of these two original compounds following pyrolysis at 600 °C were further reduced to an undetectable level and only 0.9 %, respectively. All of the compounds tested in this study generated noncondensable gases at 600 °C and were almost completely converted into noncondensable gas at 800 °C. From a comparison of the noncondensable gas yields at 600 °C [glycerol: 14.9 %, Gald–DHA (61/ 36): 52.8%, and DHA: 48.6 %, C-based], the gas-formation reactivities of Gald and DHA appear to exceed that of glycerol.

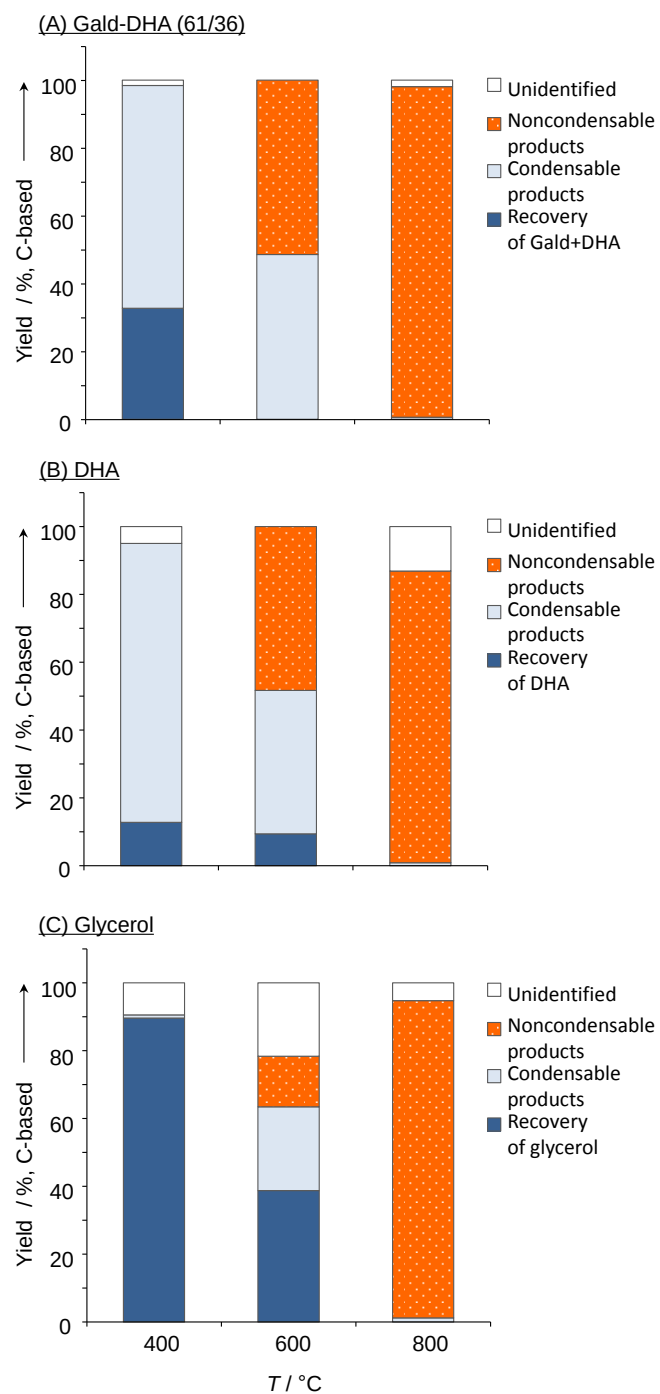


Figure 4-1. Recoveries (% , C-based) of glyceraldehyde (Gald), 1,3-dihydroxyacetone (DHA) and glycerol along with the yields (% , C-based) of condensable and noncondensable products from the pyrolysis of (A) Gald-DHA (61/36), (B) DHA and (C) glycerol at 400, 600 and 800 °C in the gas phase (residence times: 0.87–1.4 s, N₂ flow: 400 mL min⁻¹).

Accordingly, through the replacement of one C–OH group in the glycerol molecule with a C=O group, the pyrolytic reactivity in the gas phase increased dramatically at 400 and 600 °C. As described in our following paper, LG and glycerol exhibit similar reactivities.

4.1.3.3 Condensable products

The condensable products were determined from the ^1H NMR spectra of the DMSO- d_6 -soluble fractions by comparison with standard spectra. The ^1H NMR spectra obtained from the pyrolysis of Gald–DHA (61/36) at 400 and 600 °C and of glycerol at 600 °C are presented in Figure 4-2. The majority of the signals were assigned to the oxime derivatives (cis/trans isomers) of aldehydes and ketones, except for those of the unreacted glycerol and MeOH, allyl alcohol, and acetic acid. Although Wu et al. (2013) reported the formation of furanic (furfural, 5-HMF, and 5-methylfurfural) and aromatic (toluene) compounds along with char/coke from the flash pyrolysis of Gald at 500–900 °C, no NMR signals indicating the formation of these compounds were detected. Only C1–C3 products were identified from the gas-phase pyrolysis of Gald, DHA, and glycerol, and neither char nor coke was detected, although the molten-phase pyrolysis of the Gald oligomer and DHA dimer produced char/coke in the evaporator if the temperature was increased to 200 °C. Accordingly, these results confirm our previous theory for the gas-phase pyrolysis behavior of LG (*Chapter 3*): gas-phase reactions lead to clean gasification whereas coke and aromatic substances form during molten-phase pyrolysis.

The compositions (% C-based) of the condensable products obtained from Gald–DHA (61/36), DHA, and glycerol at 400, 600, and 800 °C are summarized in Figure 4-3. As described previously, the yields of the condensable products were minimal at 400 (0.9%) and 800 °C (1.2%) for glycerol, and C3 [acrolein (ACL), hydroxyacetone (HA), methylglyoxal (MeGO), and allyl alcohol], C2 [acetaldehyde (AA), glycolaldehyde (GA), acetic acid (AcOH), and glyoxal (GO)] and C1 products

[formaldehyde (FA), formic acid (FcOH), and MeOH] were identified in the total yield of 24.7% at 600 °C.

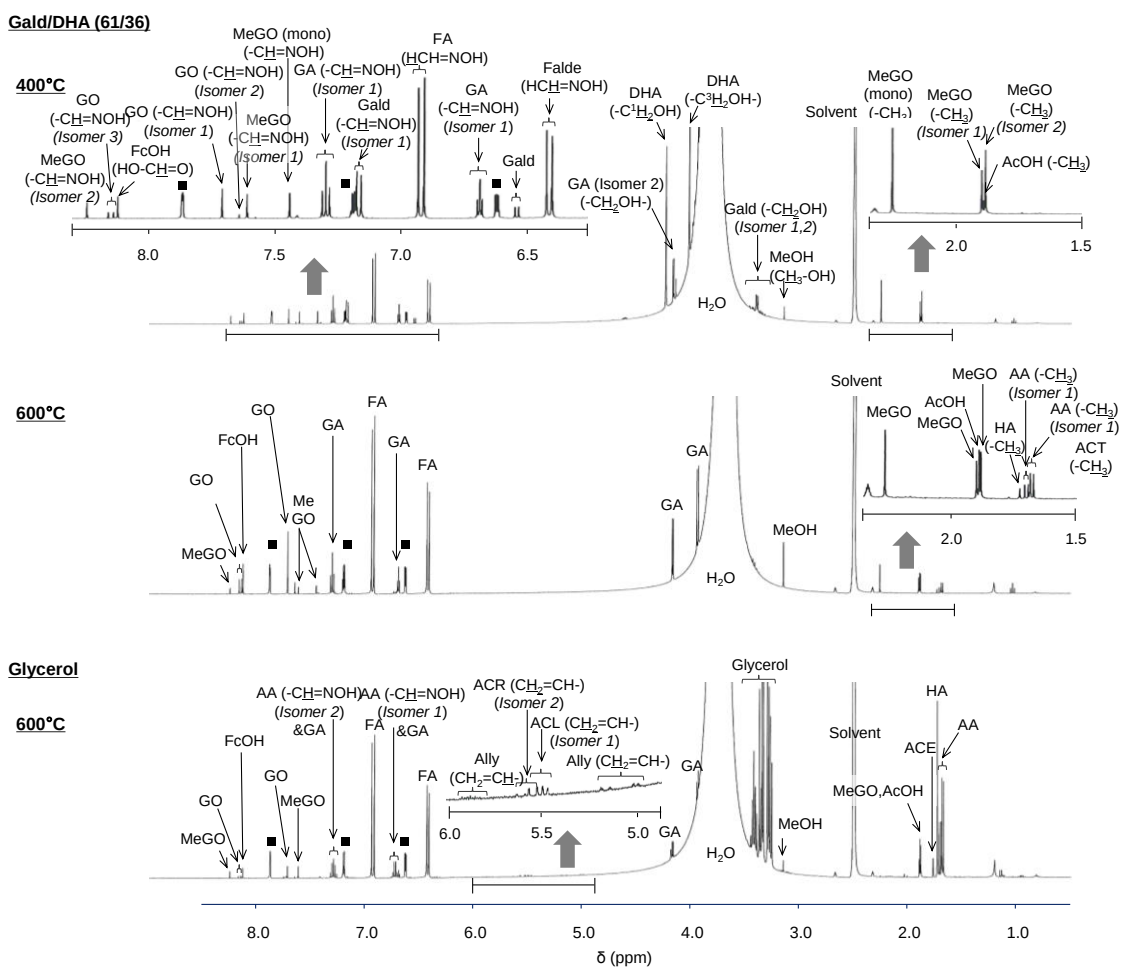


Figure 4-2. ^1H NMR spectra of the condensable products obtained from the pyrolysis of glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36) at 400 and 600 $^{\circ}\text{C}$ and glycerol at 600 $^{\circ}\text{C}$ in the gas phase (residence times: 0.87-1.4 s, N_2 flow: 400 mL min^{-1}). Legend: MeGO, methylglyoxal; HA, hydroxyacetone; ACE, acetone; GA, glycolaldehyde; GO, glyoxal; AA, acetaldehyde; AcOH, acetic acid; FcOH, formic acid; FA, formaldehyde; MeOH, methanol; ACR, acrolein; Ally, allyl alcohol

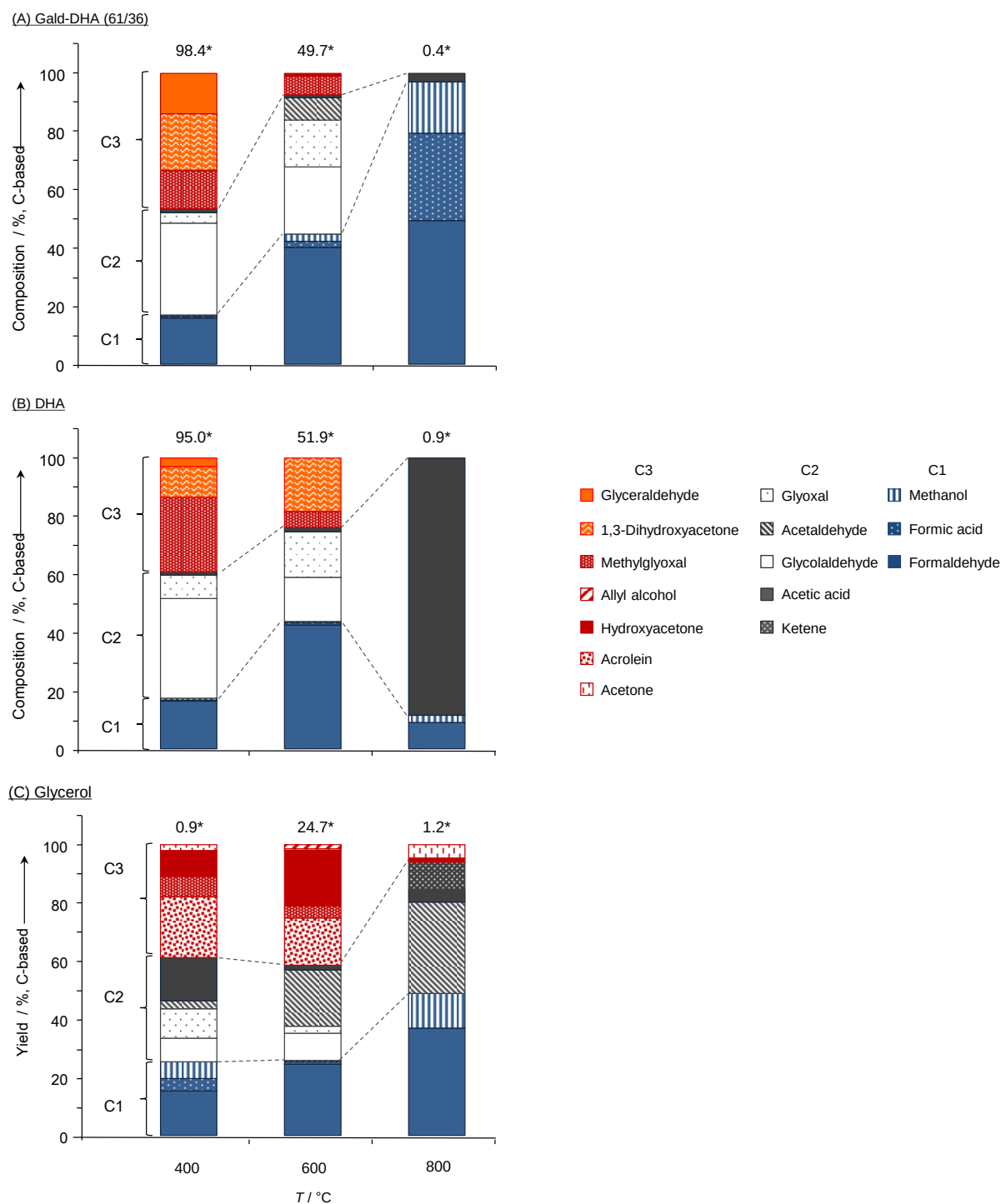


Figure 4-3. Concentrations (% , C-based) of the condensable products obtained from (A) glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36), (B) DHA and (C) glycerol at 400, 600 and 800 °C in the gas phase (residence times: 0.87-1.4 s, N₂ flow: 400 mL min⁻¹). *Yield (% , C-based) of the condensable product.

The product compositions obtained from the pyrolysis of Gald–DHA (61/36) and DHA were quite similar but very different from those of glycerol. At 400 °C, Gald–DHA (61/36) and DHA gave methyl glyoxal (MeGO), glycolaldehyde (GA), and formaldehyde (FA) quite selectively with much smaller amounts of GO, and the total yields reached 65.7 and 82.2 %, respectively. Consequently, the reactions to form these products must be enhanced by the replacement of one of the C–OH groups in the glycerol with a C=O group, as discussed below. It should also be noted that unsaturated compounds (that is, acrolein and allyl alcohol) were not produced in appreciable yields from Gald–DHA (61/36) and DHA, although the total yield of these compounds from glycerol reached 17.6% at 600 °C. This variation might be related to the different incondensable gas compositions, as discussed below. At the higher temperature of 600 °C, similar trends were observed, but the levels of GO and other minor components (AA, MeOH, and FcOH) increased.

4.1.3.4 Noncondensable products

The total yields (% C-based) and compositions (mol%) of the noncondensable products obtained from the pyrolysis of (A) Gald–DHA (61/36), (B) DHA, and (C) glycerol at 600 and 800 °C are shown in Figure 4-4. At 600 °C, glycerol produced H₂ (22.1%) and oxygenated gases [CO (56.3%) and CO₂ (4.5 %)] as the major gaseous products, and hydrocarbon gases [ethylene (9.0 %), methane (6.1 %), acetylene (0.9 %), ethane (0.8 %), and propylene (0.3 %)] were produced as minor components. An increase of the pyrolysis temperature from 600 to 800 °C increased the percentage of hydrocarbon gases slightly from 17.1 to 20.6 %, primarily because of the increase in the acetylene yield from 0.9 to 3.2 %. Acrolein, which was detected in 4.0% yield at 600 °C, was presumably converted into ethylene and acetylene at 800 °C (Stein et al., 1983).

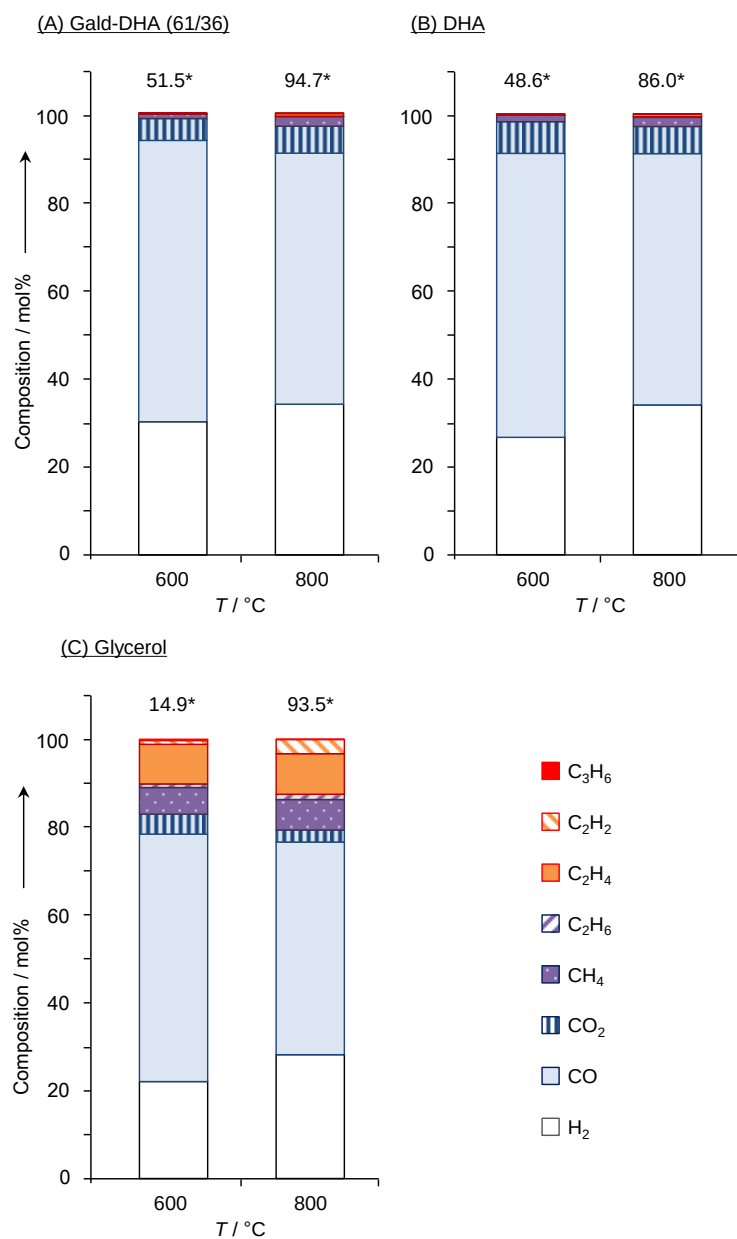


Figure 4-4. Concentrations (mol%) of the noncondensable products obtained from (A) glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36), (B) DHA and (C) glycerol at 400, 600 and 800 °C in the gas phase (residence times: 0.87-1.4 s, N_2 flow: 400 mL min^{-1}). *Yield (% C-based) of the noncondensable product.

Surprisingly, the Gald–DHA (61/36) and DHA generated only very limited levels of hydrocarbon gases of 1.3 and 1.8% (600 °C) and 3.0 and 3.0% (800 °C), respectively, with no remarkable differences between the two materials. The remainder of the gaseous products consisted of CO (56.8–65.7 %) and H₂ (27.1–34.2 %) with lower levels (5.3–6.1%) of CO₂. Thus, the introduction of C=O groups also altered the product-gas composition for these compounds. The product mixture of CO and H₂ is typically referred to as “syngas” and can be applied to the synthesis of petroleum and other chemicals; therefore, the gas-phase reactions of aldose/ketose would be applicable to syngas production. The lower yields of acrolein from the Gald and DHA as an intermediate during gas formation could be one reason for the lower levels of hydrocarbon gases.

4.1.3.5 Theoretical investigation and molecular mechanism

In the pyrolysis experiments, Gald–DHA (61/36) and DHA demonstrated very similar reactivities and gave GA, FA, and MeGO selectively at 400 °C. The GA and FA were formed at molar ratios of 1.0/1.0 [Gald–DHA (61/36)] and 1.0/1.0 (DHA), which strongly suggests the cleavage of C–C bonds in the Gald and DHA. Therefore, the bond dissociation energies (BDEs) of the C–C and C–O bonds of Gald and DHA were calculated by CCSD(T)/AUG-cc-pVTZ DFT at the (M06-2X)/6-31G+(d,p) level as a means of understanding the effects of the C=O group. As summarized in Figure 4-5, the BDEs of the C–C bonds located at the a and b positions relative to the C=O group of Gald decrease significantly from 83.5 to 77.1 kcal mol⁻¹ and from 84.5 to 73.1 kcal mol⁻¹, respectively, compared with those in glycerol. These lower BDEs result from the formation of stable formyl and C_α radicals, respectively. For the same reasons, the C–C bond in DHA also exhibits a slightly lower BDE of 81.9 kcal mol⁻¹. However, these BDEs are still too high to explain the homolytic cleavage of these bonds at a relatively low temperature of 400 °C.

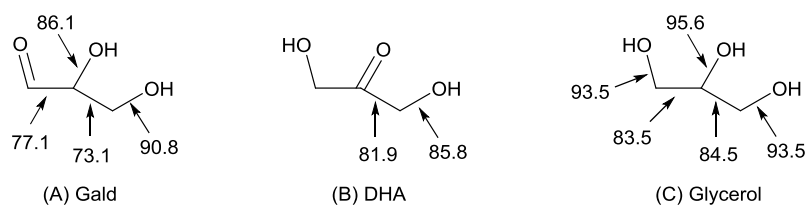


Figure 4-5. Bond dissociation energies (kcal mol^{-1}) of the C-C and C-OH bonds of (A) glyceraldehyde (Gald), (B) 1,3-dihydroxyacetone (DHA) and (C) glycerol as calculated from geometry optimization using DFT(M06-2X)/6-31+G(d,p) followed by energy calculations with CCSD(T)/AUG-cc-pVTZ.

With regard to the heterolysis (or concerted) mechanisms, the retro-aldol reaction reasonably explains the formation of GA and FA from Gald but not from DHA, as illustrated in Scheme 4-1A, on the basis of the E_a values calculated from the TS energy at the MP4(SDQ)/AUG-cc-pVTZ//DFT(M06-2X)/6-31+G(d,p) level. Owing to the stabilization effect of the cyclic transition state, the E_a of the retro-aldol reaction (A)-(a) was determined to be only $40.9 \text{ kcal mol}^{-1}$, a value that is $27.8 \text{ kcal mol}^{-1}$ lower than that ($68.7 \text{ kcal mol}^{-1}$) of the corresponding cyclic Grob fragmentation reaction (E)-(i) of glycerol. These kinetic parameters readily explain the experimental observations; AA and FA, both of which are the products of reaction (E)-(i), were generated from glycerol only at higher temperatures ($>600^\circ\text{C}$).

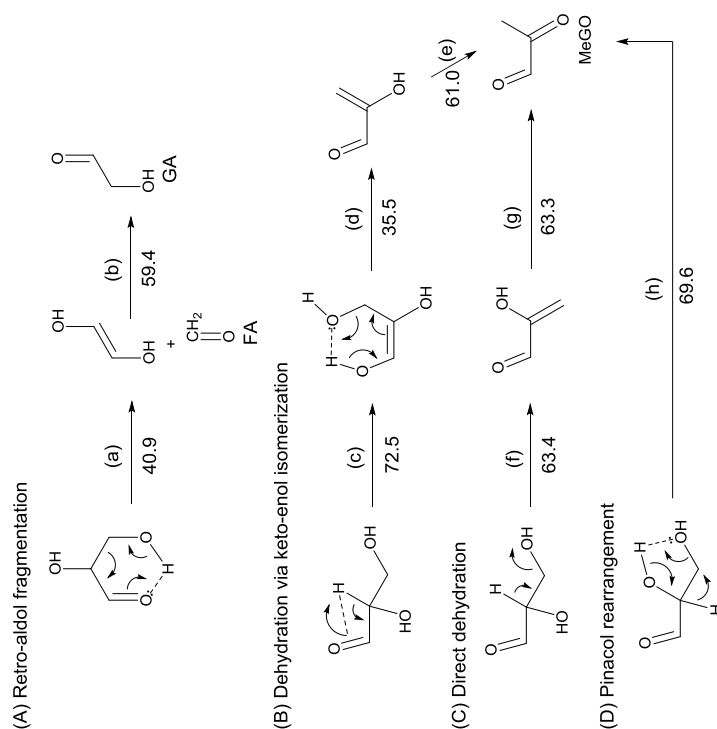
MeGO can be obtained from the cleavage of the $\text{C}_\beta\text{-OH}$ bond of Gald. However, the comparatively high BDE ($90.8 \text{ kcal mol}^{-1}$) calculated for this bond (Figure 4-6) also suggests that the homolysis pathway is not important at the relatively low temperature of 400°C . Alternatively, several heterotypic dehydration mechanisms were postulated for the formation of MeGO from Gald, including dehydration by keto-enol tautomerization (B), direct dehydration (C), and Pinacol rearrangement (D), as illustrated in Scheme 4-1. The E_a values calculated for the reactions involved in these pathways were compared with those of the corresponding reactions of glycerol [Scheme 4-1, Pathways (F) and (G)].

The direct dehydration reaction (C)-(f) eliminates C_{β} -OH and C_{α} -H and forms enol intermediates that undergo further tautomerization into MeGO through reaction (C)-(g) with an E_a of 61.0 kcal mol⁻¹. The E_a of the dehydration reaction (C)-(f) was calculated to be 63.4 kcal mol⁻¹, a value that is 13.2 kcal mol⁻¹ less than that (76.7 kcal mol⁻¹) for reaction (F)-(k) of glycerol. Thus, the dehydration reaction is enhanced substantially in the presence of a C=O group. On the contrary, the introduction of a C=O group does not affect the reactivity of the Pinacol rearrangement [reaction (D)-(h)], as the E_a (69.6 kcal mol⁻¹) for this reaction was quite similar to that (70.7 kcal mol⁻¹) of the corresponding reaction (G)-(m) of glycerol.

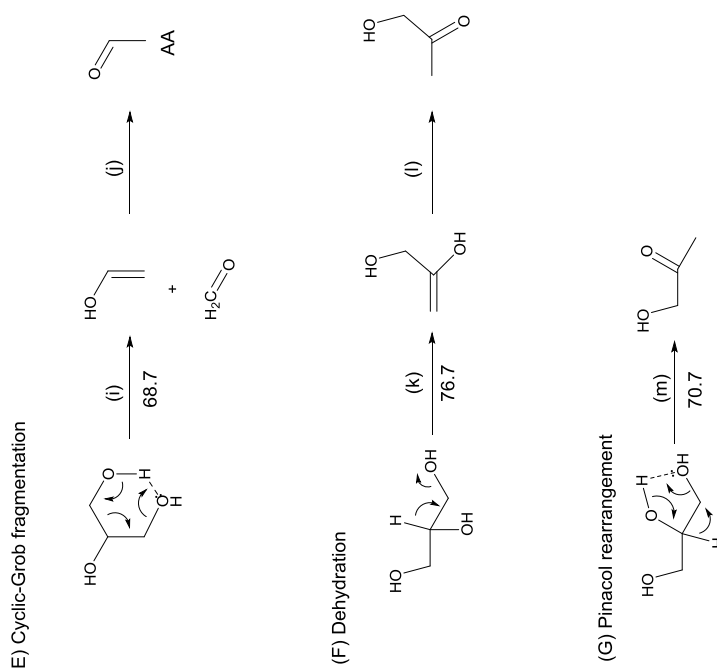
This difference is explained reasonably by considering the minimum-energy structures of the TSs of reactions (C)-(f) and (D)-(h) provided in Scheme 4-1 (Figure 4-6). During the direct dehydration, the $C_{C=O}$ - C_{α} and C_{α} - C_{β} bond lengths are reduced from 1.51 and 1.53 (reactant) to 1.44 and 1.45 Å (TS), respectively. These geometries suggest that the double-bond character of the C_{α} - C_{β} bond increases and a π -conjugated resonance structure is formed with the C=O group in the TS. This strong resonance stabilization effect reduces the energy of the TS associated with reaction (C)-(f) in Scheme 4-1. Conversely, in the TS of the Pinacol rearrangement (D)-(h), the decreased C_{α} -O and C_{α} - C_{β} bond lengths from 1.41 and 1.52 (reactant) to 1.29 and 1.44 Å (TS), respectively, indicate the carbonyl and C=C characters of these bonds, respectively, whereas no conjugated resonance is observed between the C_{α} -O and C=O groups.

In pathway (B) of Scheme 4-1, which proceeds through keto-enol tautomerization, dehydration reaction (B)-(d) with a cyclic TS was expected to proceed very effectively owing to the comparatively low E_a of 35.5 kcal mol⁻¹. Similar E_a values have also been reported by Nimlos et al. (2006) and Honma and Inohata (2014). However, the enolation step (B)-(c) has a relatively high E_a of 72.5 kcal mol⁻¹. Thus, enolation (B)-(c) is the rate-determining step in pathway (B) if it is assumed that the reactions are unimolecular.

Glyceraldehyde



Glycerol



Scheme 4-1. Concerted heterolysis mechanisms proposed for the fragmentation and dehydration of glyceraldehyde to give glycolaldehyde (GA)/formaldehyde (FA) and methylglyoxal (MeGO), respectively, along with the corresponding pathways for glycerol. The values attached to the reactions represent the activation energies (kcal mol^{-1}) obtained from the minimum energies of the transition states, as calculated at the MP4(SDQ)//DFT(M06-2X) level.

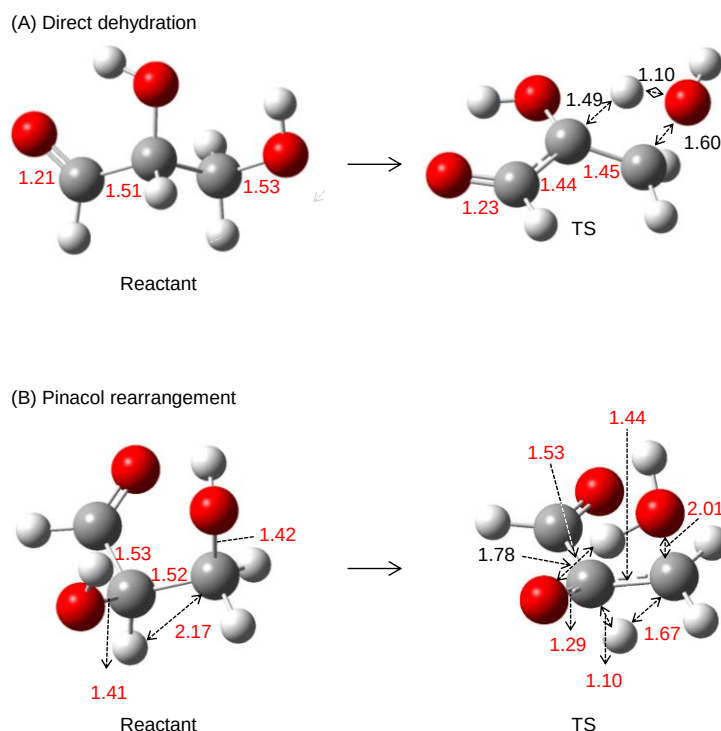


Figure 4-6. Minimum energy structures obtained for the reactants and transition states (TSs) of (A) direct dehydration and (B) Pinacol rearrangement of glyceraldehyde. Values in the structures indicate the distances (Å) between two designated atoms.

