

Abstract of the Dissertation:

VAPOR-PHASE REACTION AND ITS ROLE IN CELLULOSE GASIFICATION

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Gasification is a promising technology for utilization of lignocellulosic biomass. “Tar problems”, however, inhibit the development of reliable gasification systems. In this dissertation, molecular mechanisms of cellulose gasification, particularly vapor-phase reaction and its role, have been studied in order to improve the gasification process towards cleaner, tar-free and more efficient direction. This dissertation consists of 6 chapters.

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.

In *Chapter 2*, coke- and gas-forming reactivities of eight major volatile intermediates produced from the primary pyrolysis of cellulose have been studied in ampoule reactors under nitrogen or oxygen/nitrogen at 600°C [1]. Coking, which is defined as the formation of solid carbonized substance via volatile intermediates, is a kind of tar problem leading to clogging of the cooling lines from the gasifier. Coking from the cellulose-derived volatile intermediates is known to occur by cooling into the condensates, where liquid-phase secondary pyrolysis reactions take place. As a result, levoglucosan (LG, boiling point 385°C), which is an anhydroglucose produced from cellulose in 69.3% yield, was found to be a key volatile component for such coking reactions. In addition, furans (furfural and 5-hydroxymethyl furfural) produced coke in both vapor- and liquid-

phases, which indicates that furans are not favorable for clean cellulose gasification. Gas compositions obtained from the eight intermediates did not directly correlate to the elemental formulas, but depended on the chemical structures, which indicate that gasification reactions are controlled kinetically.

In *Chapter 3*, vapor-phase reactions of LG have been studied in contrasted with the liquid-phase pyrolysis reactions leading to coke formation. Information on the vapor-phase reactions of carbohydrates is very limited due to the intrinsic difficulty in conducting experiments. In general, pyrolysis reactions such as thermal polymerization occur in the liquid phase at temperatures which are much lower than the boiling points. For example, LG with a boiling point of 385°C decomposes at >240°C in the liquid-phase. Accordingly, experimental conditions with a two-stage tubular experimental set up were developed first to investigate only the vapor-phase reactions of LG. Careful control of the evaporator temperature around 200°C under a nitrogen flow enabled the evaporation of LG prior to the molten-phase reactions occurring.

Under these experimental conditions, the gaseous LG was pyrolyzed at 500-900°C with residence times ranging from 0.8 to 1.4 s. Interestingly, the LG vapor was stable up to 500°C, although the molten LG decomposed at >240°C. Furthermore, at the higher temperatures than 600°C, the LG vapor was selectively fragmented into noncondensable gases (CO, H₂, CO₂, methane, ethylene, acetylene, and so on) along with the condensable intermediates mainly consisting of C1-C3 carbonyl compounds and completely gasified at 900°C. No coke, benzenes, and furans were produced from the pyrolysis of LG vapor. These results suggest that the vapor-phase degradation of LG is very clean for coking problems and completion of these vapor-phase reactions of LG is important to prevent the coking problems.

Chapter 4 deals with the molecular mechanisms of vapor-phase LG degradation from the vapor-phase degradation of model compounds [carbonyls (*Section 4-1*), polyalcohols (*Section 4-2*) and methyl glucosides (*Section 4-3*)] and vapor-phase degradation kinetics of LG (*Section 4-4*). The experimental set up as exploited in *Chapter 3* has been used in this chapter, and theoretical calculations with density functional theory (DFT) method by using Gaussian 09 software have been effectively utilized to propose the degradation mechanisms.

In *Section 4-1*, degradation pathways and mechanisms have been studied for the vapor-phase pyrolysis of glyceraldehyde (a C3 aldose) and 1,3-dihydroxyacetone (a C3 ketose) as models of LG-degradation intermediates [3], because LG vapor selectively gave carbonyl compounds, particularly aldehydes, as the intermediates to the noncondensable gases. Degradation of LG and glycerol (a C3 alcohol) vapors required

relatively high temperatures $> 600^{\circ}\text{C}$, whereas glyceraldehyde and 1,3-dihydroxyacetone vapors degraded at 400°C and gave glycolaldehyde and formaldehyde (retro-aldol products) and methylglyoxal (a dehydration product). These results indicate that the introduction of $\text{C}=\text{O}$ group to polyalcohol significantly enhances the thermal degradation reactivity, which would be a reason why $>\text{C}_4$ products were hardly produced from LG vapor. Oxidation to the carbonyl intermediates is suggested to be a rate-determining step of degradation of LG and polyalcohol vapors. 1,3-Dihydroxyacetone was found to degrade via glyceraldehyde formed through keto-enol tautomerization. Based on this experimental evidence, bimolecular concerted mechanisms that effectively reduce the activation energies have been proposed for the vapor-phase keto-enol tautomerization. In addition, glyceraldehyde and 1,3-dihydroxyacetone vapors were found to give syngas (CO and H_2) selectively at higher temperatures than 800°C .

In *Section 4.2*, vapor-phase degradation of C_2 (ethylene glycol) and C_3 (glycerol and propylene glycol) polyalcohols has been studied as the simplest models of LG [4]. All polyalcohols degraded at $>600^{\circ}\text{C}$ in the vapor-phase, and dehydration reactions were found to proceed even in the vapor-phase. Heterolysis including bimolecular mechanisms and radical chain mechanisms have been proposed for the vapor-phase dehydration. The oxygenated gas (CO and CO_2)/ hydrocarbon gas (methane, ethylene, acetylene, and so on) ratio was directly related to the progression level of dehydration reactions. Based on these results, dehydration reactions have been proposed as a key process for production of hydrocarbon gases from pyrolysis of polyalcohols and LG. Radical chain mechanisms involving the α -scission of formyl radicals have also been proposed as the gas-forming