Consequently, the direct dehydration pathway (C) in Scheme 4-1 appears to be the most probable route for the formation of MeGO from Gald, as summarized in Figure 4-7. However, the E_a ($63.4 \text{ kcal mol}^{-1}$) of reaction (C)-(f) is still too high to explain why this step proceeds as a competitive reaction to the retro-aldol reaction (A)-(a) at 400°C ($E_a=40.9 \text{ kcal mol}^{-1}$). In addition, as discussed above, it is not possible to construct reasonable reaction pathways from DHA for the formation of MeGO as well as GA/FA. On the basis of these considerations, we propose bimolecular reactions for the keto–enol tautomerization of gaseous Gald and DHA (Figure 4-8). As shown in Scheme 4-2, DHA could form MeGO along with GA/FA via enol and Gald intermediates, respectively, if the keto–enol tautomerization can occur in the gas phase. Our previous investigations of gas formation from various cellulose-derived tar

components indicate that GA/FA will generate syngas ($\text{CO}+\text{H}_2$) selectively whereas MeGO, which has a methyl group, will also produce methane (*Chapter 2*).

The reaction coordinates obtained from the theoretical calculations of the bimolecular tautomerizations of Gald–Gald and DHA–DHA are shown in Figure 4-9. The six-membered cyclic TSs reduce the energy barriers significantly from 72.5 to 46.4 kcal mol^{-1} for Gald–Gald and 69.3 to 48.7 kcal mol^{-1} for DHA–DHA. These E_a values for the bimolecular reactions explain the concurrent formation of MeGO and GA/FA, even from DHA. The higher MeGO/ (GA/FA) ratio of 0.51 (C-based, 400 °C) obtained from the pyrolysis of DHA compared with that (0.27) generated by Gald–DHA (61/36) (Figure 4-3) is also explained reasonably by the preferential formation of MeGO from DHA.

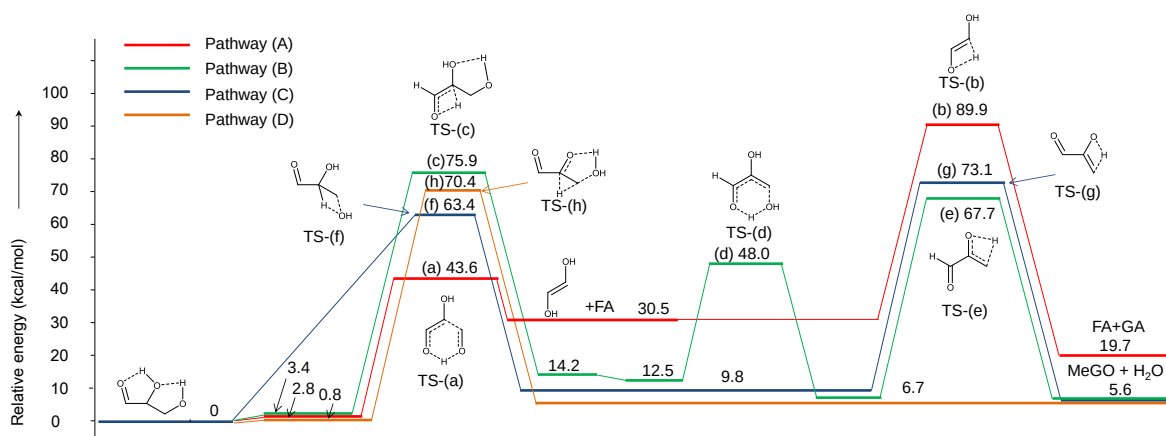


Figure 4-7. Potential energy plots for the concerted heterolysis mechanisms of glyceraldehyde, assuming unimolecular reactions.

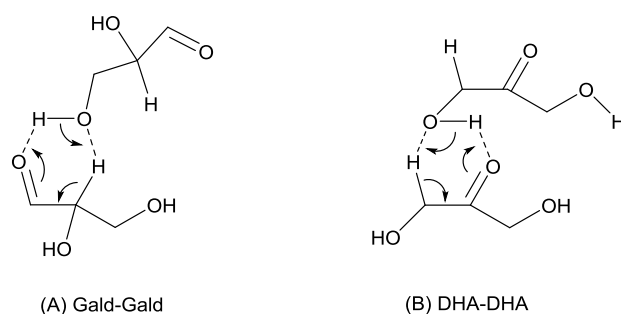
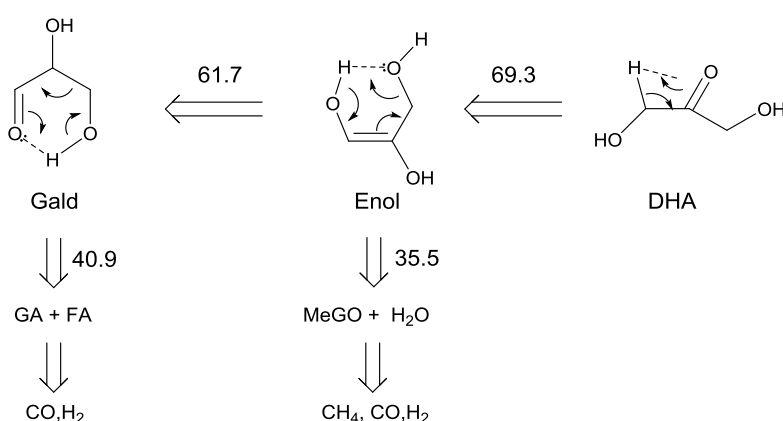


Figure 4-8. Bimolecular reactions proposed for the keto-enol tautomerizations of glyceraldehyde (Gald) and 1,3-dihydroxyacetone (DHA) starting from the (A) Gald-Gald and (B) DHA-DHA complexes in the gas phase.

In Scheme 4-2, the conversion of DHA occurs in the direction DHA→enol→Gald, and MeGO is produced from an enol intermediate that competes with the conversion to Gald, followed by retro-aldol fragmentation to give GA/FA. These results suggest that bimolecular reactions proceed during the keto–enol tautomerization, even in the gas phase, most likely as a result of the role of the C=O group as a strong hydrogen-bond acceptor.

Bimolecular reactions also reduce the energy barrier from the enol to the aldehyde/ketone, as demonstrated by the E_a values of the Gald–enol (34.2 kcal mol⁻¹) and DHA–enol (38.1 kcal mol⁻¹) enolation reactions via the same TSs. The occurrence of retro-aldol fragmentation via Gald even during the pyrolysis of pure DHA supports bimolecular Gald formation from the enol even in the gas phase, as the corresponding unimolecular reaction has a comparatively high E_a (59.1 kcal mol⁻¹). On the basis of these results, an interesting hypothesis may be proposed: the oxygen atoms in the C=O groups acts as a basic catalyst, even in the gas phase.



Scheme 4-2. Proposed pathways from 1,3-dihydroxyacetone (DHA) to methylglyoxal (MeGO) and glyceraldehyde (GA)/formaldehyde (FA) via an enol and glyceraldehyde (Gald), respectively. The values shown represent the calculated activation energies for the rate determining steps, assuming unimolecular reactions.

This hypothesis is also supported by observations reported for glucose pyrolysis studies with polyethers (Matsuoka et al., 2012). In such studies, dehydration reactions to form furanic compounds and char were inhibited completely in polyethers, a result that was reasonably explained by the hydrogen-bond theory (Matsuoka et al., 2012; Kawamoto et al., 2013; Kawamoto et al., 2014), in which proton donation through hydrogen bonding plays the same role as an acid catalyst. Even for polyethers, however, the retro-aldol reaction via a cyclic TS including a C=O group proceeds selectively, because C=O is a stronger hydrogen-bond acceptor than the polyether oxygen atoms. Unlike the present gas-phase study, dehydration products (including MeGO) were not generated by the pyrolysis of glucose in polyethers, a result that is not unexpected on the basis of the hydrogen bonds that would be formed between the glucose OH units and the ether O atoms or C=O moieties. Such bonding would make the elimination of OH difficult in reactions (B)-(d) and (C)-(f) (Scheme 4-1).

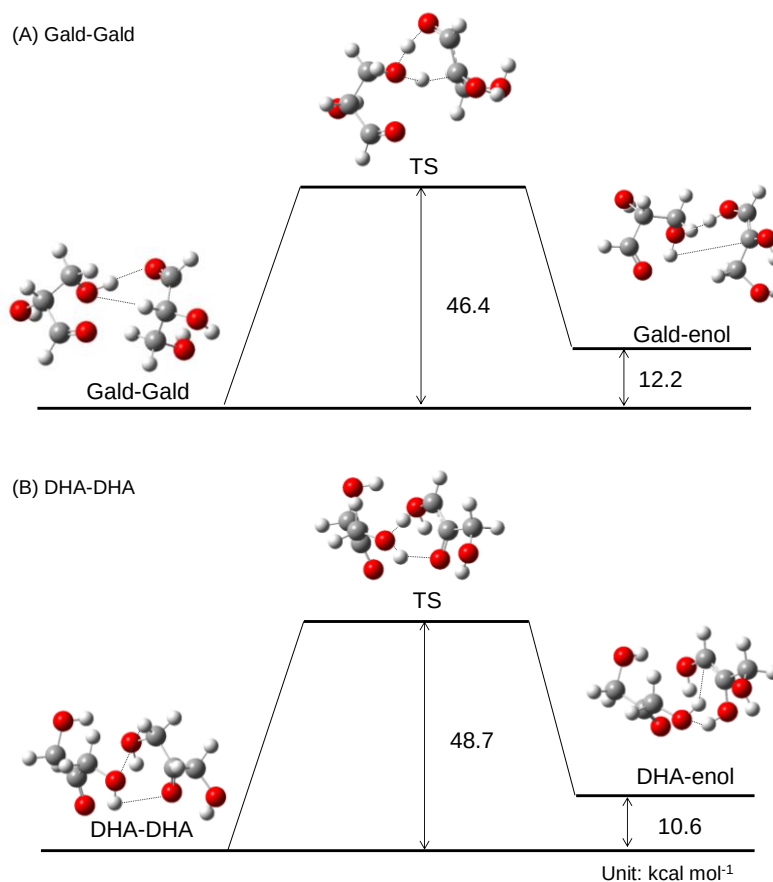


Figure 4-9. Potential energy plots for bimolecular keto-enol tautomerizations from the glyceraldehyde (Gald-Gald) and 1,3-dihydroxyacetone (DHA-DHA) complexes.

In the reaction sequence shown in Scheme 4-2, Gald is converted directly into the retro-aldol products whereas DHA requires the bimolecular enolation step for decomposition. This is consistent with the greater concentration of DHA in the recovered condensable products at 400 °C (Figure 4-3). The following discussions incorporating this finding provide insight into the role of temperature in the effectiveness of the bimolecular keto-enol tautomerization. As described in Scheme 4-2, the generation of methane and other hydrocarbon gases is dependent on the formation of MeGO as an intermediate. The MeGO yields from Gald-DHA (61/36) and DHA decreased from 12.8 and 29.3 (C-based) to 3.4 and 5.6% (C-based), respectively, as the

pyrolysis temperature increased from 400 to 600 °C. This trend is consistent with the yields of hydrocarbon gases, including methane, which were minimal [1.3–3.0% (C-based)] at 600 and 800 °C. These observations suggest that the bimolecular keto–enol tautomerization reaction becomes less effective at such high temperatures, and only small amounts of hydrocarbon gases are formed at 600 and 800 °C.

The results obtained in the present study should be very helpful with regard to understanding the gas-phase decomposition mechanisms of LG, the data for which we intend to report in the future.

4.1.4 Summary

The following gas-phase reactions were identified for glyceraldehyde (Gald), 1,3-dihydroxyacetone (DHA), and glycerol on the basis of pyrolysis experiments and theoretical calculations.

1. Gald and DHA, both of which have carbonyl moieties, decompose into fragmentation products at 400 °C whereas glycerol starts to decompose at 600 °C.
2. DHA decomposes via an enol and Gald, both of which are generated by keto–enol tautomerization.
3. Retro-aldol fragmentation to form glycolaldehyde/formaldehyde and dehydration to give methylglyoxal are the major reactions of Gald and DHA at 400 °C.
4. The E_a (40.9 kcal mol⁻¹) of the retro-aldol fragmentation is much lower than that (68.7 kcal mol⁻¹) for the corresponding cyclic Grob fragmentation of glycerol.
5. The introduction of the C=O group enhances the direct dehydration reaction (E_a =63.4 kcal mol⁻¹ for Gald, 76.7 kcal mol⁻¹ for glycerol).
6. Dehydration via the enol intermediate has a low energy barrier (E_a =35.5 kcal mol⁻¹) whereas the tautomerization from Gald to the enol was found to be the rate-determining step (E_a =72.5 kcal mol⁻¹) if it is assumed that the reactions are

unimolecular.

7. Both unimolecular pathways, that is, through direct dehydration and via the enol, do not explain the coproduction of methylglyoxal with the products of the retro-aldol fragmentation ($E_a=40.9 \text{ kcal mol}^{-1}$) from Gald at 400 °C.
8. Bimolecular keto–enol tautomerization mechanisms ($E_a= 48.7 \text{ kcal mol}^{-1}$ for Gald–Gald and $46.4 \text{ kcal mol}^{-1}$ for DHA–DHA) provide reasonable explanations for the formation of methylglyoxal at 400 °C. The ability of the C=O group to function as a strong hydrogen-bond acceptor likely allows the bimolecular reactions to proceed even in the gas phase.
9. Gald and DHA both generate hydrocarbon gases (methane, ethylene, acetylene, etc.) but only in only negligible yields, although the yield from glycerol reached 20.6% (C-based) at 800 °C. Alternatively, Gald and DHA produce syngas (H_2 and CO) selectively, along with the small amount of CO_2 .

4.2 Vapor-phase Reactions of Simple Polyalcohols

4.2.1 Introduction

Biomass gasification, which produces oxygenated (CO and CO_2) and hydrocarbon (CH_4 , C_2H_4 , and C_2H_2) gases along with H_2 , is a potential method for the sustainable production of biofuels and biochemicals. The producer gas can be used by gas turbines/engines to generate electricity. Petroleum and various chemicals can be produced over Fischer–Tropsch catalysts via syngas ($\text{CO} + \text{H}_2$). Contamination from hydrocarbon gases, however, should be eliminated for the Fischer–Tropsch process, because of the coking problem on the catalysts. Ethylene is an important industrial chemical currently produced from petroleum, and the improvement of ethylene selectivity in biomass gasification would promote replacing petroleum-derived ethylene with a biomass-based ethylene. Therefore, controlling the gas selectivity of biomass gasification is important to expand its usability.

For controlling the gas selectivity, the water-gas shift reaction (Maschio et al., 1994; Yoshida and Oshima, 2004) converts CO and H_2O into H_2 and CO_2 under steam gasification conditions. These processes produce syngas from biomass selectively. However, reports are limited for the reactions that produce hydrocarbon gases from biomass gasification.

Stein et al. (1983) reported the ethylene formation from acrolein, and they explained the formation via vinyl radical formed by the α -scission of the acrolein radical. In *Chapter 2*, we compared the gas and coke forming reactions of eight cellulose-derived volatile intermediates in an ampoule reactor at 600 °C. They showed that the intermediates bearing methyl groups (acetic acid and hydroxyacetone) produce more hydrocarbon gas (mainly methane) than that formed using glycolaldehyde, formic acid, or furanic compounds, which do not have any methyl groups. They also reported that glyceraldehyde (Gald; an aldose) and 1,3-dihydroxyacetone (DHA; a ketose) were selectively gasified into syngas (*Section 4.1*). Therefore, the gas composition from

cellulose gasification varies depending on the chemical structure of the volatile intermediate during cellulose gasification.

Levoglucosan (LG) is a major volatile intermediate in cellulose gasification, because of the large amounts (69.3% and 52.7%, C-based under nitrogen and oxygen/nitrogen conditions, respectively) detected during the pyrolysis in a flow-type reactor. The gaseous levoglucosan is stable up to around 500 °C and selectively fragments at > 600 °C into smaller compounds and finally into noncondensable gases (*Chapter 3*), although it readily degrades into polymerization and dehydration products, including coke, in the molten state by cooling. This high reactivity in the molten state has been explained using hydrogen bond theory, in which intermolecular hydrogen bonds act as acid and base catalysts (Matsuoka et al., 2012; Kawamoto et al., 2013, 2014).

The kinetic analysis of the decomposition of gaseous levoglucosan indicated the radical chain reactions acting as the rate-determining step rather than the heterolysis reactions (*Section 4.4*). From the gas compositions discussed with the radical chain reactions postulated from the C- and O-centered radicals, an interesting hypothesis has been proposed; the content of the hydrocarbon gas (methane, ethylene, and acetylene) from cellulose pyrolysis/gasification is directly related to the extent of the progression of dehydration reactions that form the intermediates bearing methyl and unsaturated alkyl groups.

To address this hypothesis, the gas-phase reactivities of three simple polyalcohols: glycerol (Gly), propylene glycol (PG), and ethylene glycol (EG) shown in Figure 4-10 were compared with those reported for Gald and DHA (*Section 4.1*) in this study, focusing on the dehydration reactions and the hydrocarbon gas formation. The experimental results are discussed with theoretical calculation results from density functional theory (DFT) conducted at MP4(sdq)/Aug-cc-pVTZ//DFT(M06-2X)/6-31+G(p,d) levels.

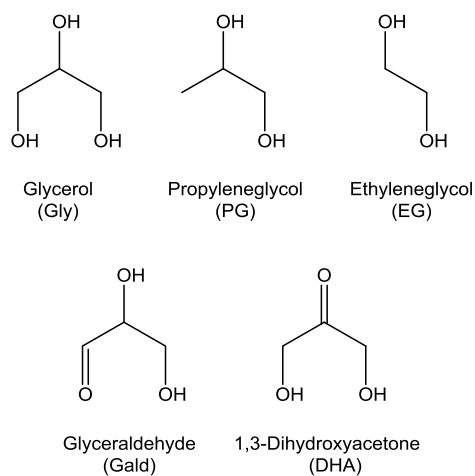


Figure 4-10. Polyalcohols used in the present investigation.

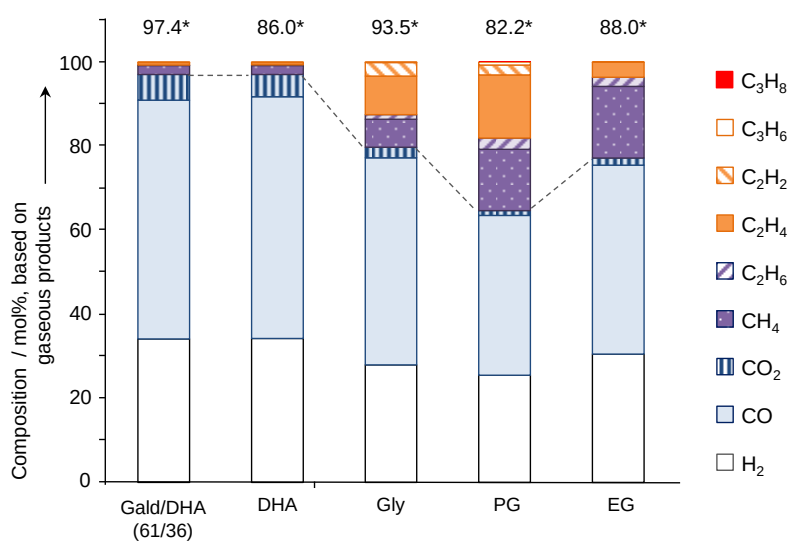


Figure 4-11. Composition (mol%) of noncondensable (gaseous) products from glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36), DHA, glycerol (Gly), propylene glycol (PG), and ethylene glycol (EG) at 800 °C and the residence time of 0.9 s under N₂ flow of 400 mL min⁻¹. *Yield (% , C-based) of the noncondensable product. The data of Gald/DHA (61/36), DHA and Gly are from *Section 4.1*.

4.2.2 Materials and methods

4.2.2.1 Materials

Ethylene glycol, propylene glycol, and glycerol, which were used for pyrolysis trials, were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). These chemicals were used as received, without further purification.

4.2.2.2 Two-stage tubular reactor

The two-stage tubular reactor (Figure 3-1) was used, that contained two cylindrical electric furnaces (internal diameter: 35 mm, length: 160 mm, Asahi Rika Seisakusho Co., Ltd.), serving as the evaporator and pyrolyzer, respectively. Each furnace included a quartz glass tube (internal diameter: 15 mm, wall thickness: 1.5 mm) and these tubes were connected to one another. The right end of the evaporator was attached to a nitrogen cylinder via a mass flow controller (Horiba SEC-400MK3) and the other end, coming from the pyrolyzer, was connected to a gas wash bottle via a glass wool filter and then to a gas bag. Air flow was supplied to the outer part of the tube coming from the pyrolyzer to quench the pyrolysis reactions. The gas wash bottle held a DMSO-*d*₆ solution (2.0 mL) containing an oximation reagent (NH₂OH•HCl) (20 mg) to recover volatile products. Aldehydes and ketones in the products were converted to the corresponding less volatile aldoximes or ketoximes (both cis and trans isomers).

4.2.2.3 Pyrolysis

In preparation for pyrolysis trials, a sample (15 mg) contained in a ceramic boat was inserted into the middle of the evaporator. A nitrogen flow (400 mL min⁻¹) was supplied for 30 min prior to conducting each pyrolysis so as to sweep out the air inside the reactor. After the pyrolyzer was preheated at a designated temperature (400, 600, or

800 °C), the evaporator was heated to 120 °C over 5 min and this temperature was maintained for an additional 5 min. The evaporator was subsequently heated to 200 °C at 16 °C min⁻¹. After holding the evaporator at 200 °C for 5 min, heating was ceased and the tube reactor was cooled by opening the furnace covers and subsequently applying an air flow. The nitrogen flow was maintained for an additional 2 min to sweep any residuals products into the gas wash bottle and gas bag.

The residence time of the pyrolyzer was defined as the period over which the gaseous substances were present in the region of the pyrolyzer with temperatures within the set value ± 25 °C. The internal temperature profiles of the pyrolyzer and evaporator were obtained for each set temperature by direct measurement during preliminary control trials conducted without the addition of sample. A constant nitrogen flow of 400 mL min⁻¹ was supplied during each experimental trial, and hence the residence time changed depending on the temperature of the pyrolyzer. The residence times at 400, 600 and 800 °C were 1.4, 1.2 and 0.9 s, respectively, which were settled to be near residence times of actual gasifications. The pressure inside the reactor was measured and found to be equal to atmospheric pressure.

4.2.2.4 Product analysis

Following each experimental trial, the condensates were washed from the internal wall with the DMSO-*d*₆ solution in the gas wash bottle. The resulting solution was directly analyzed by ¹H NMR spectroscopy using a Bruker AC-400 (400 MHz) spectrometer following the addition of 2-furoic acid as an internal standard. Quantification of the products along with any unreacted sample was performed based on the peak areas of the NMR signals as compared with those of the internal standard.

With the exception of acetylene, noncondensable gases were analyzed using a micro GC (Varian CP-4900) under the following chromatographic conditions: channel (1) column: MS5A (10 m); carrier gas: Ar; column temperature: 100 °C; column pressure: 170 kPa; detector: TCD; retention times (s): H₂ (26.4), N₂ (45.7), O₂ (35.4),

CH₄ (60.6) and 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): CO₂ (19.9), C₂H₄ (23.5), C₂H₆ (26.3), C₃H₆ (57.4) and C₃H₈ (63.2). Quantification of acetylene was conducted with a Shimadzu GC-14B under the following conditions: column: RESTEC, Rt@-Alumina BOND/N₂SO₄ (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⁻¹), 200 °C (16–20 min); detector: flame ionization detector; retention time of acetylene: 4.3 min.

4.2.2.5 Computational methods

Calculations were conducted using the Gaussian 09 software package (Frisch et al., 2009). The geometry optimizations for all reactants, products and TSs were performed by employing the DFT method (M06-2X) and 6-31+G(d,p) basis sets. Vibrational frequency calculations used the same methods and basis set. The energies of optimized geometries were calculated with the MP4(SDQ) method. The CCSD(T) method was used for single point energy calculations with the aim of estimating BDEs. The AUG-cc-pVTZ basis set was used for all energy calculations. *E_a* and BDEs were estimated as the relative energies, including zero-point energies, between the reactants and the TSs or radicals. Frequency analysis showed one imaginary mode for the TS and no imaginary modes for the reactants, products and precomplexes. In addition, we performed IRC calculations to ascertain that the TS connected the reactant and product.

4.2.3 Results and discussion

Gly, PE, and EG were pyrolyzed in the gas phase under an N₂ flow at 400, 600, or 800 °C and residence times ranging from 0.9 to 1.4 s, using an experimental setup consisting of an evaporator and a pyrolyzer, which is described in the report for the pyrolysis of gaseous Gald and DHA (Section 4.1). The gaseous polyalcohol formed from the evaporator was pyrolyzed further in the secondary gas-phase pyrolysis zone,

and the resulting condensable products were recovered in the gas-wash bottle, where the aldehydes and ketones were converted into the corresponding less volatile oxime derivatives.

A mixture of Gald-DHA (61/36) and pure DHA decomposed, even at 400 °C, and the recoveries were 32.7% and 10.7%, respectively (*Section 4.1*). Gly, PG, and EG were recovered almost quantitatively at 400 °C and became reactive at 600 °C, and the recoveries were 32.0%, 43.2%, and 53.7%, respectively. The 24.7%, 21.8%, and 15.7% (C-based) of the condensable products were identified for the pyrolyzates from Gly, PG, and EG at 600 °C, respectively, which correspond to 36.3%, 38.4%, and 33.9% (C-based) against the amounts of degraded polyalcohols, respectively. Most of the remaining components were noncondensable gases. Because polyalcohols were completely converted into the noncondensable gases by increasing the temperature to 800 °C, these condensable products are the gas-forming intermediates from the polyalcohols. Therefore, the chemical structures of the condensable intermediates (600 °C) with the final gas composition (800 °C) are discussed to understand the roles of these intermediates in hydrocarbon gas formation.

The compositions of the noncondensable gases produced from Gly, PG, and EG at 800 °C are summarized in Figure 4-11, compared with those reported for Gald-DHA (61/36) and DHA (*Section 4.1*). The gas yields (C-based) are also shown in the figure. Although the major gaseous products were syngas, the hydrocarbon (HC)/oxygenated (OX) gas ratios (HC/OX) were different depending on the chemical structure of the polyalcohol. Gald-DHA (61/36) and DHA produced OX gas (mainly CO) and H₂ selectively with the limited amounts of HC gases (2.9–3.0%, C-based), whereas the contents of the HC gases (mainly methane and ethylene) reached 20.3%, 35.3%, and 22.8% (C-based) from Gly, PG, and EG, respectively.

Discussion of the noncondensable gas formation with the elemental compositions of polyalcohols provides insight into the gas-forming reactions. As shown in Figure 4-12, the CHO ratio of Gald and DHA (C₁H₂O₁) is ideal for the production of equimolar amounts of CO and H₂. However, PG (C₁H_{2.7}O_{0.6}) has insufficient oxygen for

the production of OX gases (CO and CO₂); therefore, PG produced large amounts of HC gases (35.3%, C-based). Gly (C₁H_{2.7}O₁) and EG (C₁H₃O₁) also produced reasonable amounts of HC gases at 20.3% and 22.8% (C-based), respectively, although these polyalcohols have sufficient oxygen to produce CO. Because the yields of CO₂ were low from Gly and EG, oxygen was lost as water from these polyalcohols. These results suggest the gas compositions from these polyalcohols are controlled kinetically, not thermodynamically.

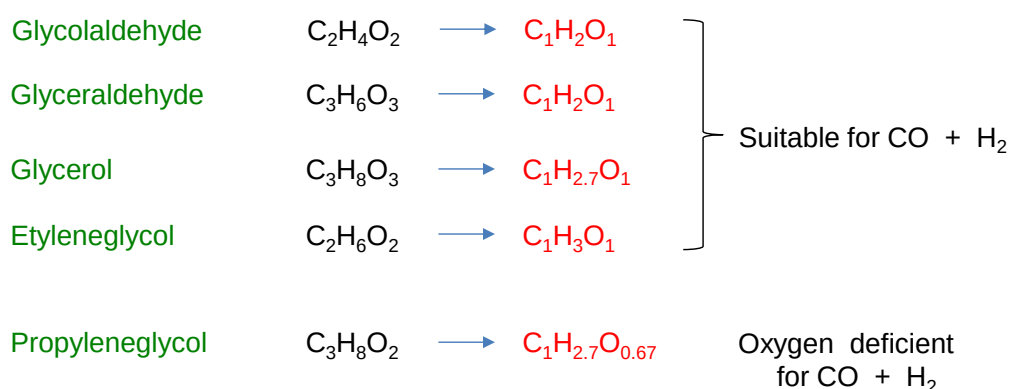


Figure 4-12. Elemental compositions of glyceraldehyde, 1,3-dihydroxyacetone, glycerol, ethylene glycol, and propylene glycol for the production of syngas (CO + H₂).

4.2.3.1 Composition of condensable intermediates

The compositions (C-based) of the condensable intermediates obtained from the pyrolyses of Gly, PG, and EG at 600 °C are shown in Figure 4-13, as compared with those of Gald and DHA at the same temperature. Gald-DHA (61/36) and DHA exhibited similar compositions including formaldehyde (FA), glycolaldehyde (GA), glyoxal (GO) and methylglyoxal (MeGO) as the major components. Gly and PG produced larger amounts of C3 products, which include hydroxyacetone (HA) and acrolein (ACR) from Gly and propionaldehyde (Pald) and allyl alcohol (AllyOH) from PG. EG, a C2

polyalcohol, formed acetaldehyde (AA) and FA selectively.

The contents (C-based on the condensable products) of the intermediates with saturated alkyl groups [acetone (ACE), MeGO, HA, acetic acid, AA, methanol, and Pald] and unsaturated alkyl groups (ACR and AllyOH and ketene) are compared in Figure 4-14. These intermediates are expected to form through dehydration reactions as discussed below. The contributions of these intermediates are small for Gald-DHA (61/36) (16.0%) and DHA (8.7%), but greater for Gly (62.4%), PG (88.1%), and EG (34.9%). These yields are proportionally correlated to the contents of the HC gases in Figure 4-11, supporting the hypothesis; the intermediates bearing alkyl groups produce hydrocarbon gases.

4.2.3.2 Roles of heterolysis and radical pathways for dehydration

Dehydration of the alcohols could proceed in the gas phase through homolysis of the C–OH bond, heterolytic dehydration, and β -scission of C-centered radicals as illustrated in Scheme 4-3. However, very high bond dissociation energies of the C–OH bonds in polyalcohols [93.5–95.6 kcal mol⁻¹ for Gly (*Section 4.1*)] indicate that the homolysis pathway is improbable even at 600 °C, where Gly, PG, and EG degraded. Therefore, heterolysis and radical pathways were considered. Along with the direct dehydration, cyclic Grob fragmentation and pinacol rearrangement were considered for the heterolysis reactions that release water (Nimlos et al., 2006).

For the radical pathways, the reactions from the C- and O-centered radicals were considered, which are formed through hydrogen abstraction from the -C–H and -O–H moieties of polyalcohols, respectively (Dagaut et al., 2009). Various radical species such as •OH and •CH₃ existing in the pyrolysis environment can abstract these hydrogens (Jodkowski et al., 1999).

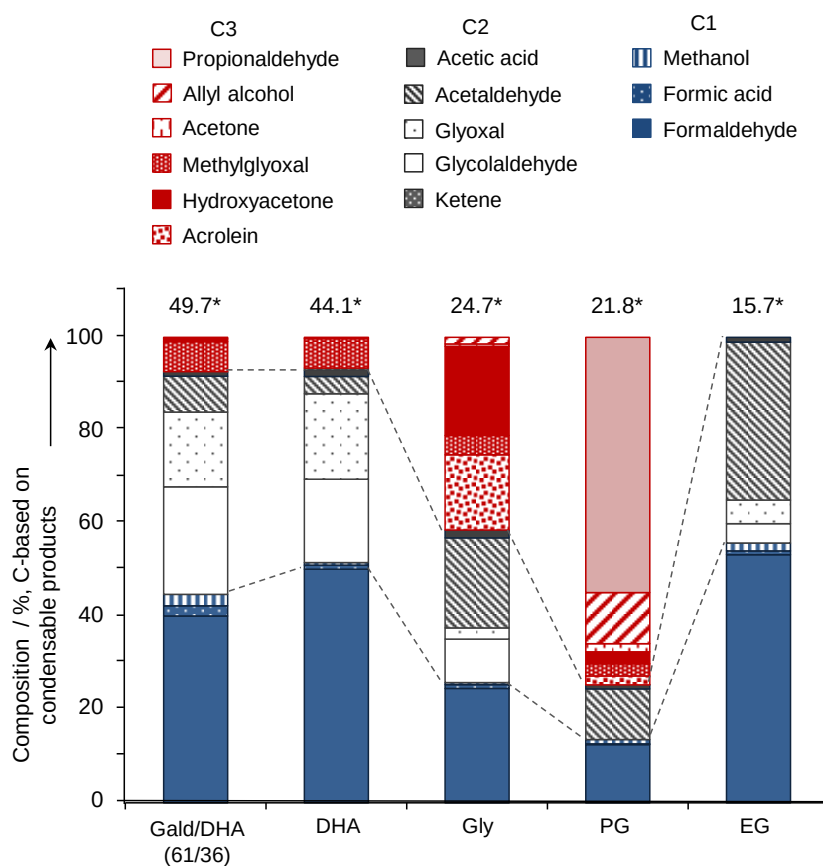


Figure 4-13. Composition (% C-based) of condensable products from glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36), DHA, glycerol (Gly), propylene glycol (PG), and ethylene glycol (EG) at 600 °C and the residence time of 0.9 s under N₂ flow of 400 mL min⁻¹. *Yield (% C-based) of the condensable product. The data of Gald/DHA (61/36), DHA and Gly are from Section 4.1.

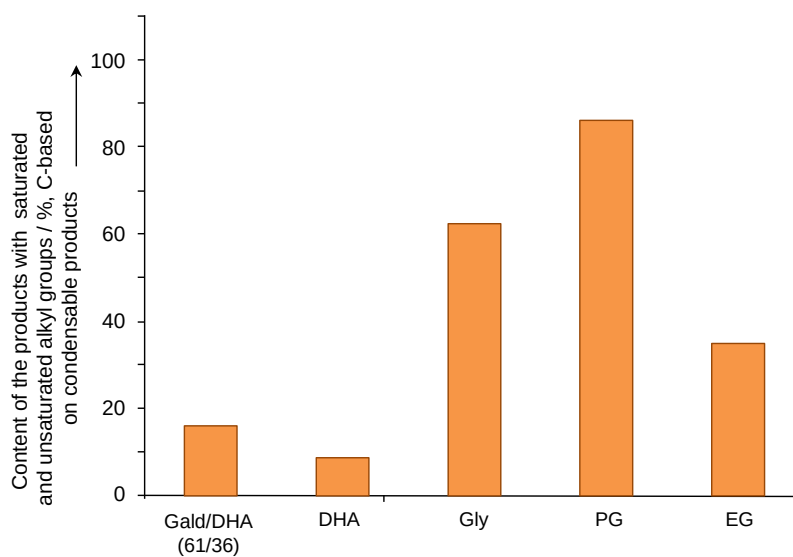
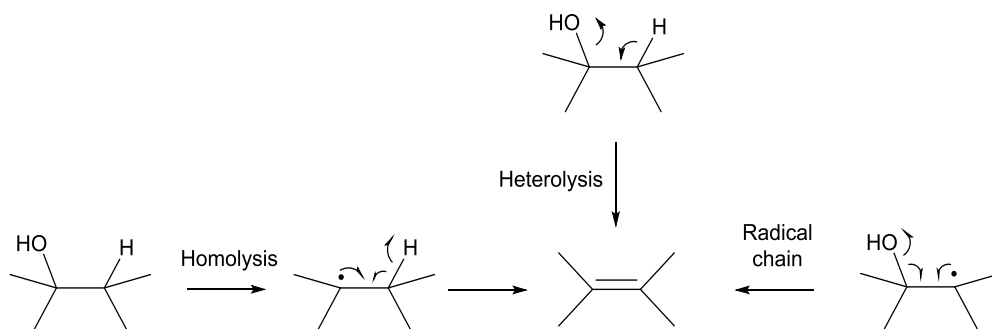


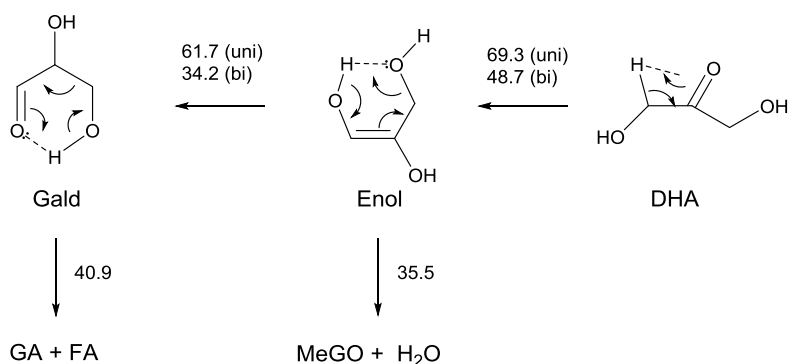
Figure 4-14. Contents (% , C-based) of the products with saturated and unsaturated alkyl groups in condensable products obtained from glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36), DHA, glycerol (Gly), propylene glycol (PG), and ethylene glycol (EG) at 600 °C. The data of Gald/DHA (61/36), DHA and Gly are from *Section 4.1*.



Scheme 4-3. Three possible dehydration pathways for polyalcohols.

Glyceraldehyde (Gald) and dihydroxyacetone (DHA)

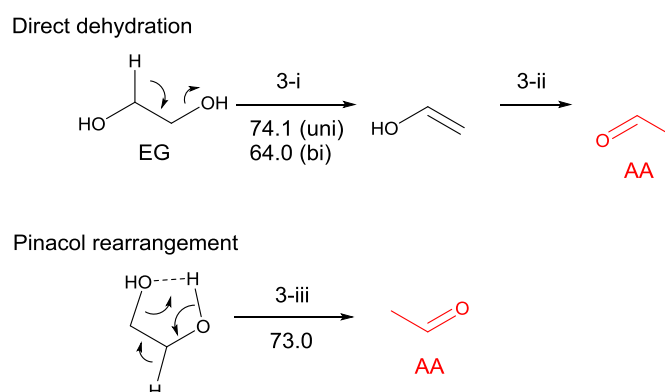
Degradation pathways of Gald and DHA (Scheme 4-3) have been discussed in detail in our previous paper (*Section 4.1*). The values next to the reaction arrows are the calculated E_a s by assuming uni- and bimolecular mechanisms. The low energy-barrier (E_a 40.9 kcal mol⁻¹) allow retro-aldol fragmentation to proceed for Gald, even at 400 °C, which produces GA and FA. DHA degrades via Gald through the proposed bimolecular keto-enol tautomerizations, which significantly reduce the E_a s. A dehydration reaction via the enol intermediate (E_a 35.5 kcal mol⁻¹), which includes a six-membered cyclic TS, was considered, because Gald and DHA formed MeGO and AA at 400 °C.



Scheme 4-4. Thermal decomposition pathways of glyceraldehyde (Gald) and 1,3-dihydroxyacetone (DHA) through retro-aldol fragmentation and dehydration via a cyclic transition state along with the keto-enol tautomerization via the bimolecular (bi) mechanisms (*Section 4.1*). The values next to the arrows represent the activation energies (kcal mol⁻¹), as calculated at the MP4(SDQ)//DFT(M06-2X) level. MeGO, methylglyoxal; GA, glycolaldehyde; FA, formaldehyde; uni, unimolecular mechanism (DHA-DHA, enol-enol).

Ethyleneglycol (EG)

EG produced AA and FA as the major condensable products. As shown in Scheme 4-5, both direct dehydration (3-i) and pinacol rearrangement (3-iii) can produce AA from EG. The E_a ($74.1 \text{ kcal mol}^{-1}$) of the unimolecular dehydration was reduced to $64.0 \text{ kcal mol}^{-1}$ by assuming the bimolecular mechanism involving two EG molecules. Bimolecular mechanisms have been proposed for the gas phase keto-enol tautomerization, $\text{DHA} \leftrightarrow \text{enol} \leftrightarrow \text{Gald}$, as illustrated in Scheme 4-4. Because the bimolecular mechanism is suggested for the conversion of enol to Gald, where only OH groups participate, similar bimolecular mechanisms can also be postulated for the dehydration of EG.

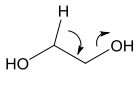
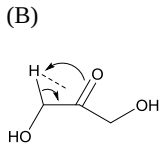
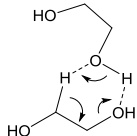
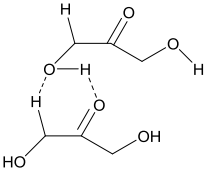
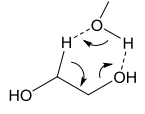
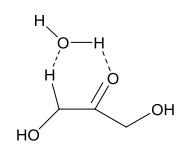


Scheme 4-5. Possible heterolytic dehydration pathways for ethylene glycol (EG). The values next to the arrows represent the activation energies (kcal mol^{-1}), as calculated at the MP4(SDQ)/DFT(M06-2X) level. AA, acetaldehyde; uni, unimolecular mechanism; bi, bimolecular mechanism (EG-EG).

To understand the roles of the bimolecular mechanisms on dehydration and keto-enol tautomerization, the $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values as calculated for EG (unimolecular), EG-EG and EG- H_2O at 25, 400, and 600 °C (Table 4-1) are compared

with those calculated for DHA (unimolecular), DHA-DHA, and DHA-H₂O. The $\Delta G^\ddagger$ of the enolation reaction from DHA was reduced from 66.4 kcal mol⁻¹ (unimolecular) to 45.4 (DHA-DHA) and 52.3 (DHA-H₂O) kcal mol⁻¹ at 25 °C. Although these values became greater at higher temperatures because of the increasing $T\Delta S^\ddagger$ values, the low $\Delta G^\ddagger$ values (400 °C) of 48.4 and 52.3 kcal mol⁻¹ for DHA-DHA and DHA-H₂O, respectively, explain the conversion from DHA to enol occurring at 400 °C.

Table 4-1. The $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values (kcal mol⁻¹) calculated for the dehydration of ethylene glycol (EG) and keto-enol tautomerization of 1,3-dihydroxyacetone (DHA) by assuming the unimolecular (uni) and bimolecular (bi, EG-EG, EG-H₂O, DHA-DHA, and DHA-H₂O) mechanisms at 25, 400, and 600 °C from the minimum energies of the transition states, as calculated at the MP4(SDQ)//DFT(M06-2X) level

(A)					(B)				
									
									
									
EG (uni)					DHA (uni)				
EG-EG (bi)					DHA-DHA (bi)				
EG-H ₂ O					DHA-H ₂ O (bi)				
		kcal mol ⁻¹					kcal mol ⁻¹		
		$\Delta G^\ddagger$	$\Delta H^\ddagger$	$T\Delta S^\ddagger$			$\Delta G^\ddagger$	$\Delta H^\ddagger$	$T\Delta S^\ddagger$
EG (uni)	25 °C	71.3	71.6	0.3	DHA (uni)	25 °C	66.4	65.7	-0.7
	400 °C	70.7	72.1	1.4		400 °C	67.2	65.6	-1.6
	600 °C	70.3	72.2	1.9		600 °C	67.8	65.5	-2.3
EG-EG (bi)	25 °C	61.0	59.3	-0.7	DHA (bi)	25 °C	45.4	43.3	-2.1
	400 °C	63.1	59.3	-2.8		400 °C	48.4	42.6	-5.8
	600 °C	64.3	59.4	-3.9		600 °C	50.2	42.4	-7.8
EG-H ₂ O (bi)	25 °C	66.5	65.3	-1.2	DHA-H ₂ O (bi)	25 °C	48.9	46.6	-2.3
	400 °C	68.2	65.1	-3.1		400 °C	52.3	45.6	-6.7
	600 °C	69.1	65.2	-3.9		600 °C	54.3	45.4	-8.9

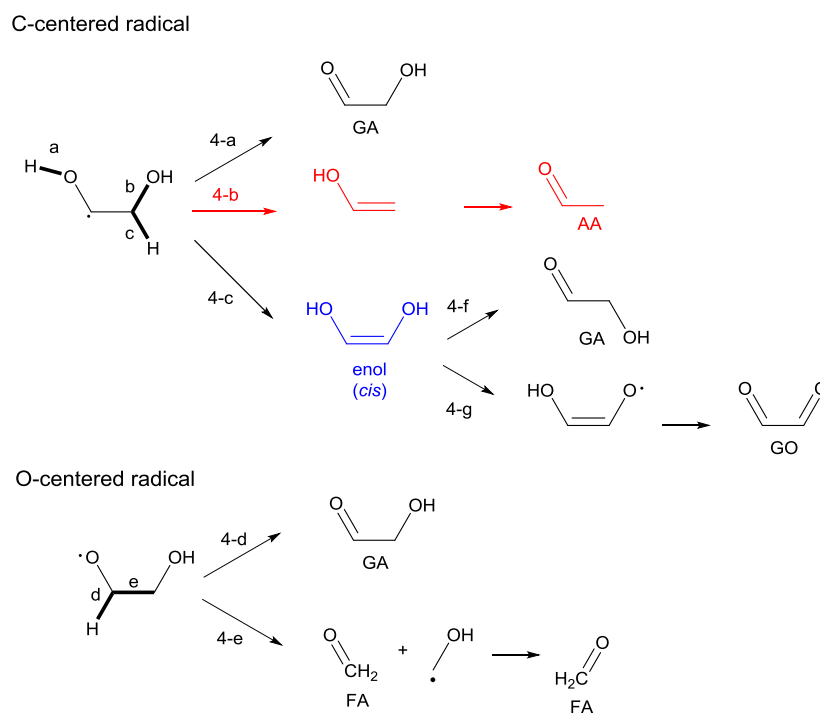
The influences of the bimolecular mechanisms on the dehydration reaction were much lower; hence, the $\Delta G^\ddagger$ values at 400 and 600 °C were in the range of 63.1–69.1 kcal mol⁻¹, even with the bimolecular mechanisms. This result is concordant with the lower pyrolytic reactivity of EG than those of Gald and DHA. Thus, dehydration reaction (3-i) is the rate-determining step for the formation of AA.

Radical pathways postulated from the C- and O-centered radicals of EG are summarized in Scheme 4-6. Reaction 4-b is a radical dehydration forming AA; therefore, AA can be produced by both heterolysis and radical pathways. Although no heterolysis pathways can explain the formation of FA, the other major product. FA can form via the β -scission of the O-centered radical of EG (4-e). The formations of GA and GO, the minor products, are possible by the radical pathways, 4-a, 4-c, and 4-d. Thus, radical pathways are necessary to explain the product formation from EG.

The radical intermediates are fragmented mainly through the β -scission reactions, which require the radical p-orbital and the σ -orbital of the C–X bond that is cleaved to lie in the same plane (Parsons, 2000). This pathway leads to the stereoselective formation of *cis* enol from EG (reaction 4-c in Scheme 4-6). As shown in reaction 3-i (Scheme 4-5), heterolytic dehydration also proceeds stereoselectively in the gas phase, which results in *cis* elimination. Therefore, the influences of these stereoisomers during the keto-enol tautomerization were studied theoretically (Figure 4-15). The *cis* enol (E_a 74.6 kcal mol⁻¹) was more stable than the corresponding *trans* isomer (E_a 58.6 kcal mol⁻¹) by assuming the unimolecular mechanisms. In the gas phase, -O–H should associate with the double bond π electron to accomplish the proton-transfer required for tautomerization to the aldehyde isomer. The hydrogen bond formed between the two OH groups in the *cis* enol make this transition difficult. For the bimolecular mechanisms including water-assisted reactions, the E_a s calculated for both isomers dramatically reduced to the levels of 40.4–43.5 kcal mol⁻¹ (*cis*) and 31.6–34.1 kcal mol⁻¹ (*trans*). Thus, even *cis* enols can be converted into keto forms through the bimolecular mechanisms (reaction 4-f in Scheme 4-6).

Alternatively, the hydrogen-bonded -O–H bond in the *cis* isomer exhibits a low

bond dissociation energy of $70.6 \text{ kcal mol}^{-1}$. Therefore, the bimolecular ketonization of *cis* enol competes with the radical reaction (4-g) to form GO, after releasing the hydrogen by hydrogen abstraction or homolytic cleavage of the O–H bond. The formation of GO from EG is explainable with this reaction sequence. The *trans* enol may be transformed to GA through the unimolecular mechanism, because of the low E_a of $58.6 \text{ kcal mol}^{-1}$.



Scheme 4-6. Possible radical chain pathways from the C- and O-centered radicals of ethylene glycol (EG). The bond with a bold line, which is located at the β -position to the radical, is expected to be cleaved through β -scission reaction. GA, glycolaldehyde; GO, glyoxal; AA, acetaldehyde; FA, formaldehyde.

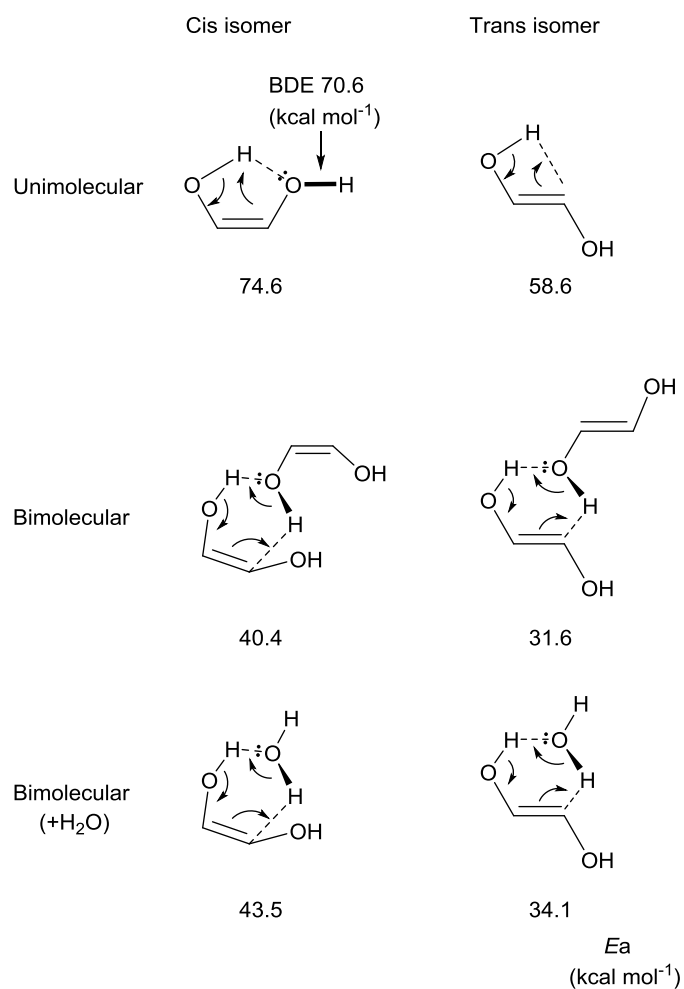
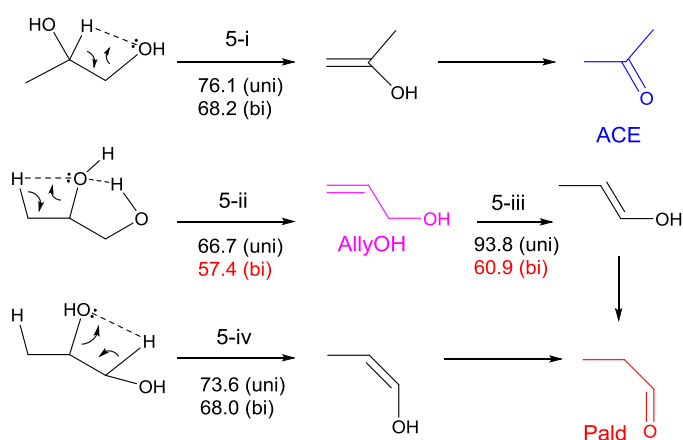


Figure 4-15. Influences of the stereochemistry of *cis/trans* enol on activation energy (kcal mol⁻¹) of keto-enol tautomerization by assuming the unimolecular and bimolecular mechanisms, as calculated at the MP4(SDQ)//DFT(M06-2X) level.

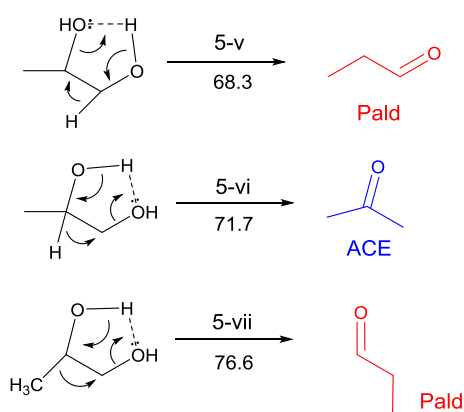
Propyleneglycol (PG)

Pald represents 54.8% of the condensable products from PG, followed by AllyOH, AA, FA, and other minor products at 600 °C. This high selectivity for the formation of Pald is explained in the following. Heterolysis and radical pathways, which were considered for the pyrolysis of PG, are summarized in Schemes 4-7 and 4-8, respectively.

Direct dehydration

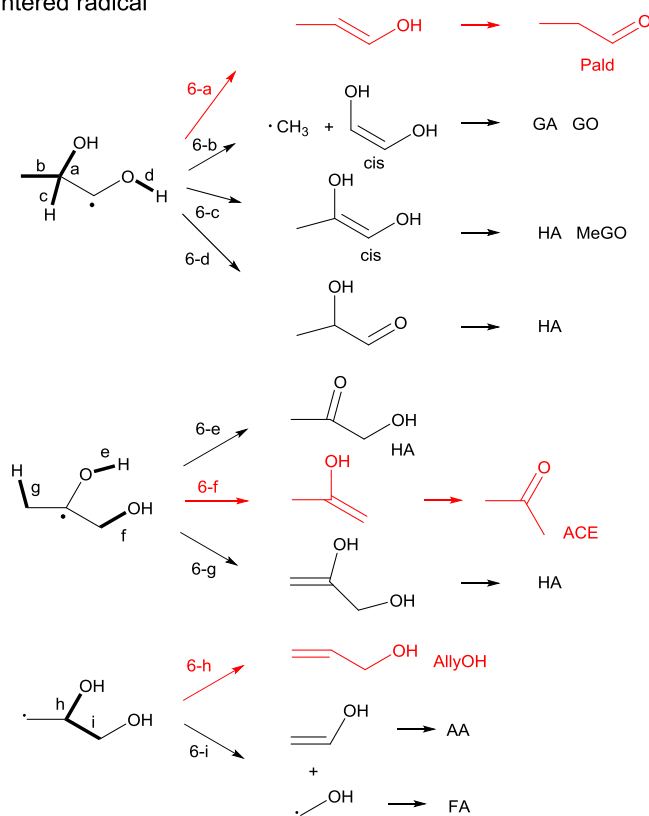


Pinacol rearrangement

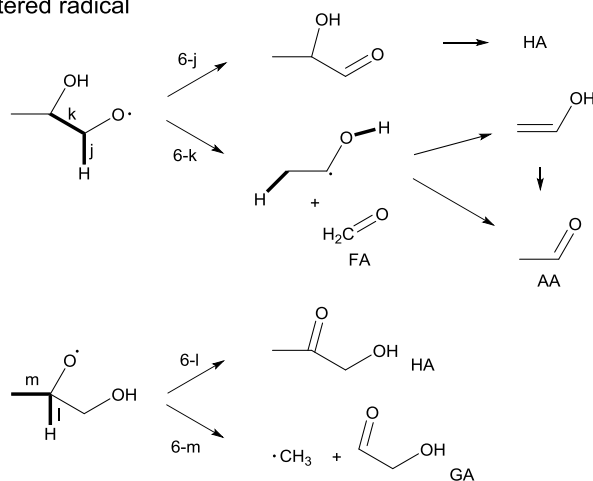


Scheme 4-7. Possible heterolytic dehydration pathways for propylene glycol (PG). The values next to the arrows represent the activation energies (kcal mol^{-1}), as calculated at the MP4(SDQ)//DFT(M06-2X) level. Pald, propionaldehyde; AllyOH, allyl alcohol; ACE, acetone; uni, unimolecular mechanism; bi, bimolecular mechanism.

C-centered radical



O-centered radical



Scheme 4-8. Possible radical chain pathways from the C- and O-centered radicals of propylene glycol (PG). The bond with a bold line, which is located at the β -position to the radical, is expected to be cleaved through a β -scission reaction. Pald, propionaldehyde; AllyOH, allyl alcohol; MeGO, methylglyoxal; HA, hydroxyacetone; ACE, acetone; GA, glycolaldehyde; GO, glyoxal; AA, acetaldehyde; FA, formaldehyde.

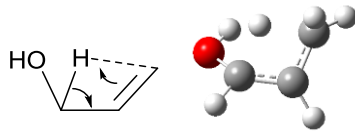
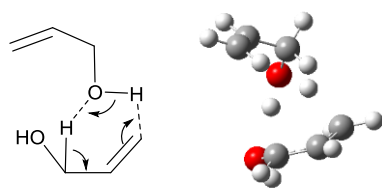
For the radical pathways, dehydration reactions, 6-a, 6-f, and 6-h occurring from the C-centered radicals, form Pald, ACE and AllyOH, respectively (Scheme 4-8). However, many other reactions can also be postulated for the radical pathways; therefore, the high selectivity of the Pald formation with the radical pathways is not explainable.

Alternatively, three reactions, 5-iv, 5-v, and 5-vii have E_a s of 73.6, 68.3, and 76.6 kcal mol⁻¹, respectively, and they can directly produce Pald by assuming unimolecular heterolysis mechanisms (Scheme 4-7). However, even the lowest E_a 68.3 kcal mol⁻¹ (5-v) is similar to that of reaction 5-vi (71.7 kcal mol⁻¹), which produces ACE. Because of the composition of ACE was low (1.7%, C-based), the difference in the E_a values is not enough to explain the preferential formation of Pald instead of ACE.

Bimolecular mechanisms significantly lower the E_a s of direct dehydration reactions, especially for 5-ii from 66.7 to 57.4 kcal mol⁻¹, which is concordant with the formation of AllyOH as the second greatest product. Furthermore, the isomerization from AllyOH to enol, which exhibited extremely high E_a (93.8 kcal mol⁻¹) via a unimolecular mechanism (reaction 5-iii), was reduced to 60.9 kcal mol⁻¹ with the bimolecular mechanism. The $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values calculated for the unimolecular and bimolecular isomerizations of AllyOH at 25, 400, and 600 °C are summarized in Table 4-2. The $\Delta G^\ddagger$ at 600 °C decreased from 95.7 (unimolecular) to 63.2 kcal mol⁻¹ (bimolecular). Consequently, the preferential formation of Pald from PG can be explained by the pathways 5-ii + 5-iii followed by the keto-enol tautomerization. These results indicate that heterolysis pathways greatly contribute to the thermal degradation of gaseous PG.

The allylic hydrogen should associate with the π electron from a direction orthogonal to the double bond plane for the isomerization of AllyOH (Table 4-2), whereas the TS with the four-membered ring increases the energy barrier of the unimolecular reaction. This concerted proton and electron transfer become much easier with the bimolecular mechanism including the cyclic TS with a six-membered ring.

Table 4-2. The $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values (kcal mol⁻¹) calculated for isomerization of allyl alcohol (AllyOH) to enol by assuming the unimolecular (uni) and bimolecular (bi) mechanisms at 25 and 600 °C from the minimum energies of the transition states, as calculated at the MP4(SDQ)//DFT(M06-2X) level

	
AllyOH (uni)	AllyOH (bi)
	kcal mol ⁻¹
	$\Delta G^\ddagger$ $\Delta H^\ddagger$ $T\Delta S^\ddagger$
AllyOH (uni)	25 °C 94.2 93.5 -0.7
	600 °C 95.7 93.2 -2.5
AllyOH (bi)	25 °C 61.6 60.6 -1.0
	600 °C 63.2 61.2 -2.0

The AA and FA formations, which cannot be explained by the heterolysis reactions, are possible through the radical pathways (6-i and 6-k). HA, a minor product, can also be explained by the radical pathways (6-c, 6-d, 6-g, 6-j, and 6-l). Therefore, radical pathways are also expected to contribute to the degradation of PG.

Glycerol (Gly)

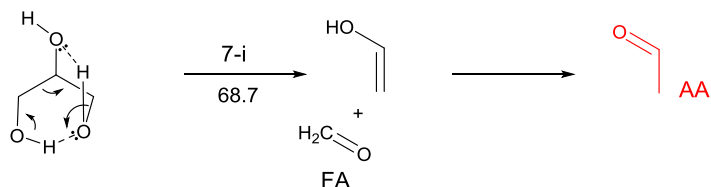
Gly forms HA, ACR, AA, GA, and FA, along with other minor products at 600 °C. The postulated heterolysis pathways as summarized in Scheme 4-9 explain the

formation of the major components except for GA. As discussed above, bimolecular mechanisms reduced the E_a values of the dehydration reactions, 7-ii and 7-iii. Cyclic Grob fragmentation (7-i, E_a 68.8 kcal mol⁻¹) forming AA and FA is a characteristic reaction of Gly. However, the route including dehydration reaction 7-iii, which has the lowest E_a (63.4 kcal mol⁻¹) with the bimolecular mechanism, followed by the retro-aldol fragmentation (7-vi, E_a 41.7 kcal mol⁻¹) was suggested to be a more probable pathway for the AA and FA formations from Gly. Dehydration reaction 7-iii forms ACR by the additional dehydration through reaction 7-iv via the cyclic TS (E_a 30.9 kcal mol⁻¹). The pinacol rearrangement (7-v), which has the third lowest E_a (66.7 kcal mol⁻¹), may compete with dehydration reaction 7-iii for starting these pathways.

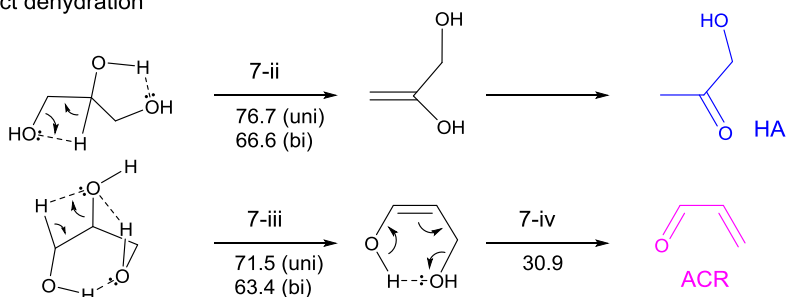
The alternative dehydration reaction 7-ii, which has the second lowest E_a (66.6 kcal mol⁻¹) with the bimolecular mechanism, forms HA. Thus, the bimolecular dehydration reactions, 7-ii and 7-iii, reasonably explain the formation of HA, ACR, AA, and FA from Gly.

As illustrated in Scheme 4-10, all of the dehydration products listed in Scheme 4-9 can be produced through radical reactions. Furthermore, many of the radical reactions explain the formation of GA, which is not expected to form by heterolysis reactions. Other minor condensable intermediates (MeGO and GO) can also be produced by the radical pathways. Therefore, consideration of the radical pathways is necessary to explain the formation of the degradation products from Gly, as concluded for the pyrolysis of EG and Pald.

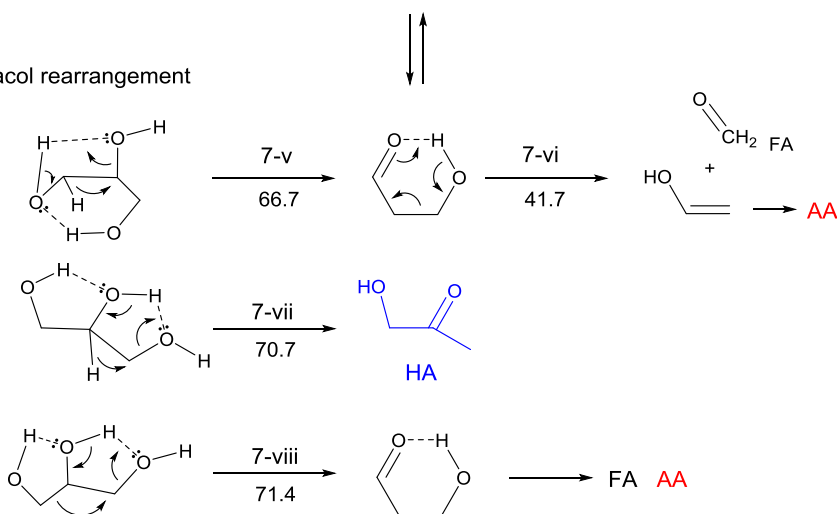
Cyclic-Grob fragmentation



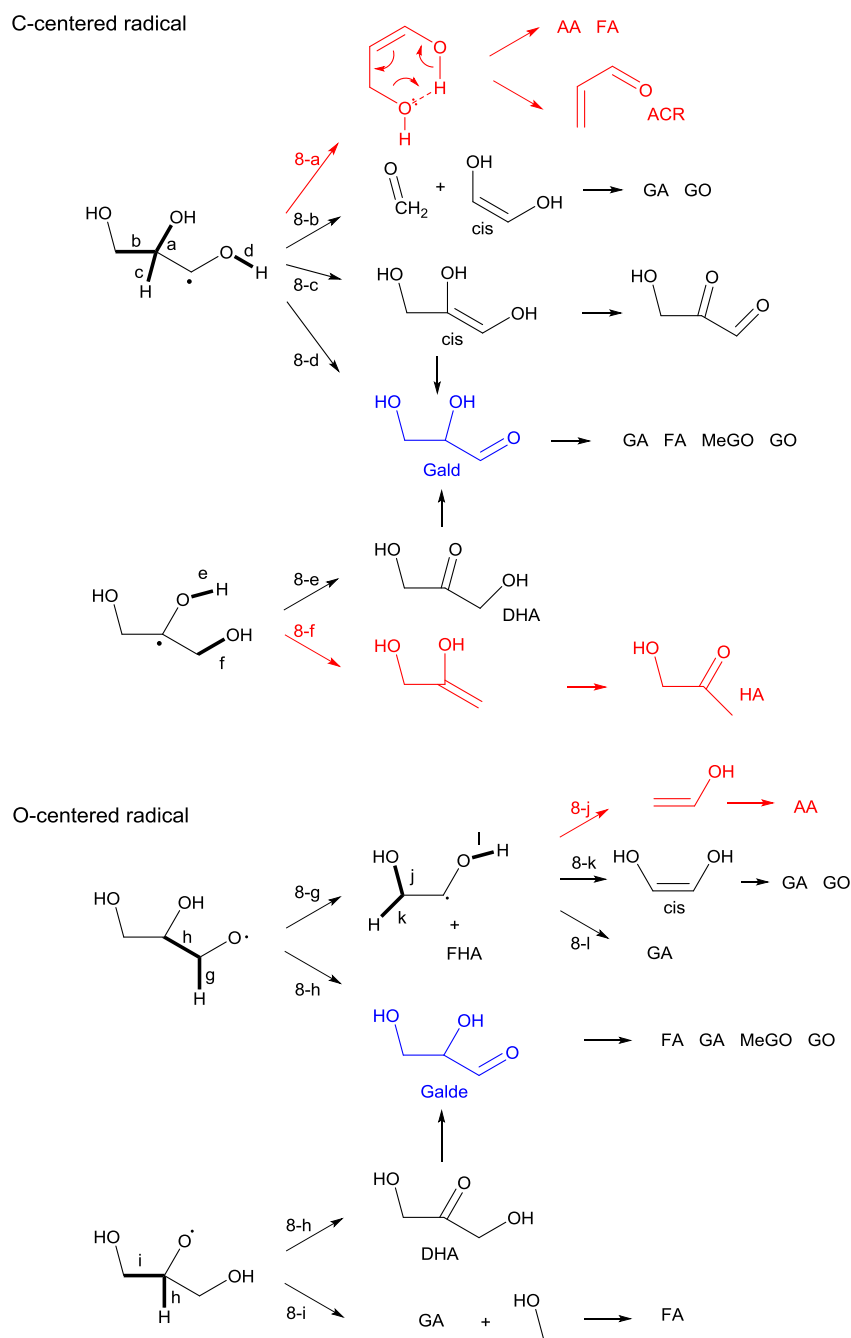
Direct dehydration



Pinacol rearrangement



Scheme 4-9. Possible heterolytic dehydration pathways for glycerol (Gly). The values next to the arrows represent the activation energies (kcal mol⁻¹), as calculated at the MP4(SDQ)//DFT(M06-2X) level. ACR, acrolein; HA, hydroxyacetone; AA, acetaldehyde; FA, formaldehyde; uni, unimolecular mechanism; bi, bimolecular mechanism.



Scheme 4-10. Possible radical chain pathways from the C- and O-centered radicals of glycerol (Gly). The bond with a bold line, which is located at the β -position to the radical, is expected to be cleaved through β -scission reaction. ACR, acrolein; MeGO, methylglyoxal; Gald, glyceraldehyde; DHA, 1,3-dihydroxyacetone; HA, hydroxyacetone; GA, glycolaldehyde; GO, glyoxal; AA, acetaldehyde; FA, formaldehyde.

4.2.3.3 Gas formation from the intermediates

As summarized in Figure 4-13, most of the condensable intermediates are aldehydes, which further fragment into the noncondensable gases. Radical chain reactions are expected for these fragmentations. Aldehydic hydrogens have been suggested as the predominant sites for hydrogen abstraction by $\bullet\text{OH}$, from experimental and theoretical investigations (Raúl Alvarez-Idaboy et al., 2001; Olivella and Solé, 2008; Castañeda et al., 2012). Prereactive complex formation between aldehyde and $\bullet\text{OH}$ has been proposed for this selective abstraction (Raúl Alvarez-Idaboy et al., 2001). Although the reactivities of alkyl radicals such as $\bullet\text{CH}_3$ remain unclear, the resulting acyl radical contributes to the fragmentation of aldehydes.

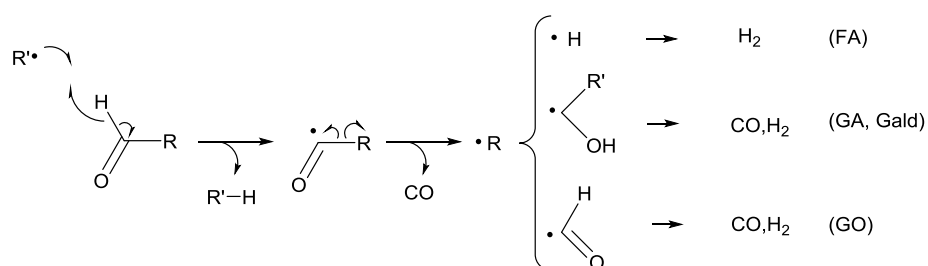
The α -scission of the acyl radical [$\bullet\text{CR}(=\text{O})$] forms CO and $\bullet\text{R}$, and then $\bullet\text{R}$ can be converted into the noncondensable gases as illustrated in Scheme 4-11. Therefore, the final gas compositions vary depending on the chemical structure of $\bullet\text{R}$. The intermediates such as FA, GA, Gald, and GO, which have sufficient O/C ratios for the CO formation, selectively produce syngas (CO and H_2). Hydrogen is produced from FA through hydrogen abstraction by the product $\bullet\text{H}$. When R is hydroxymethyl or hydroxymethyne group (for the fragmentations of Gald and GA), the resulting $\bullet\text{CR}'(\text{OH})$ fragments into $\text{CO} + \bullet\text{R}' + \bullet\text{H}$ via aldehyde [$\text{CR}'(=\text{O})$] as the intermediates. For GO (R: CHO), formyl radical ($\bullet\text{CHO}$) fragments into $\text{CO} + \bullet\text{H}$ through the α -scission reaction. These reactions cause highly selective production of syngas from polyalcohols, because these intermediates are the major products from polyalcohols through the radical chain pathways (Schemes 4-6, 4-8, and 4-10).

However, the acyl radicals with alkyl groups (AA, Pald, and ACR) can form hydrocarbon gases via the stabilization of the alkyl radical intermediates.

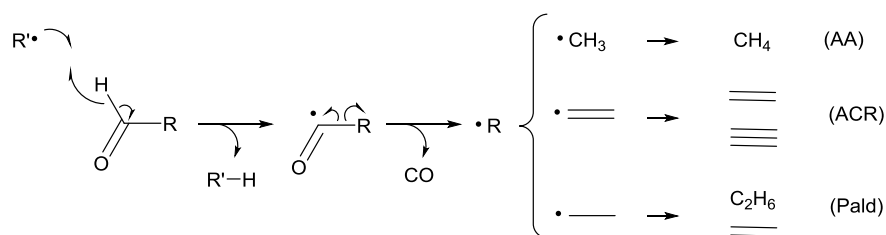
Therefore, the progression of the dehydration reactions, which lowers the O/C ratios of the intermediates (aldehydes) from polyalcohols, is a key process for the formation of hydrocarbon gases from polyalcohols, even if the elemental compositions are suitable for the production of syngas. Conversions from the hydrocarbon to the

oxygenated gases have been suggested only at a high temperature of 900 °C in our previous paper dealing with the gas-phase pyrolysis of levoglucosan. Recombination of the $\bullet\text{OH}$ formed from the product water with $\text{C}=\text{C}$ and $\text{C}\equiv\text{C}$ structures has been postulated for the explanation of these conversions.

(A) Oxygenate gas production



(B) Hydrocarbon gas production



Scheme 4-11. Oxygenated (A) and hydrocarbon (B) gas production as expected from the condensable intermediates (aldehydes) via acyl radicals.

4.2.4 Summary

Through discussion of the experimental results with the DFT calculations, the gas-forming reactions for hydrocarbons and syngas were indicated for the gas-phase pyrolysis of simple polyalcohols (glycerol, propylene glycol, and ethylene glycol) at 400, 600, and 800 °C under nitrogen flow (residence times: 0.9–1.4 s):

1. All the polyalcohols are reactive at 600 °C and produce condensable products in 15.7–24.7% yields (C-based), whereas they are completely converted into noncondensable gases at 800 °C.
2. Most of the condensable products that were gas-forming intermediates are aldehydes.
3. The noncondensable gases contain 20.3–35.3% (C-based) of hydrocarbons such as methane and ethylene along with syngas as the major components and smaller amounts of CO₂.
4. Dehydration via the bimolecular mechanism (the rate-determining step) followed by keto-enol tautomerization forms the aldehyde intermediates together with radical-induced fragmentation reactions.
5. The elimination of oxygen as water by dehydration forms hydrocarbons via aldehydes bearing alkyl groups, whereas the intermediates with hydroxymethylene and hydroxymethyne groups (such as glyceraldehyde and glycolaldehyde) are selectively converted into syngas through the α -scission of the acyl radical intermediates.
6. These findings provide insight into upgrading gasification processes and controlling the gas compositions between hydrocarbons and syngas for sustainable utilization of biomass in biofuel and biochemical applications.

4.3 Comparison of the Vapor-phase Reactivities between Levoglucosan and Methyl Glucosides

4.3.1 Introduction

Pyrolysis is the underlying principle of various thermochemical conversion technologies such as carbonization, fast pyrolysis and gasification for producing biofuels, biochemical, and biomaterials from biomass resources. Lignocellulosic biomass is the most promising bio resource, because there is a significant amount on the earth. Understanding the chemistry involved in the lignocellulose pyrolysis provides insights into the upgrading of these conversion processes.

Cellulose, which represents 40–50 wt.% of the chemical components of lignocellulose, is a crystalline polysaccharide that decomposes drastically around 350 °C, and a large amount of levoglucosan (LG) is produced (Shafizadeh et al., 1979; Kwon et al., 2007). Kwon et al. (2007) reported approximately 70 wt% of LG from the pyrolysis of microcrystalline cellulose under vacuum pyrolysis conditions. Thus, the pyrolysis behavior of LG has been studied extensively in both molten (Kawamoto et al., 2003; Hosoya et al., 2008; Bai, Johnston, and Brown, 2013) and gas (Shin et al., 2001; Hosoya et al., 2008) phases to understand the roles of intermediates during pyrolysis and gasification of cellulosic biomass.

The pyrolytic reactivity of LG is different in the molten and gas phases (Hosoya et al., 2008). As indicated in the early report of Pictet (1918), the molten LG polymerizes into polysaccharides through transglycosylation reactions at >240 °C, which is a temperature much lower than its formation temperature (around 350 °C) from cellulose. Alternatively, LG in the gas phase is stable and starts to decompose at higher temperatures >500 °C (residence time: 0.8–1.4 s), where fragmentation reactions selectively proceed to form C1–C3 aldehydes/ketones and noncondensable gases without forming any coke (*Chapter 3*). Any aromatic compounds such as benzenes and furans (furfural and 5-HMF) are not produced in the gas phase, which is explained later

by the homolysis-based fragmentation occurring at high temperatures prior to the formation of these compounds (Section 4.2). Because of these different reactivities in the molten and gas phases, extensive coking occurs only by cooling the gaseous LG produced from cellulose pyrolysis into the molten state (Hosoya et al., 2007).

LG and other sugar derivatives are stabilized in aprotic hydrogen-bond-acceptor solvents such as aromatic substances (Hosoya et al., 2006; Kawamoto et al., 2014) and polyethers (Matsuoka et al., 2012; Kawamoto et al., 2013). From these observations, hydrogen bond theory was proposed, in which intermolecular hydrogen bonds act as acid and base catalysts that promote pyrolytic reactions including transglycosylation in the molten phase. The stability of LG in the gas phase can be explained with this theory, because intermolecular hydrogen bonding is normally less important in the gas phase. However, there have been no reports to clarify whether this stability is characteristic feature of LG.

Transglycosylation forming LG and polysaccharides is the most important reaction of carbohydrates in molten-phase pyrolysis (Pictet, 1918; Wolfrom et al., 1959; Wolfrom et al., 1961; Shafizadeh and Fu, 1973). Concerted transglycosylation mechanisms have been proposed by the theoretical calculations for the gas-phase pyrolysis of methyl β -glucoside (Glc β OMe) (Hosoya, et al., 2009c) and other carbohydrates (Seshadri and Westmoreland, 2012; Hosoya and Sakaki, 2013; Mayes et al., 2014). Hosoya et al. (2009c) proposed uni- and bimolecular concerted mechanisms for the gas-phase conversion of Glc β OMe into LG, in which the $\Delta G^{0\ddagger}$ values are reduced to 47.7 and 36.4 kcal mol⁻¹, respectively. Thus, these reactions are expected to proceed at least in the gas phase. However, these reports are only based on theoretical calculations, because of the difficulty in studying only gas-phase pyrolysis of carbohydrates. Hence, the concerted transglycosylation mechanisms have not been confirmed by experimental study. Reactions do not proceed for gaseous LG at <500 °C.

In the present study, Glc β OMe, methyl α -glucoside (Glc α OMe) and LG were pyrolyzed only in the gas phase at 200, 300, 400, and 500 °C under a N₂ flow (residence times ranging from 1.2 to 2.0 s) to understand the reactivities of these compounds and

check the adaptability of the proposed concerted mechanisms.

4.3.2 Materials and methods

4.3.2.1 Materials

Glc α OMe, Glc β OMe (hydrated), and LG were purchased from Tokyo Chemical Industry Co. Ltd. (Tokyo, Japan), Sigma-Aldrich (St. Louis, MO, USA), and Carbosynth Limited (Compton, Berkshire, UK), respectively. Water trapped in the Glc β OMe crystals was eliminated before use by drying in an oven at 105 °C for 1 h, which were stored in a desiccator before use. Other chemicals were used as received without further purification.

4.3.2.2 Two-stage tubular reactor

A two-stage tubular reactor (Figure 3-1), which is fully described in our previous paper (*Chapter 3*) dealing with the gas-phase pyrolysis of LG, was used and composed of two cylindrical electric furnaces (internal diameter: 35 mm, length: 160 mm; Asahi Rika Seisakusho Co., Ltd., Chiba, Japan), serving as the evaporator and pyrolyzer. Each furnace included a quartz glass tube (internal diameter: 15 mm, wall thickness: 1.5 mm) and these tubes were connected. One end of the evaporator was attached to a nitrogen cylinder via a mass flow controller (SEC-400MK3, Horiba Ltd., Kyoto, Japan) and the other end, coming from the pyrolyzer, was connected to a gas wash bottle via a glass wool filter. A DMSO- d_6 solution (2.0 mL) containing an oximation reagent (NH₂OH•HCl) (20 mg) was placed in the gas wash bottle to recover the volatile products.

4.3.2.3 Pyrolysis

The procedure reported in *Chapter 3* was used by modifying the pyrolysis temperature and heating rate in the evaporator. A solution of Glc α OMe, Glc β OMe, or LG (5 mg) in methanol (0.1 mL) was applied to the area separated by the fringes in the evaporator tube, after which the methanol was evaporated under a nitrogen flow and the tube was completely dried in a desiccator under vacuum. A nitrogen flow (400 mL min⁻¹) was supplied for 30 min prior to conducting each pyrolysis trial to remove the air inside the reactor. The pyrolyzer was preheated at the desired temperature in the range of 200–500 °C, and the evaporator was heated to 120 °C over 12 min. The evaporator was subsequently heated to 190 °C at 5.8 °C min⁻¹. After holding the evaporator at 190 °C for 5 min, heating was stopped, and the tube reactor was cooled by opening the furnace covers and subsequently applying an air flow.

By this procedure, both glucosides were evaporated prior to molten-phase pyrolysis reactions and pushed into the pyrolysis zone, where pyrolysis reactions took place. The unreacted glucosides were recovered completely on the reactor wall outlet from the pyrolyzer and in the gas wash bottle.

The residence time of the pyrolyzer was defined as the period over which the gaseous substances were present in the region of the pyrolyzer with temperatures within the set value ± 25 °C. The residence times at 200, 300, 400, and 500 °C were estimated as 2.0, 1.6, 1.4, and 1.2 s, respectively.

The experiments were performed at least twice for each pyrolysis condition to confirm the reproducibility.

4.3.2.4 Characterization of the pyrolysis mixture

The condensates on the reactor tube interior wall and in the line between the reactor and the gas wash bottle were removed by rinsing with the solution in the gas wash bottle (2.0 mL of DMSO-*d*₆). The solution was analyzed directly by ¹H NMR spectroscopy using AC-400 (400 MHz) spectrometer (Bruker Biospin K.K., Yokohama, Japan) following the addition of 2-furoic acid as an internal standard. Quantifications of

methyl glucosides, LG, and other compounds, some of which with carbonyl groups were observed as the oxime derivatives (*cis/trans*), were performed using the peak areas of the NMR signals compared with those of the internal standard, as described in *Chapter 3*.

4.3.2.5 Computational methods

The calculations were conducted using the Gaussian 09 software package (Frisch et al., 2009). The geometry optimizations for nonradical reactants, products, and TSs were performed by employing the density functional theory method (M06-2X) and 6-31+G(d,p) basis sets. For radical products, UM06-2X/6-31+G(d,p) was employed. Vibrational frequency calculations used the same methods and basis sets. The energies of optimized geometries were calculated with same functional and 6-311+(d,p) basis set. The activation energy values and bond dissociation energies were estimated as the relative energies, including zero-point energies, between the reactants and the TSs or radicals. Frequency analysis showed one imaginary mode for the TS and no imaginary modes for the reactants, products, and precomplexes. In addition, we performed intrinsic reaction coordinate calculations to ascertain that the TS connected the reactant and product.

4.3.3 Results and discussion

4.3.3.1 Pyrolytic reactivity

Figure 4-16 shows the recoveries of methyl glucosides and LG after pyrolysis. The gaseous LG was stable in the temperature range of 200–400 °C, whereas the methyl glucosides decomposed even at the lowest temperature of 200 °C, although the conversion rates were not large. Thus, LG is clearly more stable than methyl glucosides in the gas phase.

As indicated by the ^1H NMR spectra (300 °C, Figure 4-17) of the $\text{DMSO-}d_6$ -soluble portions obtained from the pyrolysis of methyl glucosides, the major product obtained at 200 and 300 °C was LG. The yields from $\text{Glc}\alpha\text{OMe}$ and $\text{Glc}\beta\text{OMe}$ were only in the range of 3.7–14.0% (C-based), but these yields corresponded to 96.3% and 91.1% (200 °C) and 93.8% and 86.0% (300 °C), respectively, for the amounts of reacted glucosides. Transglycosylation reactions proceeded in a low temperature range, and LG is formed selectively from the gaseous methyl glucosides.

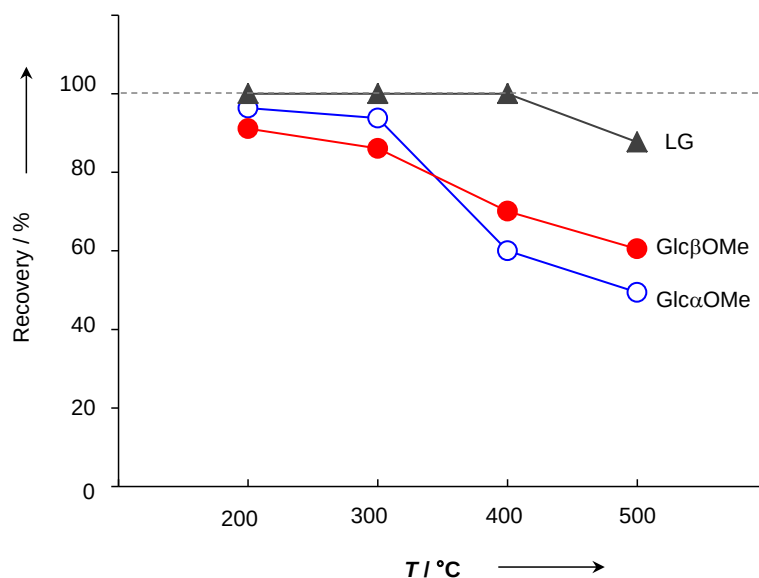


Figure 4-16. Recoveries of methyl α -glucoside ($\text{Glc}\alpha\text{OMe}$), methyl β -glucoside ($\text{Glc}\beta\text{OMe}$), and levoglucosan (LG) after the pyrolysis at 200, 300, 400, and 500 °C in the gas phase (residence time: 1.2–2.0 s, N_2 flow: 400 mL min^{-1}).

1,6-Anhydro- β -D-glucofuranose (AGF), the furanose isomer of LG, forms along with LG from the pyrolysis of cellulose and other glucose-based carbohydrates (Gardiner, 1966; Sanders et al., 2003; Patwardhan et al., 2009; Mettler et al., 2012). Microcrystalline cellulose (Avicel PH-101) gave a mixture of LG/AGF at the molar ratio of 89/11 by heating up to 500 °C (heating rate: 70 °C min⁻¹) under a N₂ flow at 400 mL min⁻¹. However, the AGF yields from the gaseous methyl glucosides were at negligible levels, as suggested by the enlarged spectra (300 °C) in Figure 4-17, where the LG/AGF molar ratios were calculated to be 96/4 (Glc α OMe) and 97/3 (Glc β OMe) from the comparison of the peak areas. These results indicate that the AGF formation proceeds mainly from the molten (liquid)-phase pyrolysis of glycosides.

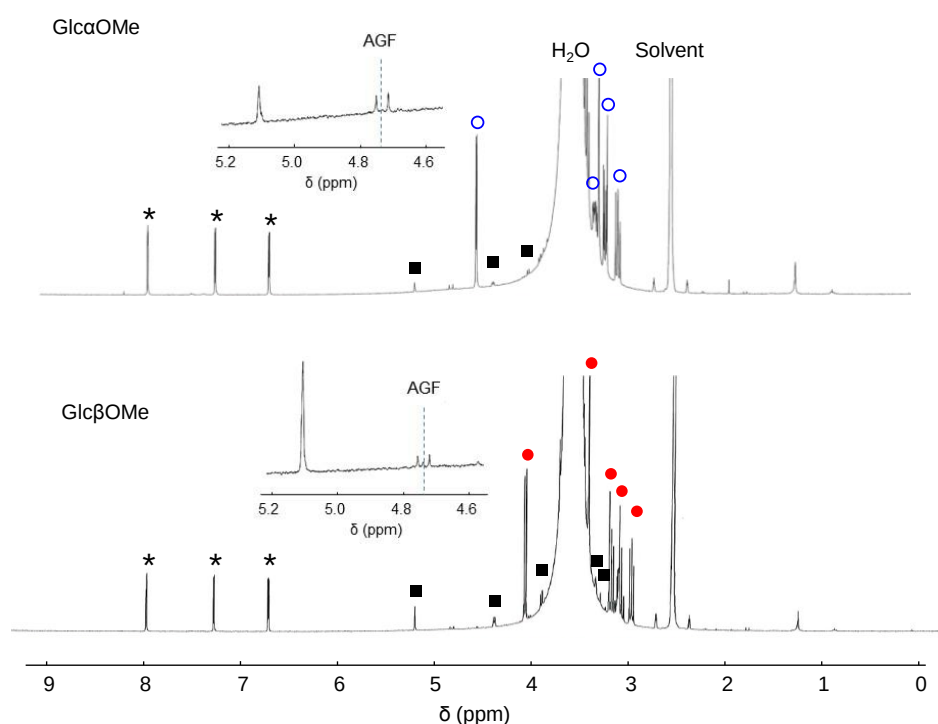


Figure 4-17. ¹H NMR spectra of the DMSO-*d*₆-soluble portions obtained from the pyrolysis of gaseous methyl α -glucoside (Glc α OMe) and methyl β -glucoside (Glc β OMe) at 300 °C with a residence time of 1.6 s under a N₂ flow of 400 mL min⁻¹. Legend: ■, levoglucosan (LG); ○, Glc α OMe; ●, Glc β OMe; *, internal standard (2-furoic acid).

By increasing the pyrolysis temperature to 400 °C, fragmentation products started to be produced from the gaseous methyl glucosides. As assigned in the NMR spectrum of Glc α OMe at 500 °C (Figure 4-18), acetic acid, formic acid and oxime derivatives (*cis/trans* isomers) of aldehydes were identified in the pyrolysis mixture along with LG. Only C1–C3 aldehydes were produced: C3 [methylglyoxal (MeGO)], C2 [glycolaldehyde (GA), glyoxal (GO), and acetaldehyde], and C1 [formaldehyde (Fald)].

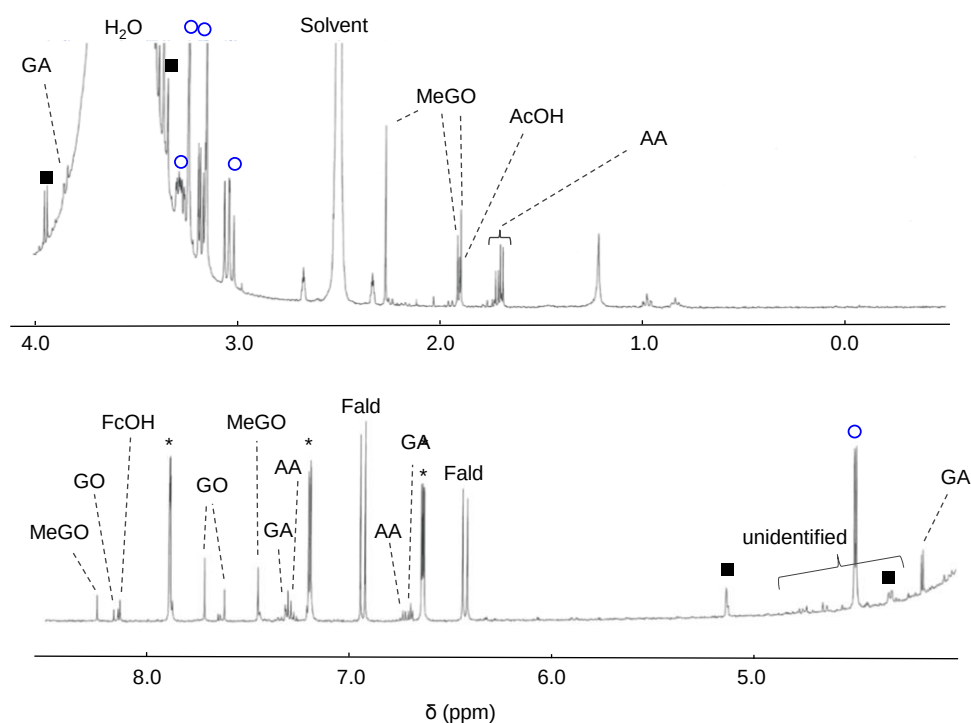


Figure 4-18. ^1H NMR spectrum of the $\text{DMSO-}d_6$ -soluble portion obtained from the pyrolysis of gaseous methyl α -glucoside (Glc α OMe) at 500 °C with a residence time of 1.2 s under a N_2 flow of 400 mL min^{-1} . Legend: ■, levoglucosan (LG); ○, Glc α OMe; *, internal standard (2-furoic acid); acetaldehyde (AA); acetic acid (AcOH); formaldehyde (Fald); formic acid (FcOH); glycolaldehyde (GA); glyoxal (GO); methylglyoxal (MeGO).

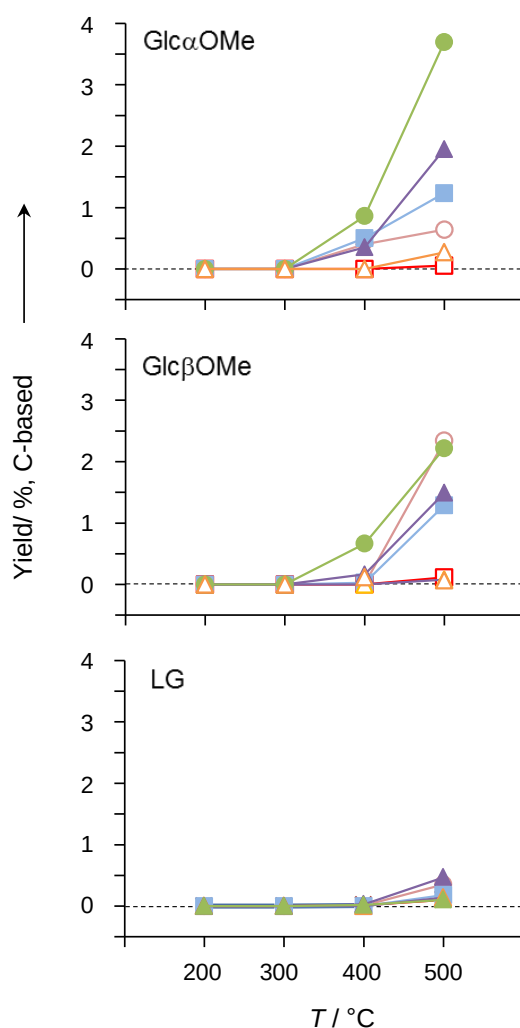


Figure 4-19. Yields of fragmentation products from methyl α -glucoside (Glc α OMe), methyl β -glucoside (Glc β OMe), and levoglucosan (LG) after the pyrolysis at 200, 300, 400, and 500 °C in the gas phase (residence times: 1.2–2.0 s, N₂ flow: 400 mL min⁻¹). Legend: ●, methylglyoxal; ▲, formaldehyde; ■, glycolaldehyde; ○, glyoxal; △, acetaldehyde; □, formic acid.

In Figure 4-19, the yields of the fragmentation products are plotted against the pyrolysis temperature and compared between methyl glucosides and LG. Fragmentation reactions of LG started at 500 °C, which is higher than the onset temperature (400 °C) of methyl glucosides. Thus, LG is more stable against fragmentation and

transglycosylation. The major fragmentation products from methyl glucosides were MeGO, Fald, GA, and GO. Noncondensable gases are also expected to form along with the condensable products by the fragmentation reactions, but any attempts to analyze the gaseous products with micro gas chromatography failed because of the low concentration by dilution with nitrogen.

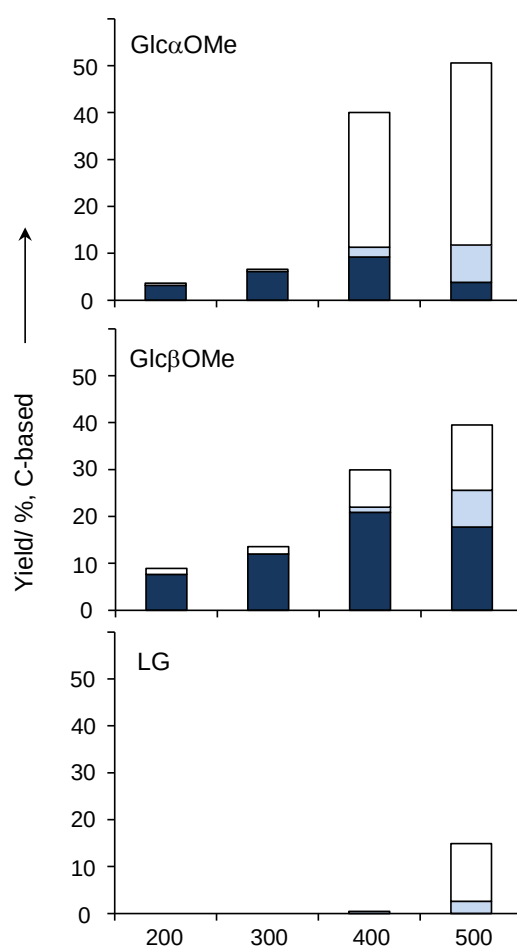


Figure 4-20. Yields of levoglucosan (LG; except for the case of LG pyrolysis), fragmentation products, and gas/unidentified products from methyl α -glucoside (Glc α OMe), methyl β -glucoside (Glc β OMe), and LG after the pyrolysis at 200, 300, 400, and 500 °C in the gas phase (residence times: 1.2–2.0 s, N₂ flow: 400 mL min⁻¹). Legend: □, gas/unidentified products; ■, fragmentation products; ■, LG

Figure 4-20 summarizes the yields of LG (except for the case of LG pyrolysis), fragmentation products and gas/unidentified products for each pyrolysis temperature. The greater stability of LG against the reactions forming these products is shown in this figure. Some different features depending on the anomer type of methyl glucosides were also identified. Transglycosylation reactivity forming LG at low pyrolysis temperatures (200–400 °C) were greater in the β -anomer, whereas the fragmentation reactivity that were greater at higher temperatures (400–500 °C) were in the opposite order ($\text{Glc}\alpha\text{OMe} > \text{Glc}\beta\text{OMe}$). These results are consistent with the temperature dependency shown in Figure 4-16, where the reactivity order for $\text{Glc}\alpha\text{OMe}$ and $\text{Glc}\beta\text{OMe}$ is reversed in the temperature range of 300–400 °C.

4.3.3.2 Gas-phase reaction mechanism

Transglycosylation

Methyl glucosides produced LG at a low pyrolysis temperature of 200 °C in the gas phase, whereas LG was stable even at 400 °C. These observations can be discussed with the concerted heterolysis mechanisms as proposed by Hosoya et al. (2009) for the conversion from $\text{Glc}\beta\text{OMe}$ to LG (Figure 4-21). In the unimolecular mechanism, conformational change from C1 to 1C is followed by the coordination of $\text{C}_6\text{-OH}$ to C_1 (glycosidic)- O , to form a four-membered cyclic TS, which makes the intramolecular nucleophilic substitution at C1 easier ($\Delta G^{0\ddagger}$ 47.7 kcal mol⁻¹). They also indicated the possibility of a bimolecular mechanism, in which the association of $\text{C}_6\text{-OH}$ and $\text{C}_1\text{-O}$ with $\text{C}_6\text{-OH}$ of another molecule forms a more stable six-membered cyclic TS, reducing the $\Delta G^{0\ddagger}$ further to 36.4 kcal mol⁻¹. The bimolecular concerted mechanism with the lower $\Delta G^{0\ddagger}$ (36.4 kcal mol⁻¹) explains the low temperature conversion at 200 and 300 °C, because the $\Delta G^{0\ddagger}$ of the unimolecular mechanism (47.7 kcal mol⁻¹) is too large for a feasible reaction.

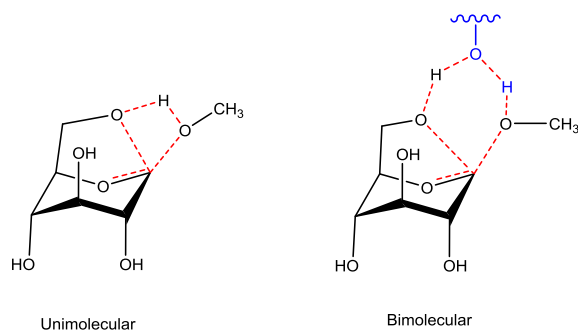


Figure 4-21. Uni- and bimolecular concerted mechanisms proposed by Hosoya et al. (2009) for the conversion from methyl β -glucoside to levoglucosan.

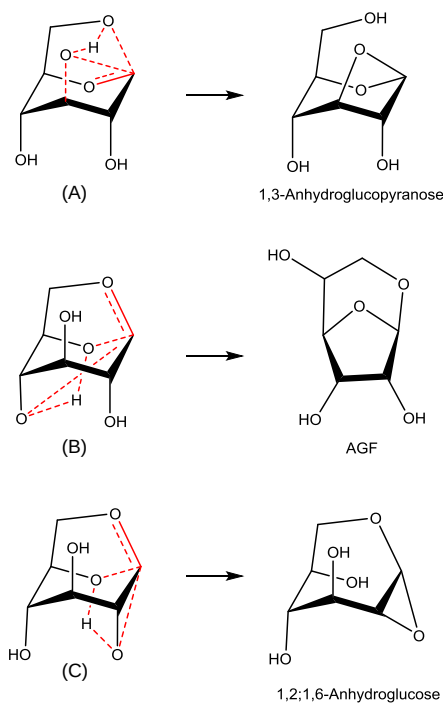


Figure 4-22. Transition states of the unimolecular concerted mechanisms for levoglucosan.

No reasonable unimolecular concerted mechanisms were made for $\text{Glc}\alpha\text{OMe}$ because of the anomeric effect, despite the selective formation of LG. The bimolecular mechanism must be adopted to explain the formation of LG from $\text{Glc}\alpha\text{OMe}$ with the concerted mechanism, although the theoretical trials to find the TSs have not been

successful. A low selectivity of the LG formation from Glc α OMe than the β -anomer at 400 °C (Figure 4-20) may be because of the missing unimolecular mechanism with the higher $\Delta G^{0\ddagger}$. Further studies are necessary to conclude these hypotheses, and the present results provide an experimental support for the concerted heterolysis mechanisms proposed by Hosoya et al. (2009c).

Several TSs can also be proposed for the concerted mechanisms of gaseous LG (Figure 4-22), but the complete recovery of the LG in the temperature range of 200–400 °C indicates that these reactions did not proceed. The instability of these TSs due to the steric effects of the bicyclic ring of LG would be an acceptable reason, and any TSs have not been identified, despite the computational trials of the theoretical calculations. 1,3-Anhydroglucopyranose and 1,2;1,6-anhydroglucose obtained from TSs (A) and (C) would be unstable because of the inclusion of a sterically hindered four-membered ring and a bicyclic acetal system with a three membered epoxide ring, respectively.

Fragmentation

Fragmentation mechanisms of the gaseous LG have been discussed in our previous paper (Section 4-4), and radical chain mechanisms are postulated instead of heterolysis reactions from the kinetic data. We discussed the different fragmentation reactivities (Glc α OMe > Glc β OMe > LG) in terms of the reactivities of the C- and O-centered radicals, which are formed through hydrogen abstractions by radical species from C–H and O–H groups, respectively. Although the selectivity of the hydrogen abstraction during pyrolysis is unclear, 1-C, 6-C, and 6-O radicals shown in Figure 4-23 were considered, because formation of these radicals are expected to be greatly different between methyl glucosides and LG. Radical type 6-O cannot be formed from LG.

To cleave the C–C and C–O bonds from radicals through β -scission reactions, these bonds must be in the same plane with the radical p orbitals (Parsons, 2000). The bonds that can be cleaved were limited as shown with the red bold lines in Figure 4-23. Although several β -scission reactions can occur for the radicals from Glc α OMe and

Glc β OMe, no bonds are cleaved from the LG radicals because of the steric effects of bicyclic ring. Thus, these LG radicals are stabilized as LG by the abstraction of hydrogen from other molecules.

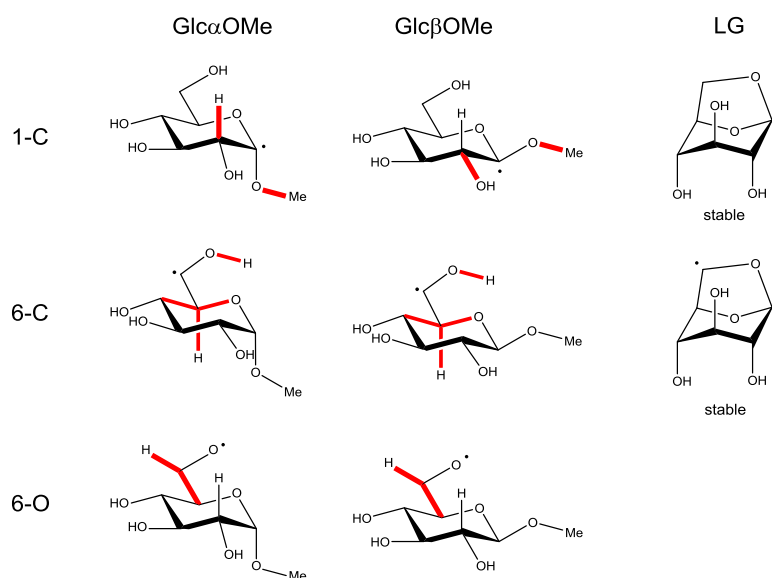


Figure 4-23. Cleavable linkages (red bold lines) through β -elimination for C- and O-centered radicals from methyl α -glucoside (Glc α OMe), methyl β -glucoside (Glc β OMe), and levoglucosan (LG).

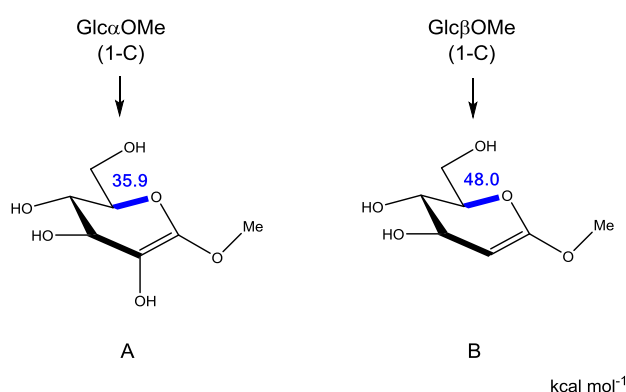
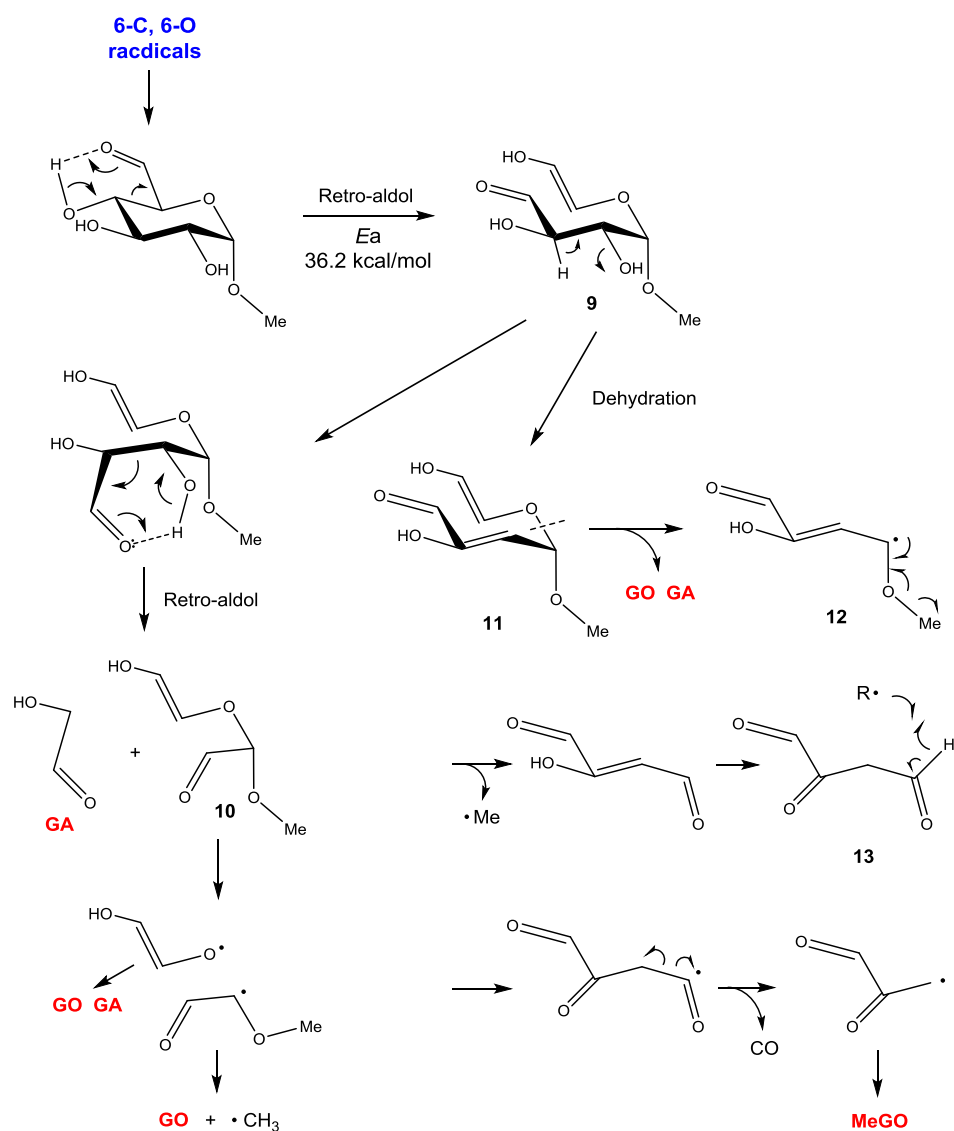


Figure 4-24. Vinyl ethers that can be formed through β -scission reactions of the 1-C radicals from methyl α -glucoside (Glc α OMe) and methyl β -glucoside (Glc β OMe) along with the bond dissociation energies of the vinyl ether C–O bonds.

Among the postulated β -scission reactions in Figure 4-23, the 1-C radicals produce vinyl ethers A and B with different oxidation states at C₂ (Figure 4-24), and they show different bond dissociation energies of the C₅–O bonds, which were calculated as 35.9 kcal mol⁻¹ for A from the α -anomer and 48.0 kcal mol⁻¹ for B from the β -anomer. In *Section 4-4*, discussing LG fragmentation, double bond formation to produce vinyl ether and conjugated carbonyl structures, are suggested to promote the fragmentation reactions through forming lower bond dissociation energy bonds, which result in cleaving homolytically to form pairs of radicals to accelerate the radical chain reactions. Thus, this efficiency is expected to be greater for Glc α OMe, which reasonably explains the fragmentation reactivity: Glc α OMe > Glc β OMe.

Using the reactivity of gaseous glyceraldehyde as a model of LG degradation intermediates compared with that of glycerol, we reported that the introduction of C=O to polyalcohol significantly accelerated the fragmentation reactions by the progression of retro-aldol fragmentation and dehydration reactions (*Section 4.1*). Dehydration reaction is accelerated by the C=O group, because the C=O group increases the acidity of the adjacent C–H group.

Fragmentation pathways via the 6-C and 6-O radicals formed from Glc α OMe are considered as illustrated in Scheme 4-12. A retro-aldol fragmentation via a six-membered TS (calculated activation energy: 36.2 kcal mol⁻¹) would proceed for the C₆=O intermediate to form intermediate **9**, which is further fragmented into GA and **10** by an additional retro-aldol fragmentation. Compound **10** with a weak vinyl ether bond would fragment further, which results in the formation of GO, GA and methyl radical. Alternatively, intermediate **9** would dehydrate to form **11** with a weak vinyl ether bond that is attached to a conjugated C=O, which is cleaved homolytically to GO, GA, along with radical **12**. This radical can be converted further into MeGO and CO. Consequently, these postulated pathways reasonably explain the formation of the major fragmentation products, i.e., MeGO, GA, and GO, from the gaseous methyl glucosides at >400 °C. Fald would be formed from the fragmentation of GA.



Scheme 4-12. Postulated fragmentation pathways for the $\text{C}_6=\text{O}$ intermediate formed from the 6-C and 6-O radicals of methyl α -glucoside, with retro-aldol fragmentation and dehydration as key reactions.

4.3.3.3 Roles of molten- and gas-phase reactions in the pyrolysis of methyl glucosides

The product compositions from the gaseous methyl glucosides were different from those of the pyrolysis including molten-phase reactions. These features provide insights into the roles of molten- and gas-phase reactions during the pyrolysis of methyl glucoside (GlcOMe) as summarized in Figure 4-25.

Along with AGF, no furans (furfural and 5-HMF) were obtained from the pyrolysis of GlcOMe (gas) and LG (gas). Thus, the transformation from the pyranose to five-membered heterocyclic rings does not effectively proceed in the gas-phase pyrolysis. Hence, AGF and furan formations probably originate from the molten-phase reactions prior to evaporation into the gas phase.

The pyran to furan ring transformation is possible via the chain structure of glucose, which may form by hydrolysis reactions. The yields of AGF and furans are reported to change depending on the degree of polymerization, i.e., content of reducing end (Gardiner, 1966; Sanders et al., 2003; Patwardhan et al., 2009; Mettler et al., 2012), which can be converted into the chain structure. For example, Gardiner (1966) reported the AGF yield decreased with the increase in the degree of polymerization: glucose (10.9 %) > cellobiose (2.8 %) > cellulose (1.5 %), and Kato (1967) reported the same tendency for the formation of furfural: glucose (11.7 %) > cellobiose (7.7 %) > cellulose (3.7 %). These reported results support the above hypothesis. Hydrolysis of cellulose proceeds effectively in a sealed reactor (Mok et al., 1992; Várhegyi et al., 1993). However, progression of the hydrolysis reactions is also reported to proceed in a quasi-sealed space formed in the cellulose cell wall and molten glycosides during pyrolysis (Várhegyi et al., 1993; Yu et al., 2012; Matsuoka et al., 2014, 2016). Thus, hydrolysis by the produced water would proceed during the molten-phase pyrolysis of methyl glucosides and LG, which results in the formation of AGF, furfural, and 5-HMF.

The evaporation process of GlcOMe and the product LG is expected to compete with the molten-phase reactions forming polysaccharides, AGF, furfural, and 5-HMF.

The GlcOMe (gas) undergoes simpler reactions in the gas phase, i.e., transglycosylation to form LG (gas) and fragmentation. The greater stability of LG (gas) may be a reason why large amounts of LG are produced from the pyrolysis of GlcOMe, cellulose, and other glucose-based carbohydrates.

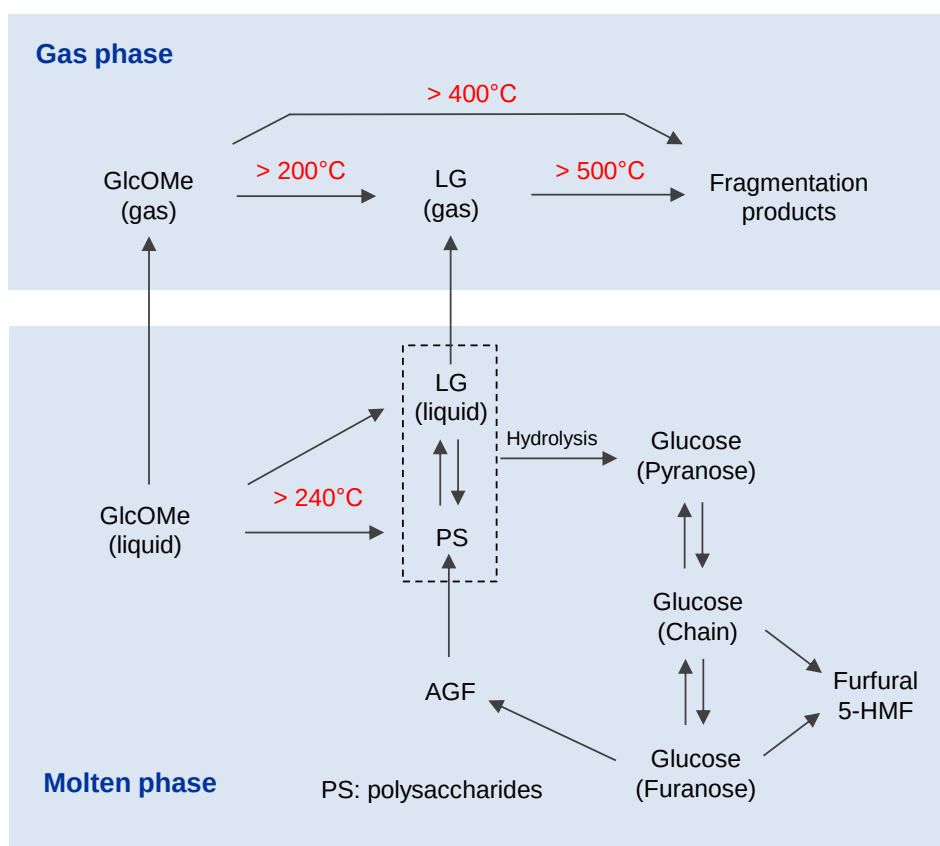


Figure 4-25. A proposed mechanism for the pyrolysis of molten methyl glucoside (GlcOMe), focusing on the molten- and gas-phase reactions.

4.3.4 Summary

Pyrolytic reactivities of GlcOMe were studied only in the gas phase for the first time and compared with that of LG. The following results were obtained:

1. The gaseous GlcOMe produces LG selectively at low pyrolysis temperatures (200 and 300 °C), at which LG is completely stable.
2. Selective transglycosylation of GlcOMe is explained with the uni- and bimolecular concerted heterolysis mechanisms as proposed from the theoretical calculations.
3. Selective LG formation from Glc α OMe (α -isomer) suggests the involvement of the bimolecular mechanism, because the unimolecular mechanism cannot occur for the α -isomer for steric reasons.
4. The greater stability of LG for transglycosylation is explained by the steric effects of the bicyclic ring system, which creates unstable transition states in the concerted mechanisms.
5. Fragmentation of GlcOMe starts at 400 °C, although higher temperatures >500 °C are required for LG.
6. Difference fragmentation reactivity (Glc α OMe > Glc β OMe) can be explained in terms of the radical chain reactivity.
7. The AGF yields are low and no furans are obtained from the gaseous GlcOMe. These compounds are suggested to originate mainly from the molten-phase pyrolysis reactions.
8. Unconventional stability of LG against transglycosylation and fragmentation reactions is suggested to be a reason for the formation of large amounts of LG from the pyrolysis of carbohydrates including GlcOMe and cellulose.
9. These findings provide insights for the efficient production of LG from glucose-based carbohydrates and efficient gasification of cellulosic biomass.

4.4 Kinetics and Molecular Mechanisms of Vapor-phase Levoglucosan Degradation

4.4.1 Introduction

Gasification can utilize biomass resources for biofuel and biochemical production. The producer gas can be used for electricity generation by gas engines/turbines and petroleum synthesis via syngas (CO and H₂) on Fischer–Tropsch catalysts. However, tar and coke by-products from biomass gasification cause problems, which include clogging pipelines from the gasifier and deactivating Fischer–Tropsch catalysts. In addition, the energy efficiency is reduced at high gasification temperatures such as 800–1000°C (L. Devi et al., 2003), which mitigate the tar/coke problem. Additional reheating processes including the injection of air (Narváez et al., 1996) and water scrubbing, to reduce tar/coke deposition, also reduce efficiency (Woolcock and Brown, 2013; Abdoulmoumine et al., 2015; Zhao et al., 2015). Understanding the fundamental chemistry in biomass gasification is helpful to establish reliable tar/coke-free clean gasification systems. This section reports the molecular mechanisms for the gas-phase degradation of levoglucosan (LG), which is the major volatile intermediate from cellulose during gasification of wood and other lignocellulosic biomass resources (Shafizadeh et al., 1979; Kwon et al., 2007).

The reactivity of LG differs in the gas and molten phases (Hosoya et al., 2008a). Molten LG decomposes (polymerized) at 250 °C, which is a temperature much lower than the formation temperature (around 350 °C) from cellulose pyrolysis. However, LG is significantly stabilized in the gas phase up to around 500 °C, and selectively fragments into C1 and C2 aldehydes/ketones and noncondensable gases at higher temperatures (Hosoya et al., 2008a). Gaseous LG does not produce any coke, furans, and aromatics, although the formation of these dehydration products occurs in the pyrolysis of molten LG. This enhanced reactivity of the pyrolytic reaction of LG in the molten phase has been explained using hydrogen bond theory, in which

intermolecular hydrogen bonds act as acid and base catalysts (Matsuoka et al., 2012; Kawamoto et al., 2013; Kawamoto et al., 2014). However, the molecular mechanisms of the gas-phase fragmentation of LG remain unclear, although this is an important process for tar/coke-free clean biomass gasification. Elucidating the molecular mechanisms provides insight into the control of gasification and the development of low-temperature clean gasification systems.

There are limited reports on the gas-phase reactions of LG (Antal, 1983; Evans and Milne, 1987; Li et al., 2001; Shin et al., 2001; Morf et al., 2002; Norinaga et al., 2013). Shin et al. (2001) reported the E_a , 44.1 kcal mol⁻¹, for the pyrolytic degradation of gas-phase LG using a two-stage flow-type reactor. However, the furanic compounds, which are not produced from gas-phase LG, were detected in their experimental results. Thus, these experiments may include the pyrolytic reactions of molten LG, which may occur prior to evaporation. In *Chapter 3*, the degradation behavior of gas-phase LG has been reported with a similar two-stage flow-type reactor by controlling the evaporator temperature to selectively vaporize molten LG prior to their reactions occurring. However, no kinetic investigations were conducted with this system.

Therefore, in this section, the results of kinetic analysis of the gas-phase LG are described, and the molecular mechanisms are discussed from the reactivities of model compounds (permethylated LG, glycerol, propylene glycol, and ethylene glycol; Figure 4-26) as well as theoretical calculation results with DFT. The degradation mechanisms of gaseous glyceraldehyde (aldose) and 1,3-dihydroxyacetone (ketose) suggested in *Section 4.1* are also included for discussion. These compounds are reactive C3 model compounds that contain carbonyl groups in the degradation of gas-phase LG.

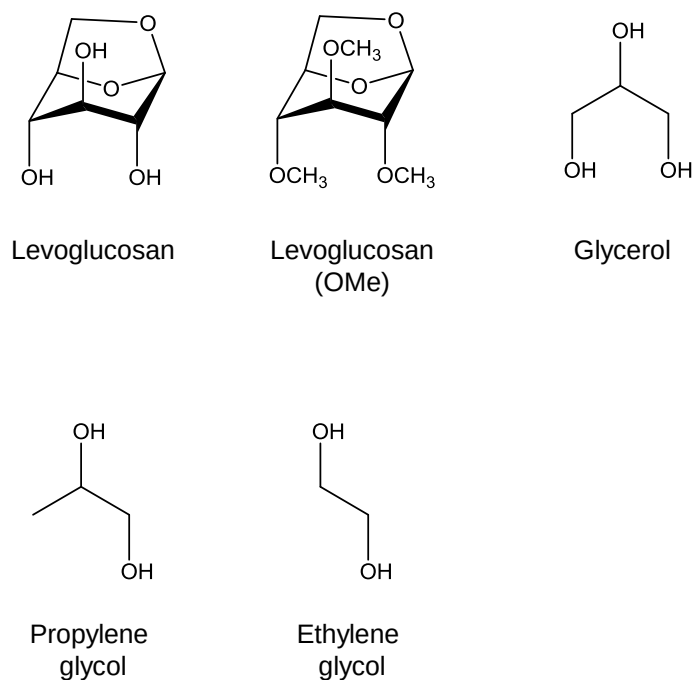


Figure 4-26. Levoglucosan and model compounds used in this study.

4.4.2 Materials and methods

4.4.2.1 Materials

LG used for pyrolysis trials was purchased from Carbosynth Ltd. (Berkshire, UK), which was used as received, without further purification. Other reagents and solvents were obtained from Nacalai Tesque, Inc. (Kyoto, Japan). Permethylated LG was prepared by the methylation of LG with methyl iodide in the presence of sodium hydride in dimethylformamide (DMF) and used for the pyrolysis after purification using silica gel column eluted with 5% methanol/ CHCl_3 (82.1 % yield).

4.4.2.2 Two-stage tubular reactor

The two-stage tubular reactor (Figure 3-1) was used and composed of two cylindrical electric furnaces (internal diameter: 35 mm, length: 160 mm, Asahi Rika Seisakusho Co., Ltd.), serving as the evaporator and pyrolyzer, respectively. Each furnace included a quartz glass tube (internal diameter: 15 mm, wall thickness: 1.5 mm) and these tubes were connected to one another. The right end of the evaporator was attached to a nitrogen cylinder via a mass flow controller (Horiba SEC-400MK3) and the other end, coming from the pyrolyzer, was connected to a gas wash bottle via a glass wool filter. Air flow was supplied to the outer part of the tube coming from the pyrolyzer to quench the pyrolysis reactions. The gas wash bottle held methanol (100 mL).

4.4.2.3 Pyrolysis

The procedure reported in *Chapter 3* and *Section 4.1* was utilized by modifying the nitrogen flow rate to change the residence time. A solution of LG (15 mg) in methanol (0.20 mL) was applied to the area separated by the fringes in the evaporator tube, after which the methanol was evaporated under a nitrogen flow and the tube was completely dried in a desiccator under vacuum. A nitrogen flow ($1000\text{--}3500\text{ mL min}^{-1}$) was supplied for 30 min prior to conducting each pyrolysis trial so as to sweep out the air inside the reactor. The pyrolyzer was preheated at the desired temperature in the range of $550\text{--}700\text{ }^{\circ}\text{C}$ and the evaporator was heated to $120\text{ }^{\circ}\text{C}$ over 5 min and this temperature was maintained for an additional 5 min. The evaporator was subsequently heated to $200\text{ }^{\circ}\text{C}$ at $16\text{ }^{\circ}\text{C min}^{-1}$. When the temperature reached approximately $185\text{ }^{\circ}\text{C}$, the LG melted and began to vaporize. After holding the evaporator at $200\text{ }^{\circ}\text{C}$ for 5 min, heating was stopped and the tube reactor was cooled by opening the furnace covers and subsequently applying an air flow. Three times of experiments were performed for each pyrolysis condition.

The residence time of the pyrolyzer was defined as the period over which the gaseous substances were present in the region of the pyrolyzer with temperatures within the set value ± 25 °C. The internal temperature profiles of the pyrolyzer and evaporator were obtained for each set temperature by direct measurement during preliminary control trials conducted without the addition of LG. The residence times as estimated at the four nitrogen flow rates, 1000, 1900, 2300, and 3500 mL min⁻¹ were 0.45, 0.24, 0.20, and 0.13 s for 550 °C; 0.43, 0.23, 0.19, and 0.12 s for 600 °C; 0.40, 0.21, 0.18, and 0.12 s for 650 °C; 0.38, 0.20, 0.17, and 0.11 s for 700 °C, respectively. The pressure inside the reactor was measured and was found to equal atmospheric pressure.

Pyrolysis experiments of the model compounds including permethylated LG were conducted basically with the similar procedures except for the nitrogen flow rate (400 mL min⁻¹, residence time: 1.2 s), and the results were compared with those of LG at the same flow rate. The details of the experimental procedure for the pyrolysis of glycerol, propylene glycol and ethylene glycol are described in the literature.

4.4.2.4 Quantification of levoglucosan

The condensates on the reactor tube interior wall and in the line between the reactor and the gas wash bottle were removed by rinsing with the solution in the gas wash bottle (100 mL of methanol), and the solution was evaporated in vacuo. The resulting residue was solubilized in 1 mL of DMSO-*d*₆ and analyzed directly by ¹H NMR spectroscopy using a Bruker AC-400 (400 MHz) spectrometer following the addition of 2-furoic acid as an internal standard. Quantifications of LG and permethylated LG were performed based on the peak areas of the NMR signals as compared with those of the internal standard.

4.4.2.5 Computational methods

The calculations were conducted using the Gaussian 09 software package

(Frisch et al., 2009). The geometry optimizations for nonradical reactants, products, and TSs were performed by employing the DFT method (M06-2X) and 6-31+G(d,p) basis sets. For radical products, UM06-2X/6-31+G(d,p) was employed. Vibrational frequency calculations used the same methods and basis set. The energies of optimized geometries were calculated with same functional and 6-311+(d,p) basis set. The E_a values and BDEs were estimated as the relative energies, including zero-point energies, between the reactants and the TSs or radicals. Frequency analysis showed one imaginary mode for the TS and no imaginary modes for the reactants, products and precomplexes. In addition, we performed IRC calculations to ascertain that the TS connected the reactant and product.

4.4.3 Results and discussion

4.4.3.1 Gas-phase degradation kinetics of levoglucosan

Gaseous LG was pyrolyzed at 550, 600, 650, and 700 °C with residence times in the range 0.11–0.45 s. A two-stage tubular reactor was used for the pyrolysis to study only gas-phase LG by controlling the evaporator temperature. We assumed that the rate-determining step for the decomposition of gaseous LG obeys a first order reaction and not zero and second order reactions, because the test plots of the rate equations for zero and second order reactions were not linearly proportional.

The plots of natural log of the recovery of LG ($-\ln [LG]/[LG]_0$) against the residence time are shown in Figure 4-27, where $[LG]$ and $[LG]_0$ represent the amounts of LG recovered after pyrolysis and the initial amount used in the experiment, respectively. When the reaction is first order, these relationships must exhibit a linear equation. This criterion is satisfied at 550 °C, the lowest temperature used in this study, and for short residence times at 600–700 °C. For longer residence times, however, these plots deviated from linear relationships. These results indicate that the degradation of gaseous LG starts as a first order reaction, but the reaction rate increases with increasing

residence time. These features indicate the initiation and the following radical chain mechanism.

Therefore, the rate constants, which may obey first order reactions, were evaluated from data points obtained at the shortest residence time for each pyrolysis temperature of 600–700 °C. The Arrhenius plots from the resulting rate constants are shown in Figure 4-28. These plots cannot be explained with a single straight line, which indicates that the rate-determining step changes depending on the pyrolysis temperature. Thus, two lines are provisionally provided for data sets of the plots of 550/600 °C and 600/650/700 °C with kinetic parameter sets of E_a : 35.1 kcal mol⁻¹/ A : 2.03 × 10⁹ and E_a : 16.7 kcal mol⁻¹/ A : 3.03 × 10⁵, respectively. These E_a values, which are much smaller than those of the heterolysis reactions discussed below, cannot explain the gas-phase degradation of LG only with a heterolysis mechanism.

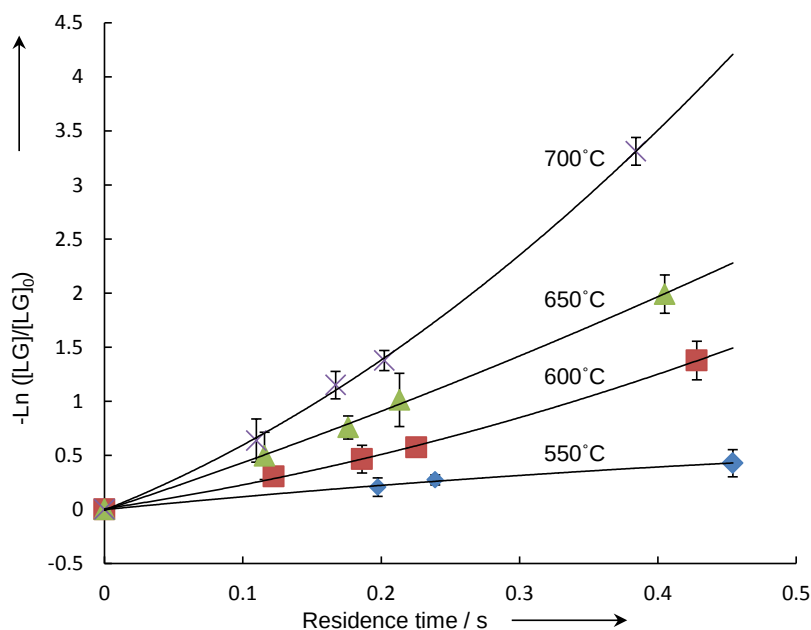


Figure 4-27. $-\ln ([\text{LG}]/[\text{LG}]_0)$ plotted against residence time during the pyrolysis of gaseous levoglucosan (LG) at 550, 600, 650, and 700 ° C. Error bars represent the standard deviation ($n=3$).

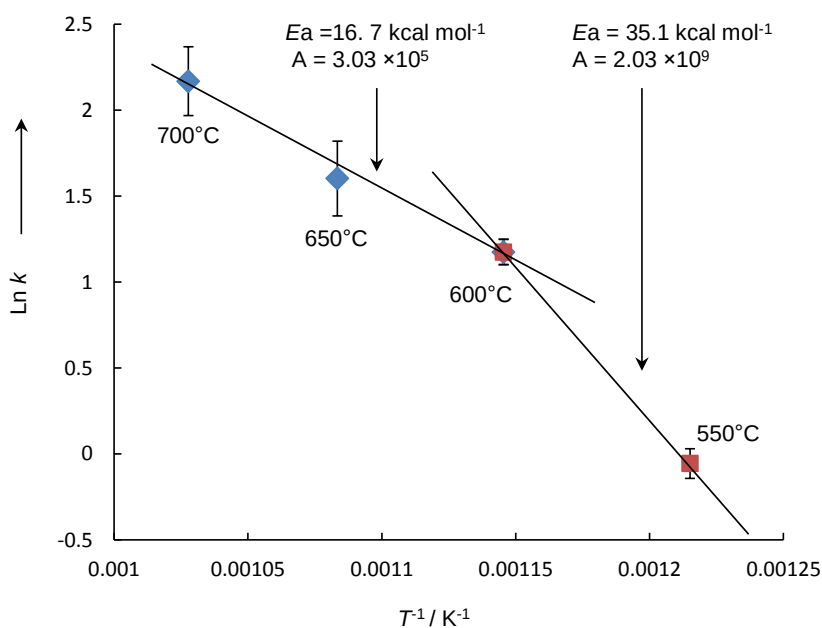


Figure 4-28. Arrhenius plots of the decomposition rates (k) of levoglucosan in the gas phase. Error bars represent the standard deviation ($n=3$).

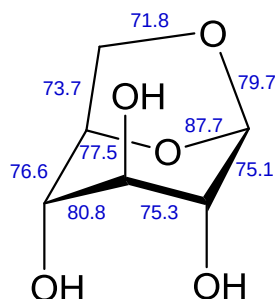


Figure 4-29. Bond dissociation energies (kcal mol^{-1}) of the C–C and C–O bonds of levoglucosan as calculated from geometry optimization using DFT(M06-2X)/6-31+G(d,p) followed by energy calculations with DFT(M06-2X)/6-311+G(d,p). DFT(UM06-2X) was used for the calculations of radicals.

4.4.3.2 Model compound reactivity

A cyclic Grob reaction via the 6-membered transition state, direct dehydration, and pinacol rearrangement have been postulated from theoretical calculations (Nimlos et al., 2006). To understand the roles of these heterolysis reactions, gas-phase reactivities of 2,3,4-tri-*O*-methyl-1,6-anhydro- β -D-glucopyranose (permethylated LG) and several C2–C3 polyalcohols (Figure 4-26) were investigated at 400–800 °C with similar methods as those used for LG. The pyrolytic reactions of these model compounds were discussed in *Section 4.1* and *4.2* with other experimental and computational results. As observed for LG, these compounds became reactive by increasing the pyrolysis temperature to 600 °C, where the recovery decreased in the order of LG (19.3 %) < permethylated LG (28.6 %) < glycerol (32.0 %) < propylene glycol (43.2 %) < ethylene glycol (53.7 %).

LG and glycerol, in which cyclic Grob reactions are possible, exhibited lower recovery rates, 19.3 and 32.0 %, respectively, but the other model compounds also decomposed at 600 °C. These results indicate that the cyclic Grob reaction does not exhibit a critical role for the pyrolytic degradation of these compounds in the gas phase at 600 °C.

4.4.3.3 Homolysis/heterolysis reactions and the influence of bicyclic ring system of levoglucosan

To investigate the contribution of the homolysis and heterolysis reactions during the decomposition of gaseous LG, the BDEs of the C–C and C–O bonds in LG, and the *E_{as}* of specific heterolytic reactions were calculated with DFT (M06-2X) and the 6-311+(d,p) basis set. The results were compared with the experimental results.

Bond dissociation energy

The BDEs of the C–C and C–O bonds in LG are summarized in Figure 4-29, which varied from 71.8 to 87.7 kcal mol^{−1}. These values are concordant with those

reported by Zhang et al. (2012). The C–O bonds of the acetal moiety exhibited especially high BDEs (79.7 and 87.7 kcal mol⁻¹). The weakest bond was the C₆–O bond, but 71.8 kcal mol⁻¹ is still too high to conclude that gaseous LG decomposes through homolysis pathways at 600 °C. The relatively small *E*_{as} (35.1 and 16.7 kcal mol⁻¹) obtained by kinetic analyses agree with this conclusion.

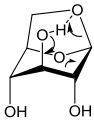
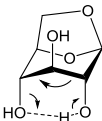
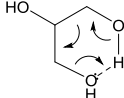
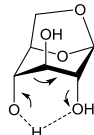
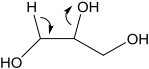
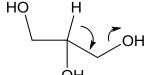
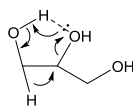
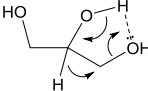
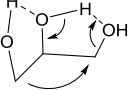
Heterolysis reaction including a bimolecular mechanism

The *E*_{as} of cyclic Grob reaction, direct dehydration, and pinacol rearrangement as calculated with DFT (M06-2X)/ 6-311+(d,p) are compared between LG and glycerol in Table 4-3 by assuming unimolecular mechanisms. Glycerol was used as a model because it is free of steric restrictions, unlike the bicyclic ring in LG.

The direct dehydration eliminating C₃–OH and C₂–H was high at 80.7 kcal mol⁻¹, whereas other dehydrations exhibited a similar range of *E*_{as} (72.7–73.2 kcal mol⁻¹) to those of glycerol (69.6 and 73.0 kcal mol⁻¹). These results indicate that the influences of the bicyclic ring is minor for the direct dehydration reactions of LG, except for those forming C₁=C₂ and C₄=C₅ double bonds, which cannot proceed because of steric hindrance from the bicyclic ring.

However, the *E*_{as} of cyclic Grob reactions and pinacol rearrangements were different between LG and glycerol. For the pinacol rearrangements with the shift of hydrogens, TSs were not obtainable by theoretical calculations. The other rearrangements, in which carbon atoms are rearranged instead of hydrogens, exhibited *E*_{as} ranging from 75.2 to 81.4 kcal mol⁻¹, which are greater than that of glycerol (71.2 kcal mol⁻¹). These differences are explained because of the influence of the LG bicyclic ring, as illustrated in Figure 4-30, where the pinacol rearrangements start from the boat conformer of LG. To accomplish the rearrangement of hydrogen, the hydrogen must attack the adjacent carbon from behind the OH that is cleaved. This criterion cannot be achieved for LG because of steric hindrance from the bicyclic ring. The reactivity for

Table 4-3. Activation energies of cyclic Grob reactions, direct dehydrations, and pinacol rearrangements calculated for LG and glycerol by assuming unimolecular reactions. Minimum energies of the transition states were calculated at a DFT(M06-2X)/6-311+G(d,p) level

Levogluconan	E_a / kcal mol ⁻¹	Glycerol	E_a / kcal mol ⁻¹
Cyclic Grob		Cyclic Grob	
R1 	57.4		
R2 	87.1		65.7
R3 	91.2		
Dehydration		Dehydration	
Combination of OH / H			
C ₂ / C ₃	72.9		69.6
C ₃ / C ₂	80.7		
C ₃ / C ₄	73.2		73.0
C ₄ / C ₃	72.7		
Pinacol rearrangement		Pinacol rearrangement	
Combination of H / OH ^[a]	— ^[c]		66.4
Combination of C / OH ^[b]			70.3
C ₄ / C ₂	76.5		71.2
C ₁ / C ₃	81.0		
C ₅ / C ₃	81.4		
C ₂ / C ₄	75.2		

[a] Hydrogen rearranged / OH eliminated. [b] Carbon rearranged / OH eliminated. [c] Could not find any transition states.

the rearrangement of carbon atom is suppressed by the formation of unstable products because of the strain in five-membered bicyclic rings.

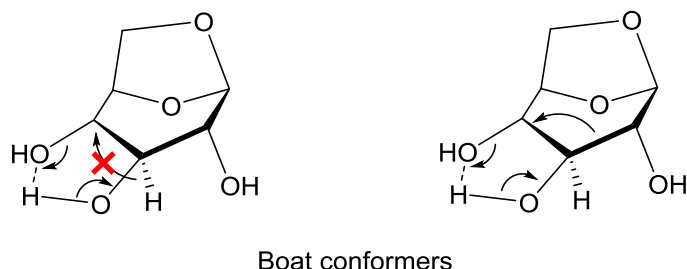


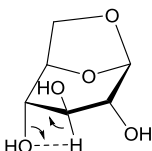
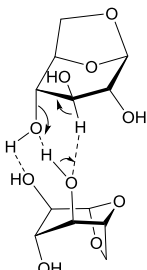
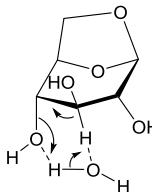
Figure 4-30. Pinacol rearrangement mechanisms for levoglucosan.

Cyclic Grob reactions R2 and R3 exhibited extremely high E_{as} of 87.1 and 91.2 kcal mol⁻¹, respectively, although the E_{a} of glycerol was only 65.7 kcal mol⁻¹ (Table 4-3). These differences are also because of the influence of the bicyclic ring of LG. In reactions R2 and R3, the six-membered ring is cleaved, which increases the double bond character of $>\text{C}=\text{C}<$ and $>\text{C}=\text{O}$. However, the remaining five-membered ring restrains these substructures from adopting the required geometries (in plane). Consequently, the transition states of reactions R2 and R3 become unstable compared with that of glycerol. Alternatively, reaction R1, in which both of five- and six-membered rings are cleaved, exhibited lower E_{a} (57.4 kcal mol⁻¹), because the transition state is stabilized by releasing the strain energies from the bicyclic ring.

Bimolecular mechanisms have been proposed for the gas phase keto-enol tautomerization, 1,3-dihydroxyacetone $\leftrightarrow$ enol $\leftrightarrow$ glyceraldehyde by comparing the experimental and theoretical calculation results (Section 4.1). Because the bimolecular mechanism is suggested for the conversion of enol to glyceraldehyde, where only OH groups participate, similar bimolecular mechanisms can be postulated for direct dehydration. Therefore, the influence of the bimolecular mechanism was investigated theoretically by assuming the LG-LG and LG-H₂O types of bimolecular reactions for

the dehydration reaction with the lowest E_a of 72.7 kcal mol⁻¹. The $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values obtained at 25 and 600 °C are summarized in Table 4-4 and compared with those of the unimolecular reaction.

Table 4-4. The $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values [kcal mol⁻¹] calculated for the direct dehydration of levoglucosan (LG) by assuming unimolecular and bimolecular (LG-LG and LG-H₂O) mechanisms. Minimum energies [kcal mol⁻¹] of the transition states were calculated at a DFT(M06-2X)/6-311+G(d,p) level

Unimolecular		Bimolecular (LG-LG)		Bimolecular (LG-H ₂ O)	
					
		kcal mol ⁻¹			
		$\Delta G^\ddagger$	$\Delta H^\ddagger$	$T\Delta S^\ddagger$	
Unimolecular	25 °C	71.7	73.3	1.6	
	600 °C	73.9	70.9	-3.0	
Bimolecular (LG-LG)	25 °C	59.4	57.4	-2.0	
	600 °C	63.9	59.3	-7.4	
Bimolecular (LG-H ₂ O)	25 °C	55.8	53.5	-2.3	
	600 °C	60.9	52.9	-8.0	

The $\Delta G^\ddagger$ values decreased from 71.7 kcal mol⁻¹ for the unimolecular reaction to 59.4 (LG-LG) and 55.8 (LG-H₂O) kcal mol⁻¹ at 25 °C. These values for the unimolecular reaction, (LG-LG), and (LG-H₂O) were higher at 73.9, 63.9, and 60.9 kcal mol⁻¹, respectively, at 600 °C, because of the increasing $T\Delta S^\ddagger$ values. These theoretical

results suggest that the bimolecular and water-assisted dehydration of LG and the cyclic Grob reaction R1 are candidates for the heterolysis reactions occurring at 600 °C.

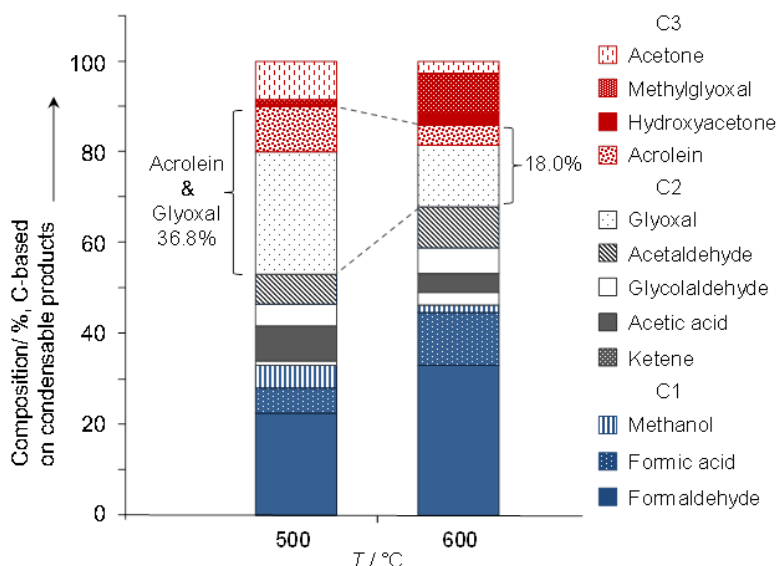
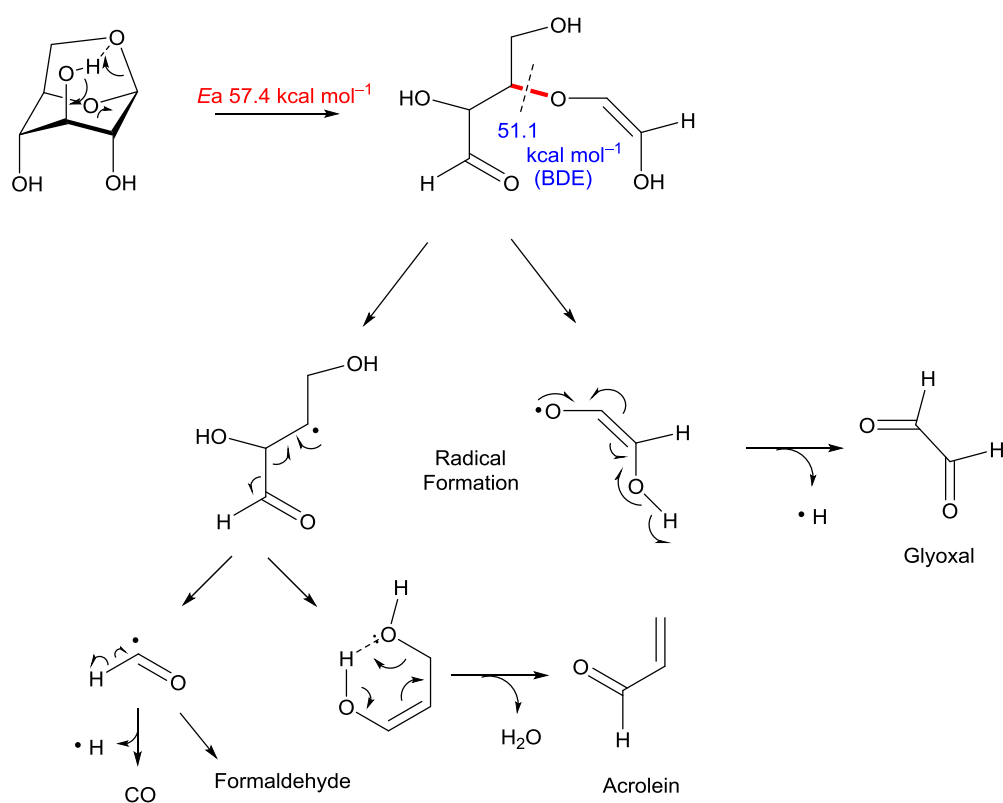


Figure 4-31. Compositions (% C-based) of the condensable products obtained from the pyrolysis of levoglucosan at 500 and 600 °C in the gas phase (residence times: 1.1–1.2s, N₂ flow: 400 mL min⁻¹).

Figure 4-31 shows the compositions of the condensable products from the pyrolysis of gaseous LG, as reported in *Chapter 3*, which uses a similar experimental system to that of the present study. Although the yield of condensable product was low (2.2 %, C-based), acrolein and glyoxal were produced more selectively at 500 °C (38.8 % in total) than that at 600 °C (18.0 % in total). These products may form through the cyclic Grob reaction R1 as shown in Scheme 4-13, via the reactive vinyl ether intermediate, which has a weak C–O bond (BDE 51.1 kcal mol⁻¹). Therefore, the subsequent homolysis of this bond forms two radical species, which can start radical chain reactions. Acrolein and glyoxal formations are explained from these radicals through the β -scission reactions.

These results indicate one of the cyclic Grob reactions (E_a 57.4 kcal mol⁻¹)

proceeding for the gaseous LG at 500 °C, although the efficiency is low. The direct dehydration reactions through bimolecular mechanisms (E_{as} 57.9 and 54.4 kcal mol⁻¹ for the reactions LG-LG and LG-H₂O in Table 4-4, respectively) are also suggested. The large E_{a} (35.1 kcal mol⁻¹) obtained at 550/600 °C (Figure 4-28) agrees with this conclusion. However, the E_{a} became lower (16.7 kcal mol⁻¹) in the high temperature range (600–700 °C), which suggests that the contribution of these heterolysis reactions decreases at high temperatures.



Scheme 4-13. Possible fragmentation pathways of levoglucosan through a cyclic Grob reaction via a vinyl ether intermediate bearing a weak C-O bond. Bond dissociation energy (BDE) (kcal mol⁻¹) was calculated at a DFT (M06-2X, UM06-2X)/6-311+G(d,p) level.

4.4.3.4 Radical chain reactions

Radical species may abstract hydrogens from LG to form C- and O-centered radicals, which are expected to degrade through β -scission reactions. The β -scission reaction can proceed only when the radical p-orbital and the σ -orbital of the C–X bond that is cleaved lie in the same plane (Parsons, 2000) as illustrated in Figure 4-32. Therefore, the linkages (shown with the red bold lines in Figure 4-33), which can be cleaved through β -scission reactions, are limited because of the conformational restriction of the bicyclic ring-system. No such bonds exist for **1-C**, **5-C**, and **6-C** radicals; hence, these radicals are expected to be stable for β -scission reactions. From each of the **2-C**, **3-C**, and **4-C** radicals, one or two C–O bonds and one O–H bond can be cleaved, forming C=C and C=O double bonds, respectively, whereas any of the C–C bonds are not cleaved from these C-centered radicals. For the O-centered radicals (**2-O**, **3-O**, and **4-O**) formed by hydrogen abstraction from the OH groups, all three bonds, which are located at the β -position to the radicals, can be cleaved, because the C–O• bonds can rotate freely to adopt conformations satisfying the stereoelectronic requirement for β -scission reactions. Unlike the C-centered radicals, C–C bonds can be cleaved from the O-centered radicals, opening the six-membered rings of LG to form aldehyde ends.

The degradation pathways starting from **2-C**, **3-C**, **4-C**, **2-O**, **3-O**, and **4-O** radicals are considered and most of the reactions were similar for the subgroup of C- and O-centered radicals. Therefore, possible degradation pathways from **2-C** and **2-O** radicals are discussed below as examples.

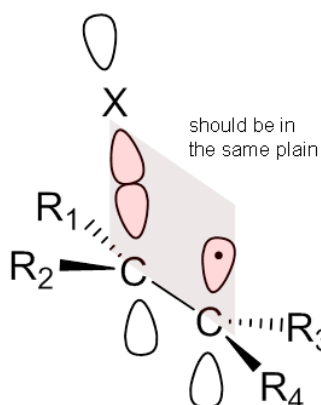


Figure 4-32. Stereoelectronic geometry required for the progression of a β -elimination reaction from a radical.

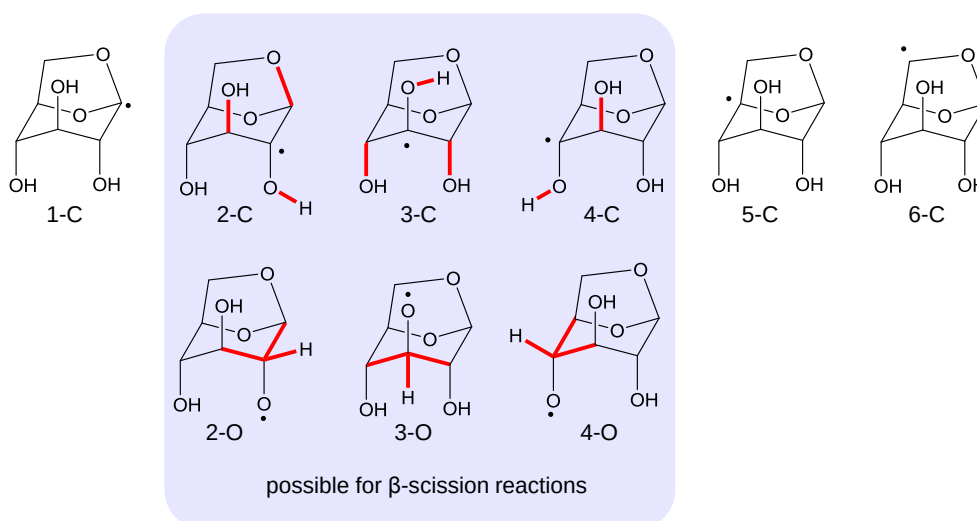


Figure 4-33. Cleavable linkages (red bold lines) through β -elimination for C- and O-centered radicals from levoglucosan.

Pathways from the C-centered radical

Scheme 4-14 illustrates the degradation pathways from the **2-C** radical. The values next to the arrows and at the linkages represent the *E*_{as} and BDEs, respectively, which were calculated theoretically. Three pathways from the different β -scission reactions are denoted as pathways a, b, and c. Pathway a is an oxidation reaction to form

a C=O structure directly. In *Section 4.1*, the conversion of one C-OH group of glycerol into C=O dramatically enhanced the subsequent pyrolytic reactivity for retro-aldol fragmentation and dehydration reactions. As indicated by these findings, the dehydration reaction d (E_a 56.4 kcal mol⁻¹) was accelerated because of the increasing acidity of the C₃-H by the adjacent electron-attracting C=O group. A bimolecular reaction would further reduce the E_a . The resulting conjugated C=O structure of intermediate **14** weakens the C₅-O and C₅-C₆ bonds at BDEs 52.4 and 52.1 kcal mol⁻¹, respectively, cleaving homolytically at 600 °C. Therefore, the oxidation of LG to the C=O intermediates would be followed by the radical fragmentation reactions. Alternatively, the electron-attracting C=O increased the E_a of the dehydration reaction e (74.7 kcal mol⁻¹).

The intermediate formed through pathway b includes an enol moiety, which can be transformed into a ketone derivative by keto-enol tautomerization f (E_a 54.6 kcal mol⁻¹). This E_a is from a unimolecular mechanism, whereas the bimolecular mechanism reduces the E_a . The following dehydration reaction g (E_a of 57.0 kcal mol⁻¹) converts the ketone derivative into intermediate **16** bearing a conjugated C=O structure. Although the BDEs of the allylic C₄-C₅ and C₁-O₆ (or O₅) bonds in the enol intermediate are low at 63.6 and 66.0 kcal mol⁻¹, respectively, the additional conjugation of C=C with the C=O group reduces the BDEs of the allylic C₅-O (54.0 kcal mol⁻¹) and C₅-C₆ (55.3 kcal mol⁻¹) bonds in **16**. The release of strain energy from the five-membered ring also contributes to the reduction of BDEs. Therefore, pathway b accelerates the following fragmentation into radical species.

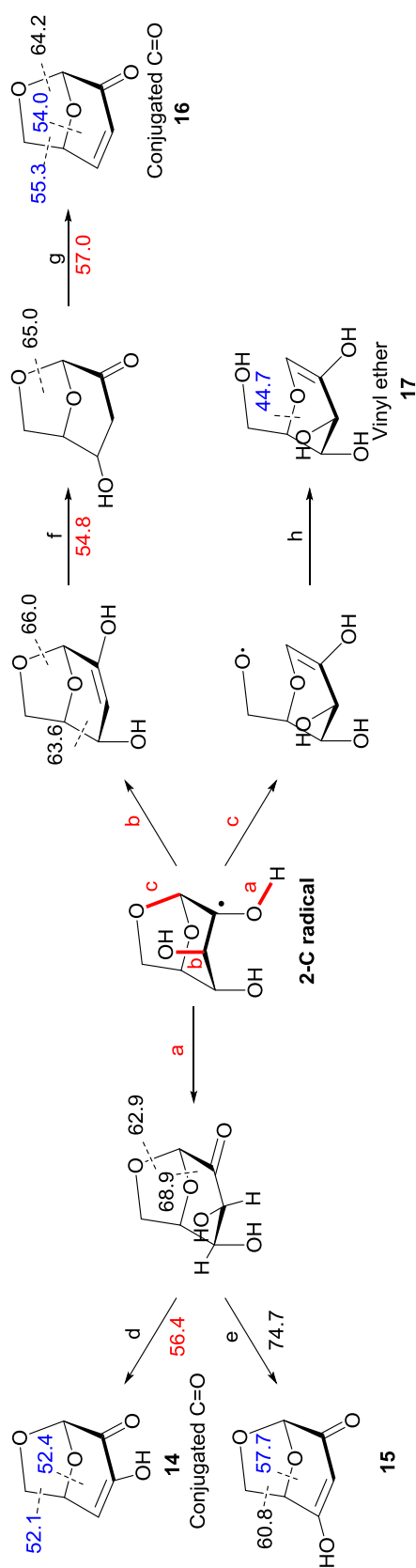
A C=C double bond is formed through pathway c by cleaving the C₁-O₆ linkage. The resulting vinyl ether intermediate **17** has a weak bond (BDE 44.7 kcal mol⁻¹), which can be readily cleaved homolytically. Consequently, these considerations with the theoretical calculation results suggest that the **2-C** radical can be fragmented simultaneously via the more unstable intermediates than LG formed through pathways a-c. These pathways increase the concentration of radicals in the pyrolysis environment, which accelerates the radical chain reactions.

The fragmentation pathways from intermediates **14**, **16**, and **17** in Scheme 5-2 are illustrated in Schemes 4-15, 4-16, and 4-17, respectively. The homolysis of the C₅–O bond (a) of **14** followed by the β-scission of the C₆–O bond form a linear formyl radical **14-1** and a formate radical (Scheme 4-15). Successive α-scission reactions of the formyl radical **14-1** release two CO molecules, and the resulting propenyl radical is stabilized as propene by the abstraction of hydrogen. The formate radical can convert into CO₂ or formic acid, which is degraded into CO, H₂, and CO₂. This pathway is concordant with the origin of formic acid from C₁ reported for glucose pyrolysis using deuterium-labeled glucose derivatives (Ponder and Richards, 1993). Alternatively, the homolysis of the C₅–C₆ bond (b) of **14** forms intermediate **14-2** by releasing methane. Compound **14-2** fragments into CO and methane, probably via a similar formyl radical intermediates as that for **14-1** at 600 °C, because the BDE of the O=C–C=O bond was comparatively large (64.1 kcal mol⁻¹). Therefore, intermediate **14** is expected to fragment into CO, low amounts of CO₂, and hydrocarbon gases (methane and propene).

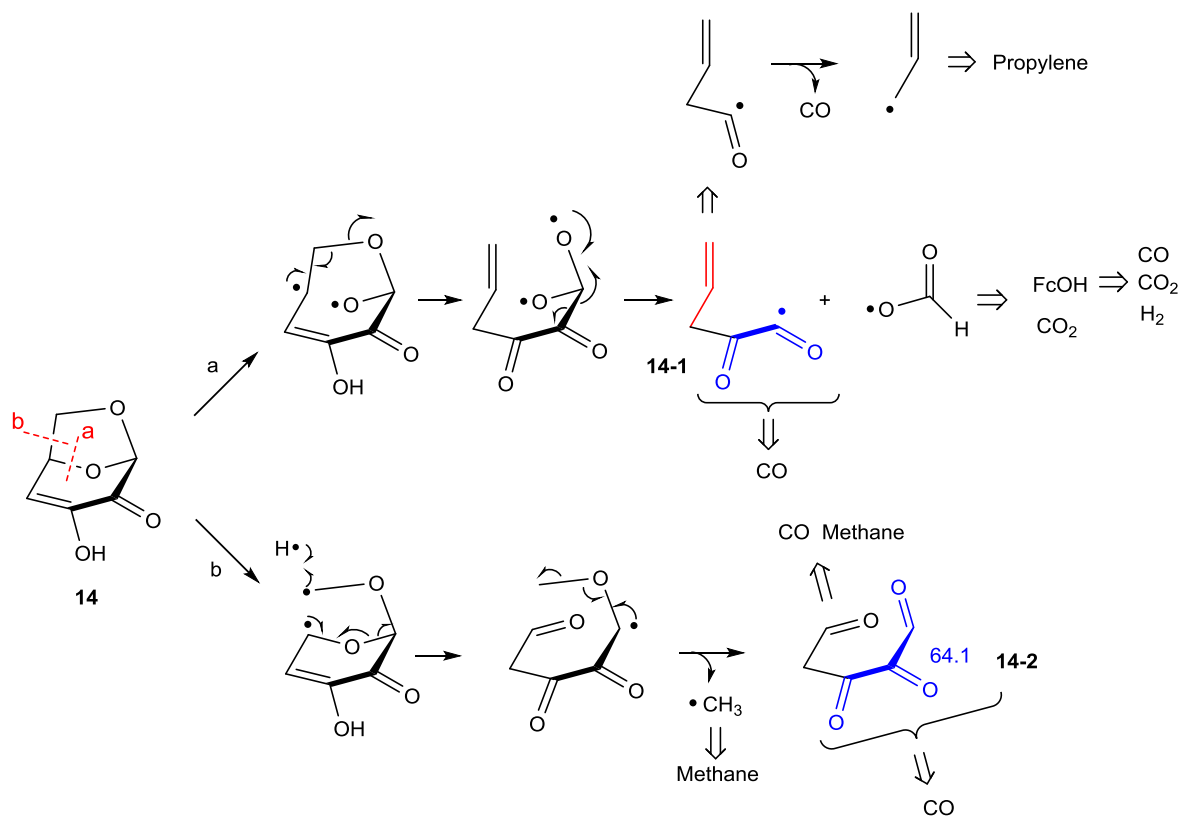
Intermediate **16** is an analog of compound **14**. Because the OH group at C₃ is eliminated, **16-1** and **16-2** formed from **16** have additional C=C double bonds compared with **14-1** and **14-2** from **14** (Scheme 4-16). These double bonds form unsaturated hydrocarbons such as ethylene and acetylene from **16** instead of CO. The butadiene-moiety of **16-1** can be further converted into 1,3-butadiene or ethylene + acetylene. A low amount of 1,3-butadiene (0.4 % C-based at 600 °C) was obtained from gaseous LG. The fragmentation of **16-2** produces CO and acrolein radical, which is further degraded into acetylene, ethylene, and CO. Therefore, intermediate **16**, which is in a more dehydrated state, produces larger amounts of hydrocarbon gases than those of **14**. The hydrocarbon/oxygenated (HC/OX) gas ratio (C-based) is 1.0 (**14**) and 2.0 (**16**) for pathway a, and 0.5 (**14**) and 1.0 (**16**) for pathway b. These results provide an interesting hypothesis; the HC/OX gas ratio is determined by the progression of dehydration.

As illustrated in Scheme 4-17, the homolysis of the vinyl ether C₅–O bond converts intermediate **17** into **17-1**, which includes an aldose-type structure. We

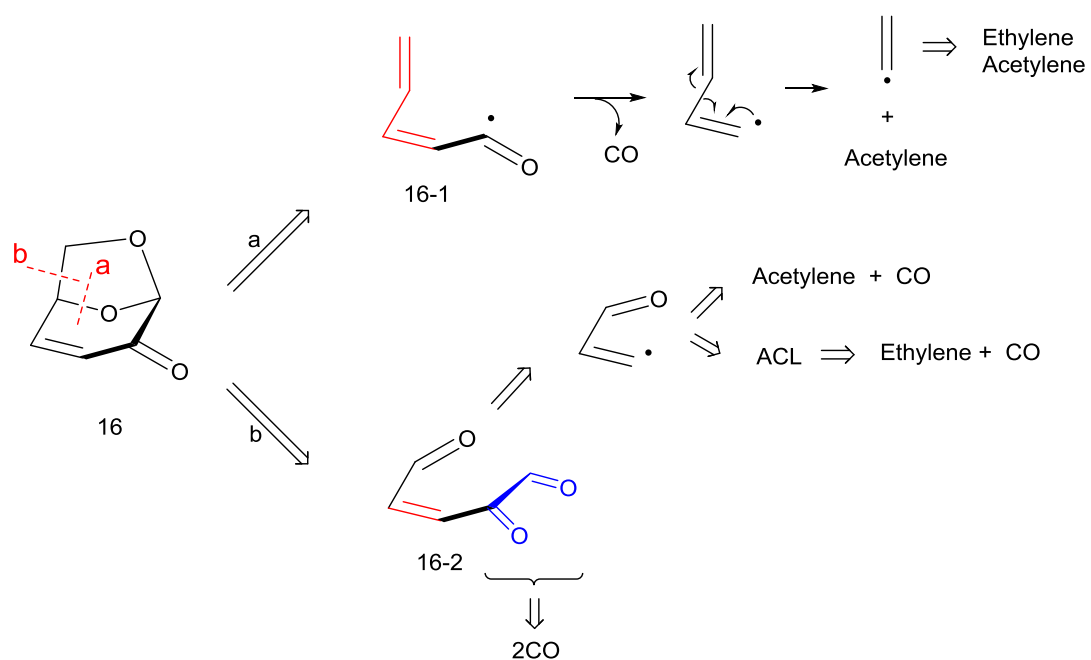
reported that glyceraldehyde, an aldose, is selectively fragmented into syngas (CO and H₂) during gas-phase pyrolysis (*Section 4.1*). Therefore, this aldose moiety is expected to fragment into CO and H₂ through a successive formyl radical formation followed by α -scission releasing CO. These reactions convert intermediate **17-1** into CO and H₂ selectively with a low amount of methane. The HC/OX gas ratio (C-based) of this pathway is relatively low at 0.2, which is concordant with the above hypothesis. Dehydration reactions are not involved in this pathway.



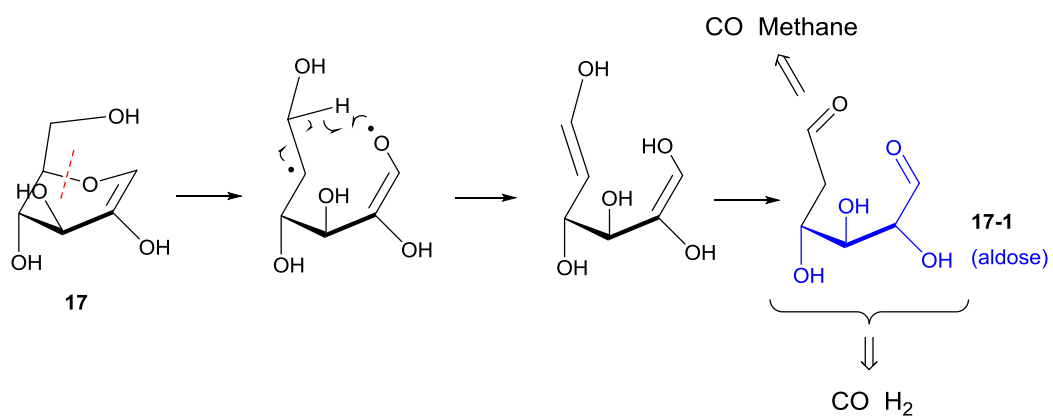
Scheme 4-14. Degradation pathways expected from a 2-C radical, which include reactive intermediates **14**–**17**. The red values below the reaction arrows represent the activation energies (kcal mol^{-1}) obtained from the minimum energies of the transition states, as calculated at a DFT(M06-2X)/6-311+G(d,p) level. The blue values at the bonds represent the bond dissociation energies (kcal mol^{-1}) calculated using DFT (M06-2X, UM06-2X).



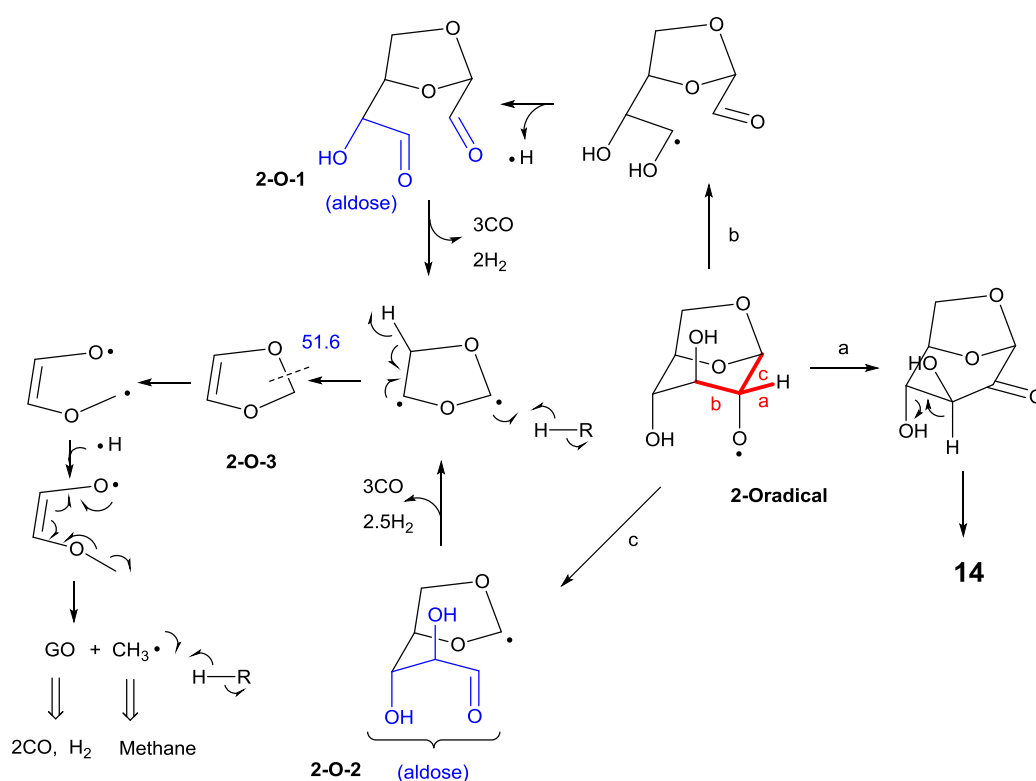
Scheme 4-15. Fragmentation pathways expected from intermediate **14**. The bond dissociation energy of **14-2** (64.1 kcal mol⁻¹) was calculated using DFT (M06-2X, UM06-2X).



Scheme 4-16. Fragmentation pathways expected from intermediate **16**.



Scheme 4-17. Fragmentation pathway expected from intermediate **17**.



Scheme 4-18. Fragmentation pathways expected from **2-O** radical. The bond dissociation energy in blue for **2-O-3** (51.6 kcal mol⁻¹) was calculated using DFT (M06-2X, UM06-2X).

These considerations provide insights into the formation of furanic compounds (furfural and 5-hydroxymethyl furfural), which were not observed in the gas-phase pyrolysis of LG. Dehydration reactions are suggested to proceed even in the gas phase only at high temperatures >500–600 °C by the present investigations, but the resulting C=C double bond formations make the allylic C–C and vinyl ether C–O bonds very reactive for homolysis at 600 °C, causing fragmentation instead of forming furanic compounds.

Pathways from the O-centered radical

For the O-centered radicals, the expected fragmentation pathways of **2-O**

radical are shown in Scheme 4-18. The β -scission of the C₂–H bond (pathway a) produces compound **14** as an oxidation product, which is formed from **2-C** radical (Scheme 4-14). Thus, this intermediate can be fragmented as discussed in Scheme 4-15.

The cleavages of the C₂–C₃ (pathway b) and C₁–C₂ (pathway c) bonds convert **2-O** radical to **2-O-1** and **2-O-2**, respectively. These compounds have aldose-type structures, which degrade into CO and H₂ with **2-O-3**, a cyclic acetal. The homolysis of the weak C–O bond (BDE 51.6 kcal mol⁻¹) causes fragmentation into CO, H₂, and methane. Thus, syngas (CO and H₂) is produced more selectively from the **2-O** radical [the HC/OX gas ratio (C-based): 1.0 and 0.5 (a), 0.2 (b) and 0.2 (c)] than that of the **2-C** radical.

4.4.3.5 Hydrocarbon/oxygenated gas selectivity

As summarized in Table 4-5, the HC/OX gas ratio from the O-centered radicals is lower than that from the C-centered radicals, because dehydration reactions proceed more readily for the C-centered radicals. Alternative direct dehydration reactions (heterolysis) may not play a critical role, even though the bimolecular and water-assisted mechanisms are considered. These results provide an interesting hypothesis; the contributions of the radical chain reactions via the C- and O-centered radicals of LG determine the HC/OX gas ratio during the pyrolysis of LG, cellulose, and other lignocellulosic biomass.

The HC/OX gas ratio obtained from the pyrolysis of gaseous LG conducted under similar conditions to the present study are included in Table 4-5 for comparison (*Chapter 3*). The ratios of 0.33 (600 °C), 0.36 (700 °C), 0.36 (800 °C), and 0.22 (900 °C) suggest dehydration reactions occur, because the expected HC/OX gas ratio without any dehydration reactions is 0.2. Further study is necessary to understand the roles of the C- and O-centered radicals in cellulose pyrolysis/gasification. The lower HC/OX gas ratio at 900 °C has been explained tentatively by the reactions of unsaturated hydrocarbon gases with active oxygen species such as •OH in our previous

paper, which converts hydrocarbons to oxygenated gases.

Table 4-5. Comparison of the hydrocarbon (HC)/oxygenated (OX) gas ratios (C-based) for the noncondensable gases obtained experimentally and theoretical pathways from C- and O-centered radicals and a cyclic Grob reaction

			HC/ OX gas ratio (C-based)
Experimental	600 ° C		0.33
	700 ° C		0.36
	800 ° C		0.36
	900 ° C		0.22
Theoretical			
C-centered radical			
Scheme 4-15	a		1.0
	b		0.2
Scheme 4-16	a		2.0
	b		0.5
Scheme 4-17	a		0.2
O-centered radical			
Scheme 4-18	a		1.0, 0.2
	b		0.2
	c		0.2
Cyclic Grob			
Scheme 4-13	a		0.5

4.4.4 Summary

The kinetic analysis of the pyrolysis of gaseous LG and model compound reactivities discussed with the theoretical calculation results indicate the following conclusions for the fragmentation reactions of gaseous LG during pyrolysis, as illustrated in Figure 4-34:

1. The vapor-phase degradation of LG at 550–700 °C obeys a first order reaction for short residence times, but the reaction rates increase with increasing residence times, indicating a radical chain mechanism.
2. Arrhenius plots from the data of the short residence times are not explained with a single straight line, but with two first order reactions depending on the pyrolysis temperature: E_a : 35.1 kcal mol⁻¹/ A : 2.03×10^9 (550/600 °C) and E_a : 16.7 kcal mol⁻¹/ A : 3.03×10^5 (600/650/700 °C).
3. The LG reactivity is close to those of model compounds (permethylated LG, glycerol, propylene glycol, and ethylene glycol).
4. Restraint in the LG bicyclic ring significantly affects cyclic Grob reactions and pinacol rearrangements (heterolysis). One cyclic Grob reaction (E_a 57.4 kcal mol⁻¹) can occur with bimolecular dehydrations, but these contributions are not significant.
5. Radical chain pathways from the C- and O-centered radicals of LG can contribute to the noncondensable gas formation, whereas the bicyclic ring-system of LG affects the reactions significantly.
6. Double bond formation causes fragmentation rather than furanic and aromatic compounds because of the formation of reactive intermediates with low-BDE bonds, which explains the direct fragmentation of LG into smaller (<C3) fragments in the gas phase.
7. The pathways from the C-centered radicals, which include dehydration, produce more hydrocarbons. Thus, their contribution is a key factor affecting the hydrocarbon/oxygenated gas compositions from LG and cellulose.
8. These lines of information provide insights into the development of clean and efficient gasification systems for cellulosic biomass and control of the hydrocarbon and syngas productions for production of renewable fuels and chemicals.

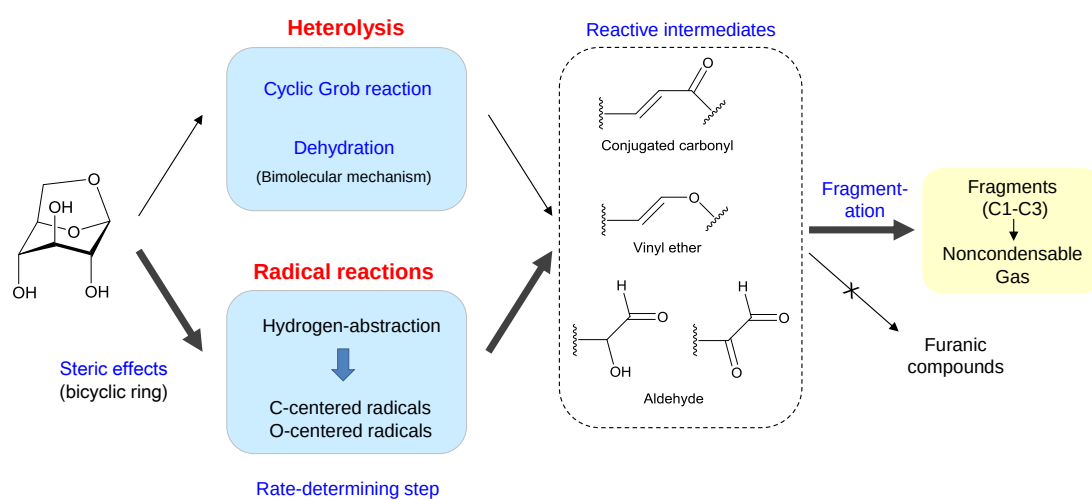


Figure 4-34. Proposed fragmentation mechanisms of levoglucosan.

Chapter 5

Role of Vapor-phase Reactions of Levoglucosan during Cellulose Gasification

5.1 Introduction

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 reactions. 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 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 (LG) is a major volatile intermediate of a high yield (up to around 70 %) from cellulose pyrolysis (Shafizadeh et al., 1979; Kwon et al., 2007).

Although many papers describe the pyrolysis of cellulose, studies of the gas-phase secondary reaction stage of the volatile intermediates have been limited

(Antal, 1983; Evans and Milne, 1987; Li et al., 2001; Shin et al., 2001; Morf et al., 2002; Norinaga et al., 2013). Evans and Milne (1987) 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 CO₂ from the MS data. With a similar system, Shin et al. (2001) compared the gas-phase reactions of LG, 5-HMF and hydroxyacetone as cellulose-derived volatile intermediates. Li et al. (2001) analyzed CO, CO₂, H₂O, CH₄, C₂H₄ 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. (2002) developed a 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. (2013) determined 25 products including gas and tar components by the direct analysis of the mixtures using 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 (Hosoya et al., 2008a). 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 (*Chapter 3*). Intermolecular hydrogen bonding acting as an acid catalyst has been proposed to explain the enhanced transglycosylation (polymerization) and dehydration reactivities in the liquid phase (Hosoya, et al., 2009c; Matsuoka et al., 2012; Kawamoto et al., 2013; Kawamoto et al., 2014).

In *Chapter 3*, we reported the details of pyrolytic reactions of the gaseous LG by the careful control of the evaporator conditions to prevent liquid-phase reactions. We also proposed molecular mechanisms, in which radical chain reactions contribute greatly, from the kinetic analysis data (*Section 4.4*) and the gas-phase reactions of model compounds (*Section 4.1* and *4.2*) including polyalcohols such as glycerol and glyceraldehyde/1,3-dihydroxyacetone. Further discussion with the results of theoretical investigations (*Section 4.4*) suggest that heterolysis reactions of the gaseous LG are limited because of the strain of the bicyclic ring, compared with simple polyalcohols, which included bimolecular mechanisms proposed for polyalcohols and glyceraldehyde/1,3-dihydroxyacetone. One type of cyclic Grob fragmentation with the calculated E_a of $57.3 \text{ kcal mol}^{-1}$ may be involved in the gas-phase heterolysis of LG, and the possibility of the bi-molecular and water-assisted dehydrations, which showed $\Delta G^\ddagger$ at 600°C of 63.9 and $60.9 \text{ kcal mol}^{-1}$, respectively. 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 chapter, 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. Influences of oxygen are discussed to understand the cellulose gasification under partial oxidation conditions.

5.2 Materials and Methods

5.2.1 Materials

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%.

5.2.2 Two-stage tubular reactor

The two-stage tubular reactor (Figure 5-1) 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 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 CO₂ in air. During the trials under inert condition, the end was only connected to N₂ 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 DMSO-*d*₆ solution (2.0 mL) containing an oximation reagent (NH₂OH·HCl, 20 mg) to recover volatile products.

5.2.3 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 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 °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 ± 25 °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 mL min⁻¹ was supplied during each experimental trial under inert conditions, while a constant nitrogen flow of 250 mL min⁻¹ and air flow 150 mL min⁻¹ for O₂/N₂ 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.

5.2.4 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 (DMSO-*d*₆, 2.0 mL) containing an oximation reagent (NH₂OH·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 ¹H 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: TCD; retention times (s): H₂ (26.4), N₂ (45.7), O₂ (35.4), CH₄ (60.6), and 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): CO₂ (19.9), C₂H₄ (23.5), C₂H₆ (26.3), C₃H₆ (57.4), and C₃H₈ (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/N₂SO₄ (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⁻¹), 200 °C (16—20 min); detector: flame ionization detector; retention time (min): propadiene (4.2), acetylene (4.3), trans-2-butene (5.7), 1-butene (5.8), isobutylene (6.1), cis-2-butene (6.2), 1,3-butadiene (7.5), and methyl acetylene (7.6).

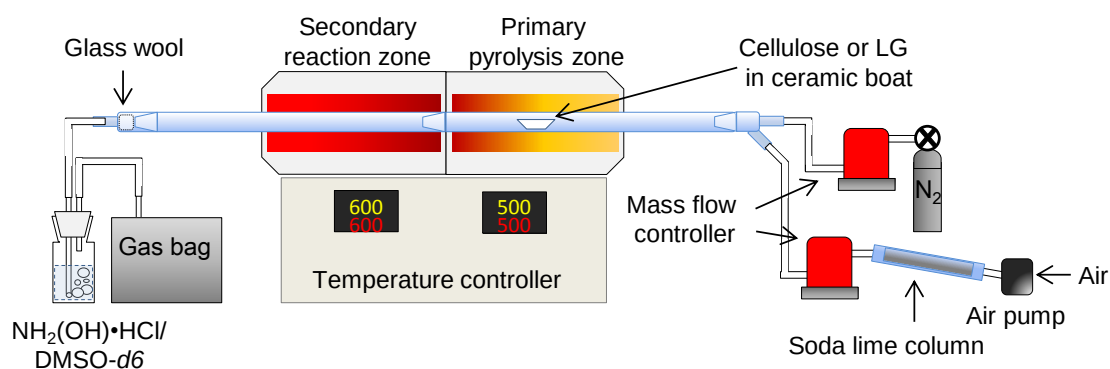


Figure 5-1. A flow-type two-stage tubular reactor that consists of primary pyrolysis and gas-phase secondary reaction zones along with product-recovery units.

5.3 Results and Discussion

The ^1H NMR spectra obtained from the pyrolysis/gasification of cellulose-derived volatiles at 400, 500, 600 and 900 °C under N_2 or 7 % O_2/N_2 flow are shown in Figure 5-2. 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) (Shoji et al., 2014). 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 AGF. The identification of these products is described in detail on the pyrolysis of gaseous LG in *Chapter 3*. In addition, the signals of benzene and methanol were observed in the spectra obtained under N_2 and 7 % O_2/N_2 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 5-3. The pyrolysis of LG created solid carbonized product (char) in the primary pyrolysis zone, which indicates that liquid-phase pyrolysis reactions (polymerization and dehydration) compete with the direct evaporation of LG at its boiling point of 385 °C (Shoji et al., 2014). 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 in *Chapter 3* are shown in Figure 5-4.

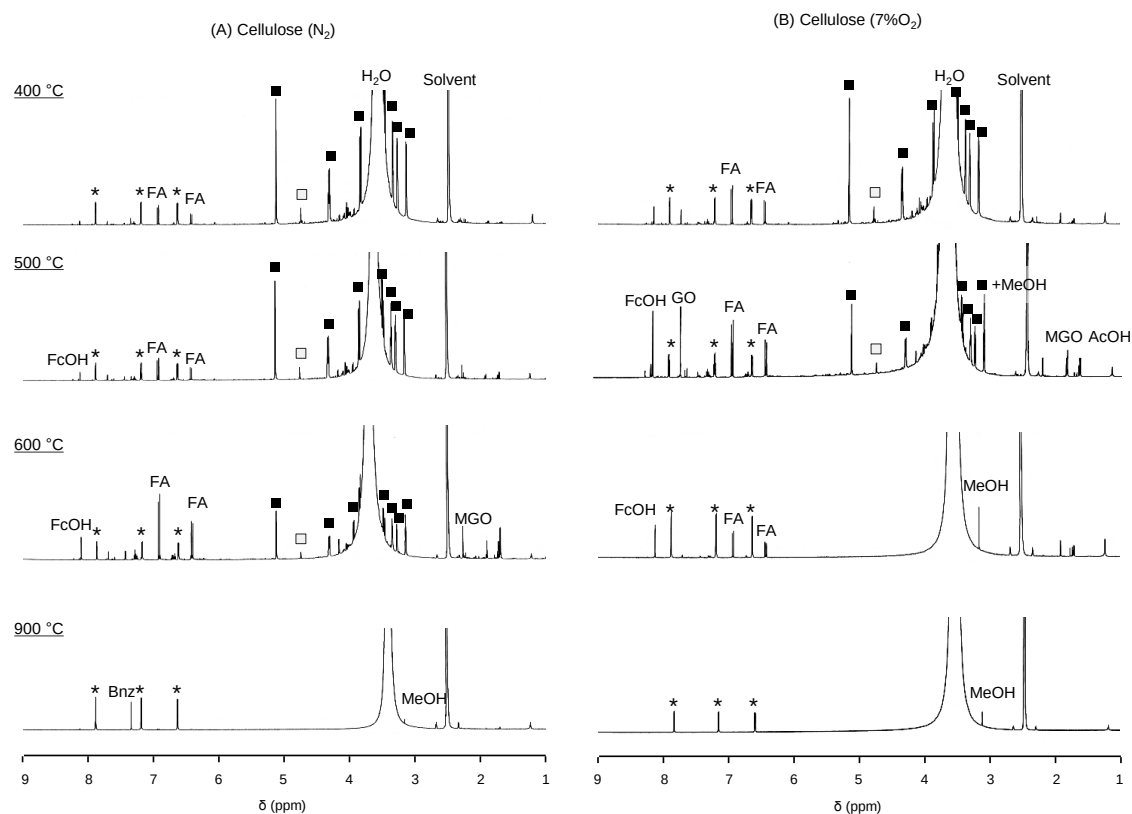


Figure 5-2. ^1H NMR spectra of the condensable products recovered in the gas-wash bottle ($\text{DMSO}-d_6$) including the oxidation reagents during the pyrolysis of cellulose at the second-stage temperatures of 400, 500, 600 and 900 $^\circ\text{C}$ under N_2 and 7 % O_2/N_2 flow (primary pyrolyzer: 500 $^\circ\text{C}$).

■: 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 and Bnz: benzene.

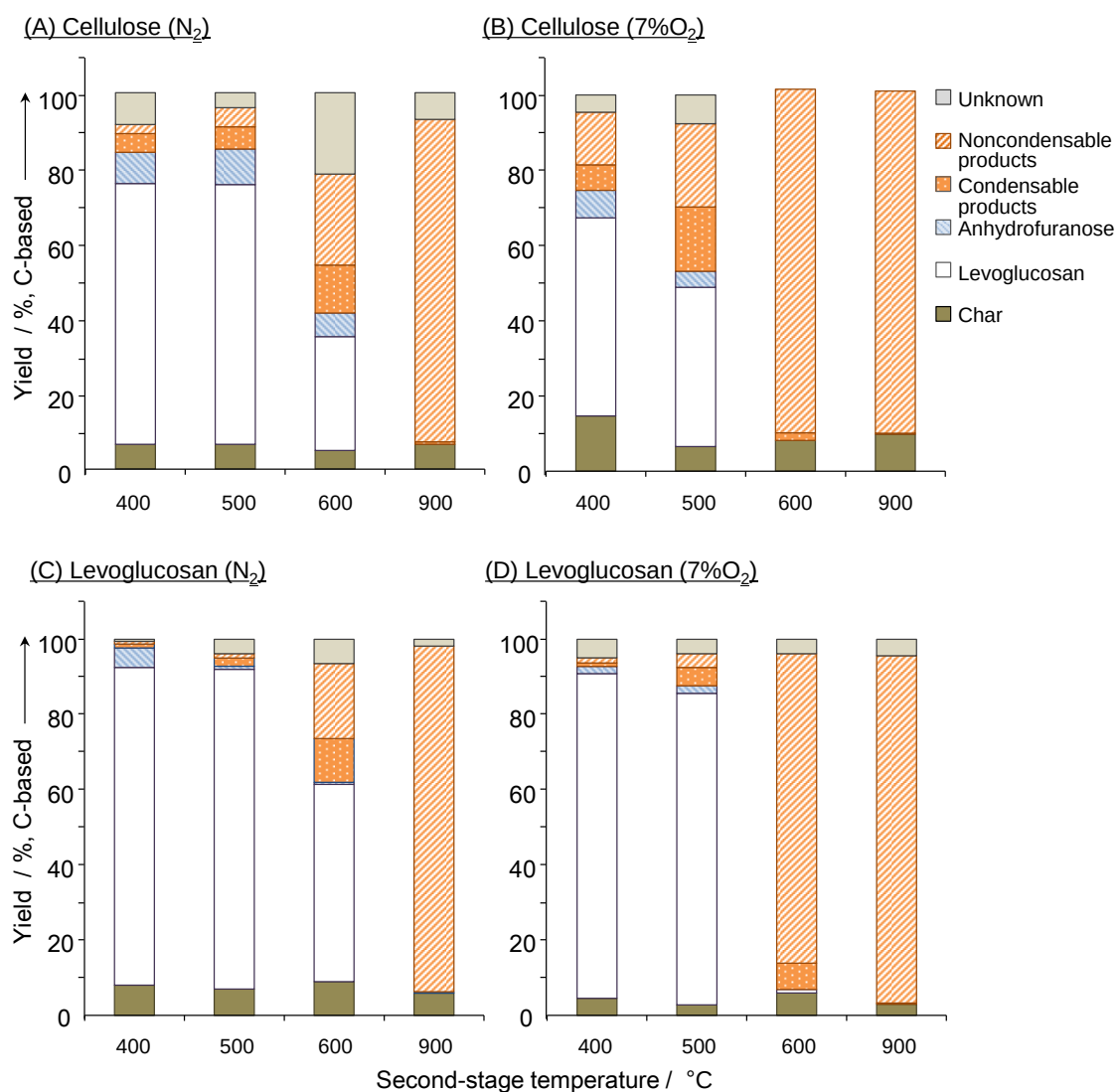


Figure 5-3. Product compositions from the pyrolyses of cellulose (A, B) and levoglucosan (C, D) at the second-stage temperatures of 400, 500, 600 and 900 °C under N₂ and 7 % O₂/N₂ flow (primary pyrolyzer: 500 °C).

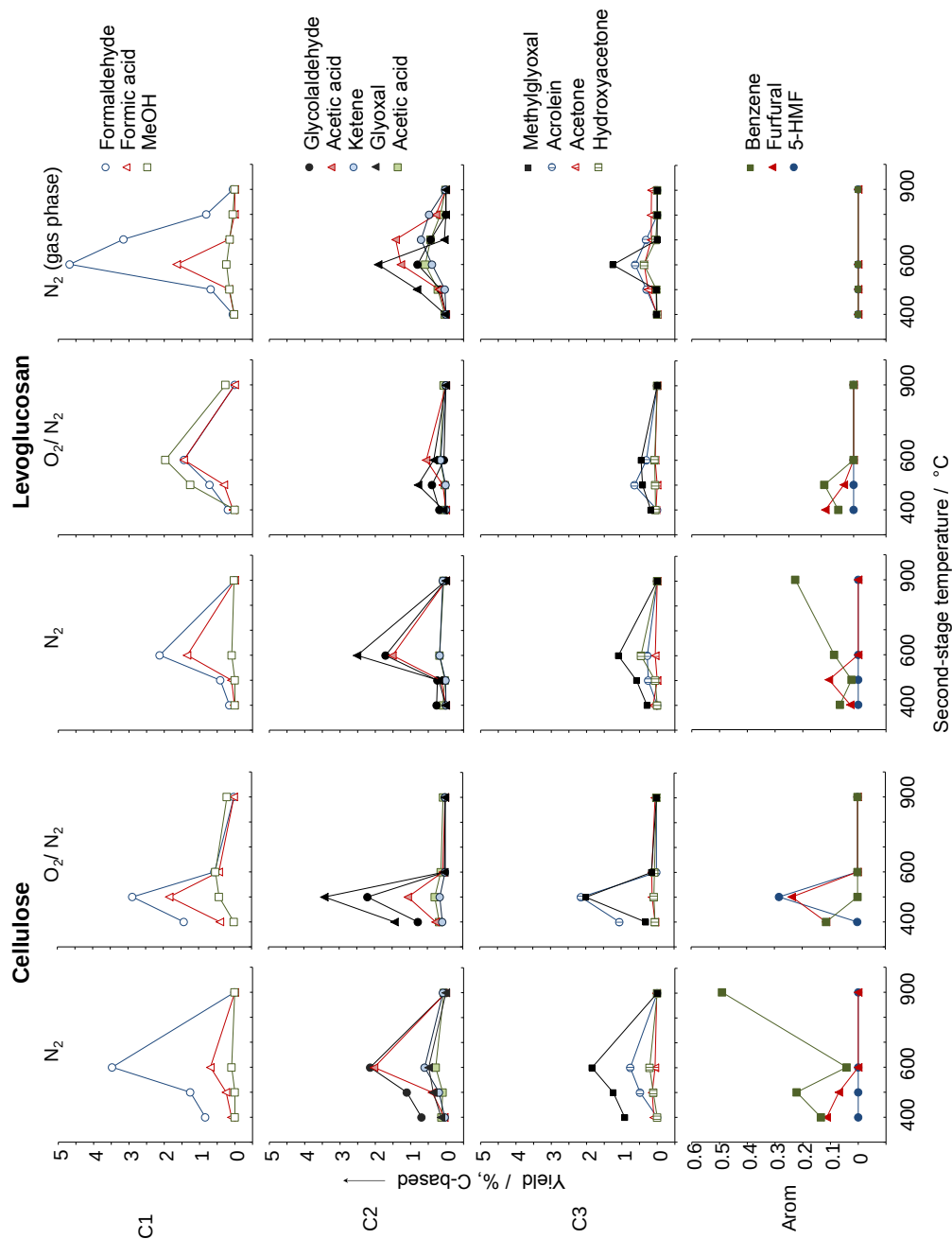


Figure 5-4. Change in the composition of the condensable products from cellulose and levoglucosan by increasing the second-stage temperature from 400 to 900 °C under N₂ and 7 % O₂/N₂ flow (primary pyrolyzer: 500 °C), along with previous results using gaseous levoglucosan (*Chapter 3*).

5.3.1 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 N₂, which confirms LG as the major volatile intermediate during cellulose gasification. This situation did not change under 7 % O₂/N₂ 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 (Shafizadeh and Bradbury, 1979; Shen et al., 2013).

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 5-4). Because the formation of these compounds is completely inhibited in the pyrolysis of gaseous LG (*Chapter 3*), these products may form in the liquid-phase pyrolysis of LG. Although the literature (Evans and Milne, 1987; Norinaga et al., 2013) 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 reducing sugar moiety has been indicated for the formation of furans and AGF (Gardiner, 1966; Kato, 1967). This proposal is supported by the experimental results, because the yields of furans and AGF decrease in the order of glucose > cellobiose > cellulose (Gardiner, 1966). 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 (*Chapter 3*). Recent literature (Matsuoka et al., 2011; Yu et al., 2012) 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. (1997), using pyrolysis-GC analyses of preheated cellulose samples, where the products depend on the pretreatment temperature: anhydrosugars ($< 250\text{ }^{\circ}\text{C}$) $\rightarrow$ furans $\rightarrow$ benzenes ($> 350\text{ }^{\circ}\text{C}$). The conversion, furans $\rightarrow$ benzenes, was extensively studied for the hydrothermal carbonization of reducing sugars using solid-state NMR (Titirici et al., 2008; Baccile et al., 2009; C. Falco et al., 2011). These findings indicate that the benzene obtained at $400\text{ }^{\circ}\text{C}$ 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 $> 500\text{--}600\text{ }^{\circ}\text{C}$ in the gas phase (*Section 4.2*), the dehydration of glyceraldehyde (an aldose) can occur at $400\text{ }^{\circ}\text{C}$ through highly reactive dehydrations via the cyclic transition states of enol intermediates. (*Section 4.1 and 4.2*) A similar dehydration mechanism has been proposed for the glucose dehydration into 5-HMF and furfural via 3-deoxyglucosone (Perez Locas and Yaylayan, 2008; van Putten et al., 2013).

5.3.2 Gas-phase secondary reactions

The pyrolysis products changed by increasing the second-stage temperature (Figures 5-3 and 5-4), 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 ($500\text{ }^{\circ}\text{C}$) is insufficient for the gasification of char and the heating period of char fraction is only 2 min after reaching $500\text{ }^{\circ}\text{C}$. The changes in the compositions of the noncondensable

gases are summarized in Figures 5-5 and 5-6.

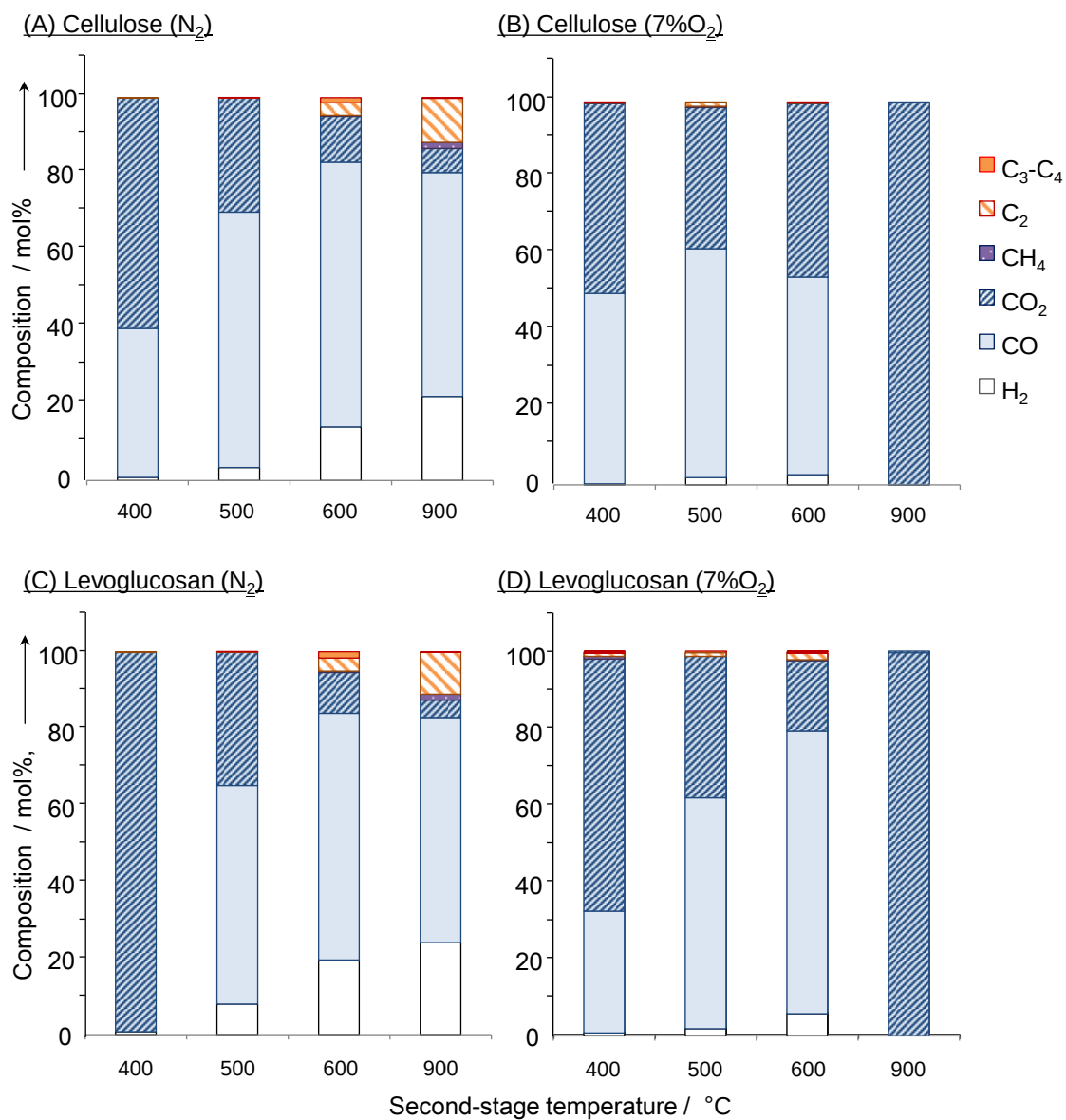


Figure 5-5. Compositions of the noncondensable gases from the pyrolyses of cellulose (A, B) and levoglucosan (C, D) at the second-stage temperatures of 400, 500, 600 and 900 °C under N₂ and 7 % O₂/N₂ flow (primary pyrolyzer: 500 °C).

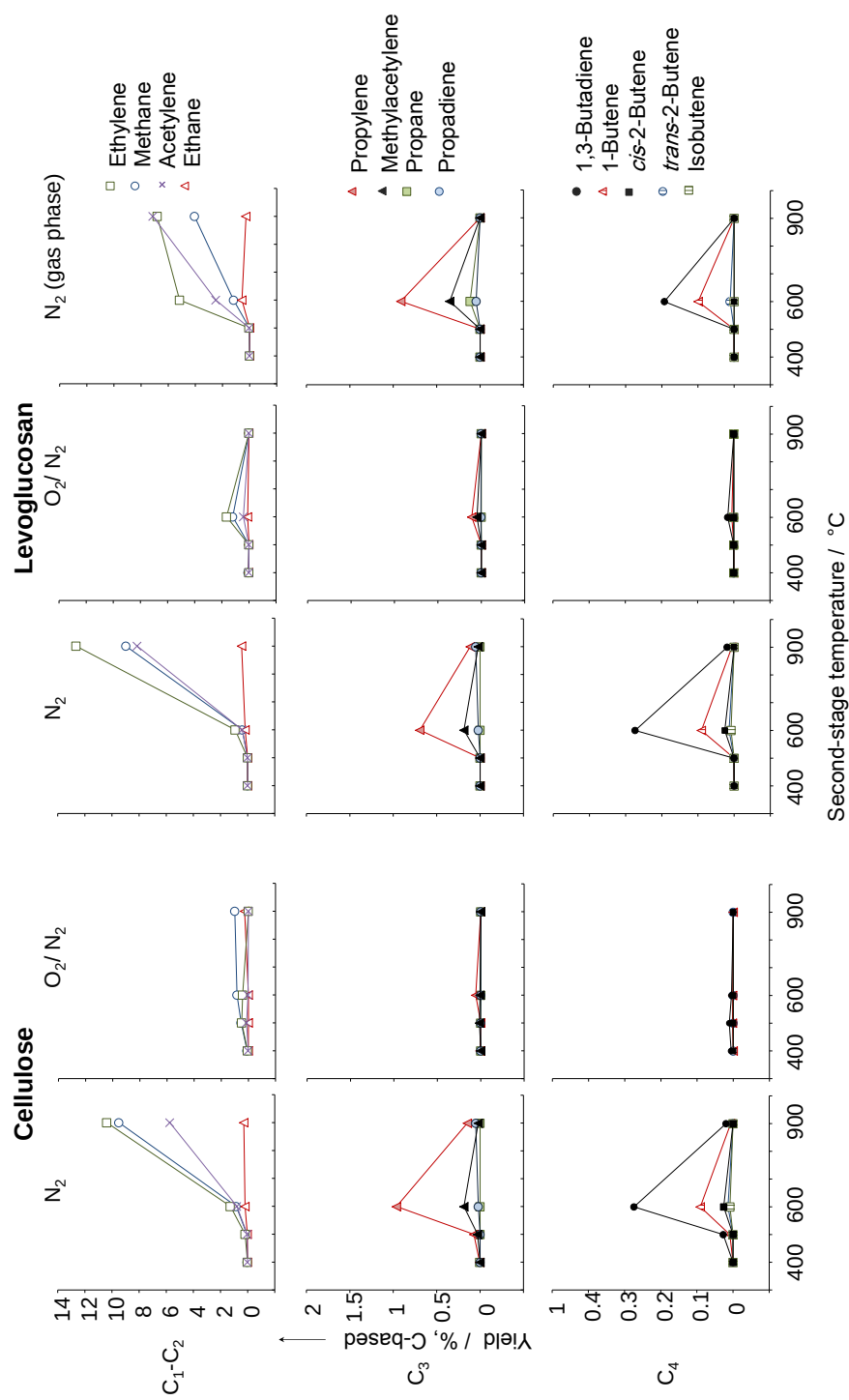


Figure 5-6. Change in the composition of the noncondensable gases from cellulose and levoglucosan by increasing the second-stage temperature from 400 to 900 °C under N₂ and 7 % O₂/N₂ flow (primary pyrolyzer: 500 °C), along with previous results using gaseous levoglucosan (*Chapter 3*).

Under N₂ 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 H₂, CO₂, unsaturated hydrocarbons (ethylene and acetylene) and methane (Figure 5-5). These results are concordant with those of the pyrolysis of gaseous LG in *Chapter 3*. 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 5-4), which include C3 [hydroxyacetone, acetone, acrolein and methylglyoxal], 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 N₂ cellulose pyrolysis.

Some unsaturated C4 hydrocarbons were identified as noncondensable gases, including 1,3-butadiene, 1-butene, *cis/trans*-2-butene and isobutene (Figure 5-6). 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 (Lifshitz et al., 1998; Norinaga et al., 2014), 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 (*Chapter 3*), 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 5-4).

The oxygen in the N₂ 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 5-3). 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. Synergetic effects of O₂ and volatiles from cellulose can enhance the acceleration effects, even at temperatures 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 N₂ flow (Figures 5-2 and 5-4), the inclusion of O₂ 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 5-5 and 5-6), the contents of unsaturated hydrocarbons from cellulose and LG pyrolyses decreased dramatically 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, CO₂ became predominant by complete oxidation.

These influences of O₂ can be discussed with a biradical mechanism. *Section 4.4* suggested that the radical chain mechanisms are important for the gas-phase fragmentation of LG. Therefore, the addition of radical species such as O₂ (biracial) accelerates fragmentation reactions. Radicals add to the unsaturated C=C and C≡C to form oxygenated structures (Parsons, 2000), which converts the unsaturated hydrocarbons including benzene into oxygenated gases. The radical coupling of •CH₃ with oxygen (biradical) forms MeOH via the peroxide intermediate, which reduces the methane yield.

5.3.3 Molecular mechanisms of cellulose gasification

Building on the literature information, the molecular mechanisms of cellulose gasification are proposed as illustrated in Figure 5-7, which included solid/liquid- and gas-phase conversions.

Cellulose has a heterogeneous layered structure (Salmén, 2004; Salmén and Burgert, 2009; Terashima et al., 2009), 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 (Zickler et al., 2007), 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 (Matsuoka et al., 2014).

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 (Hosoya et al., 2007). LG, glycolaldehyde, furfural and 5-HMF have been suggested to contribute to these coking reactions (*Chapter 2*).

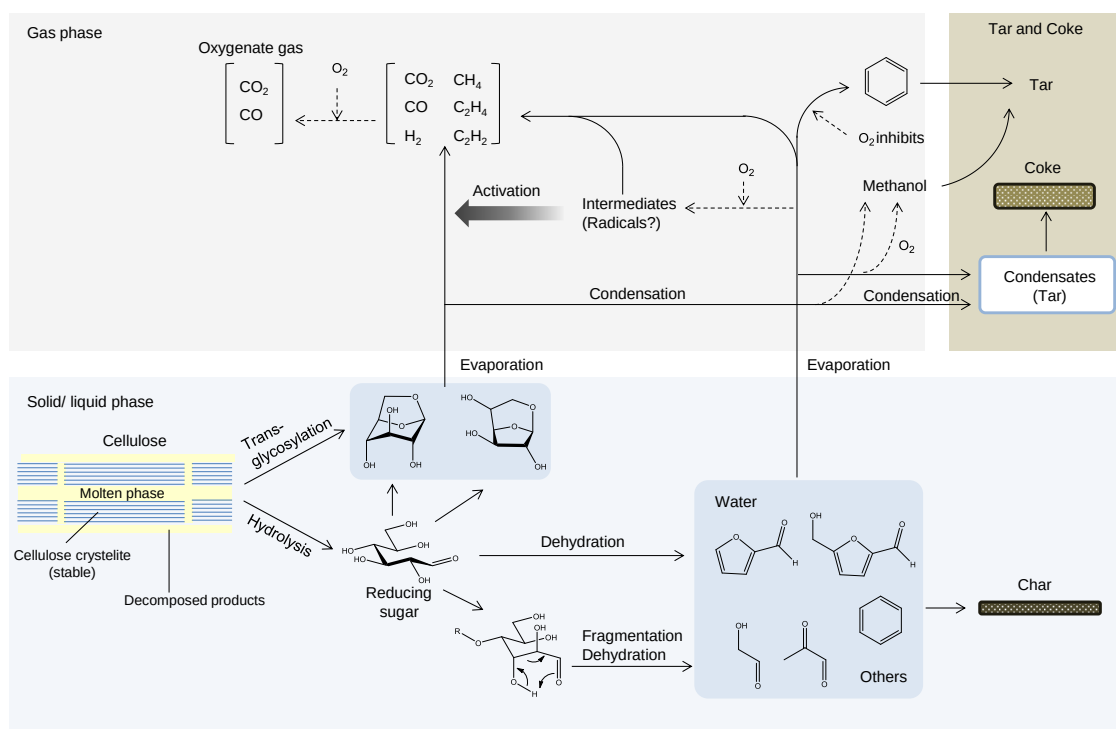


Figure 5-7. Proposed gasification mechanisms of cellulose.

5.4 Summary

The results of the present investigations provide the information for the gas-phase conversions as summarized in the following 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 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 hydrocarbon 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 N₂, and methanol and smaller amounts of acetic acid and acetone under 7 % O₂/N₂.

Chapter 6

Concluding Remarks

In this dissertation, the molecular mechanisms of cellulose gasification were investigated mainly from the vapor-phase reactions of levoglucosan as an important intermediate of cellulose gasification. The following conclusions are obtained.

Coke/soot- and gas-forming reactivities of eight cellulose gasification intermediates were found to be different depending on their chemical structures. Levoglucosan and furans (furfural and 5-HMF) produced coke in the molten-phase pyrolysis, while coking reactions of furans occurred also in the vapor-phase. Gas-forming reactivity was inversely correlated with BDE of the weakest bond in the molecule. Homolysis followed by fragmentation was proposed as gas-formation mechanism. Oxygen enhanced gas formation at 500 °C but promoted soot formation from furans at 600 °C by reducing the gas formation.

Experimental conditions using a two-stage flow type reactor were established to study only the vapor-phase reactions of levoglucosan as the gasification intermediate from cellulose. With this system, cellulose produced 69.3 % (C-basis) of levoglucosan in a short heating time, which confirms that studying the vapor-phase degradation of levoglucosan is quite effective for understanding the roles of vapor-phase reactions in cellulose gasification.

With this reactor system, the vapor-phase reactivity of levoglucosan was clarified for the first time. Levoglucosan was stable up to ~500 °C and selectively degraded into noncondensable gas (CO, H₂, CH₄, ethylene, acetylene, etc.) via C1-C2 aldehydes as the major condensable intermediates, without forming any coke, furans, and benzenes. Thus, the vapor-phase degradation of levoglucosan was suggested to lead to the clean-gasification of cellulose. Coking occurred only upon cooling of levoglucosan vapor to form the molten phase, in which intermolecular hydrogen

bonding serves as an acid catalyst to promote dehydration.

Because the vapor-phase degradation of levoglucosan gave C1-C2 aldehydes selectively as the condensable intermediates, formation of carbonyl group was expected to be a key process for the vapor-phase degradation of levoglucosan. To study the degradation mechanisms, vapor-phase reactivities of glyceraldehyde (aldose) and 1,3-dihydroxyacetone (ketose) were studied and compared with those of simple polyalcohols (glycerol, propyleneglycol, and ethyleneglycol). Theoretical calculations were also effectively utilized to propose the degradation mechanisms.

Glyceraldehyde (aldose) and 1,3-dihydroxyacetone (ketose) decomposed in the vapor phase at as low as 400 °C and were converted selectively to CO and H₂ via methyl glyoxal (a dehydration product) and glycolaldehyde and formaldehyde (retro-aldol fragmentation products) as the intermediates. The decomposition temperature of 400 °C was much lower than those (600 °C) observed for levoglucosan and simple polyalcohols. Thus, conversion into aldehydes is suggested to be a rate-determining step for the vapor-phase degradation of levoglucosan. Bimolecular keto-enol tautomerization mechanisms were also proposed for the vapor-phase degradation of glyceraldehyde and 1,3-dihydroxyacetone.

From the reactivities of the simple polyalcohols supported by theoretical calculations, heterolytic and radical chain dehydration mechanisms were suggested to occur to produce aldehydes from the simple polyalcohols. The extent of the progression of dehydration reactions was also suggested to be a key step for the production of hydrocarbon gases such as methane, ethylene, and acetylene.

By comparing the vapor-phase reactivity, levoglucosan with a ¹C₄ conformer was found to be more stable than methyl glucosides as a model of the majority of glucosides (α- and β-anomers) with ⁴C₁ conformers. Levoglucosan was stable up to 500 °C in the vapor phase, while the vapor-phase methyl glucosides were selectively converted into levoglucosan even at 200 and 300 °C and fragmentation products at temperatures >400 °C. Concerted heterolysis mechanisms can explain the levoglucosan formation from methyl glucosides, along with the radical chain fragmentation

mechanisms for the vapor-phase methyl glucosides. Thus, the vapor-phase levoglucosan is characteristically stable at high temperatures, and the steric hindrance arising from the bicyclic ring of levoglucosan was proposed for this stability.

Kinetic analysis of the vapor-phase degradation of levoglucosan could not explain by only first order reactions, but rather indicated radical chain mechanisms. One type of cyclic Grob reactions followed by the homolytic cleavage of weak vinyl ether linkage of the resulting intermediate was suggested to be an initiation reaction. Theoretical investigations of chain reactions from various C- and O-centered radicals of levoglucosan indicated the molecular mechanisms of vapor-phase degradation of levoglucosan; β -scission type reactions play key roles for formation of C=C double bonds which are rearranged into reactive carbonyl species through keto-enol tautomerization; The carbonyl formation further promotes retro-aldol fragmentation and dehydration at the adjacent hydroxymethylene groups forming conjugated carbonyl species; homolytic cleavage of very weak C–C and C–O bonds of the conjugated carbonyl species occurs, which promotes fragmentation.

Finally, roles of vapor-phase reactions in cellulose gasification were clarified by comparing the reactivity of cellulose gasification with those of vapor-phase levoglucosan as the major volatile intermediate (max. 69.3 %, C-based). Cellulose and levoglucosan intermediate started to be gasified at 600 °C and completed at 900 °C. Gas- and tar-forming behaviors during cellulose gasification were largely explained by the vapor-phase degradation of levoglucosan. Benzenes, furans and anhydrofuranose were only detected from cellulose gasification that include molten-phase reactions before forming volatile intermediates. Synergetic effects of oxygen and volatile intermediates from the molten-phase reactions of cellulose primary pyrolysis were found to accelerate the conversion of volatiles into gases.

These lines of information guide the development of effective tar/coke-free clean gasification systems for cellulosic biomass by controlling the primary and secondary reactions involved in the gasification.

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List of Publications

Original Papers

1. Fukutome, A., Kawamoto, H., and Saka, S. (2014). Gas- and coke/soot-forming reactivities of cellulose-derived tar components under nitrogen and oxygen/nitrogen. *Journal of Analytical and Applied Pyrolysis*, **108**, 98-108. (Chapter 2)
2. Fukutome, A., Kawamoto, H., and Saka, S. (2015). Processes forming gas, tar, and coke in cellulose gasification from gas-phase reactions of levoglucosan as intermediate. *ChemSusChem*, **8** (13), 2240-2249. (Chapter 3)
3. Fukutome, A., Kawamoto, H., and Saka, S. (2016). Gas-phase reactions of glyceraldehyde and 1,3-dihydroxyacetone as models for levoglucosan conversion during biomass gasification. *ChemSusChem*, **9** (7), 703-712. (Chapter 4-Section 4.1)
4. Fukutome, A., Kawamoto, H., and Saka, S. (2016). Molecular mechanisms for the gas-phase conversion of intermediates during cellulose gasification under nitrogen and oxygen/nitrogen. *Chemical Industry and Chemical Engineering Quarterly*, 22(4), 343-353. (Chapter 5)
5. Fukutome, A., Kawamoto, H., and Saka, S. Kinetics and molecular mechanisms for the gas-phase degradation of levoglucosan as a cellulose gasification intermediate. *Journal of Analytical and Applied Pyrolysis*, in press (DOI:10.1016/j.jaap.2016.12.010). (Chapter 4-Section 4.4)
6. Fukutome, A., Kawamoto, H., and Saka, S. Gas-phase reactions of methyl glucosides and levoglucosan at high temperatures. *Journal of Wood Science* (submitted) (Chapter 4-Section 4.3)

7. Fukutome, A., Kawamoto, H., and Saka, S. Dehydration as a key reaction for hydrocarbon gas production in gasification of simple C2 and C3 alcohols. (in preparation) (*Chapter 4-Section 4.2*)

International conferences

1. Fukutome, A., Kawamoto, H., and Saka, S. Molecular-based study of gas and coke formation in gasification of cellulosic biomass, 3th International cellulose conference, Oct 10-12, 2012, Sapporo, Japan. (*Chapter 2*)
2. Fukutome, A., Kawamoto, H., and Saka, Gas- and liquid-phase reactions of levoglucosan as a key intermediate of cellulose gasification, International Symposium on Wood Science and Technology 2015, March 15-17, 2015, Tokyo, Japan. (*Chapter 3*)
3. Fukutome, A., Kawamoto, H., and Saka, Molecular mechanisms in pyrolysis of gaseous levoglucosan as a cellulose gasification intermediate, 18th International Symposium on Wood, Fiber and Pulp Chemistry, September 9-11, 2015, Vienna, Austria. (*Chapters 3 and 4*)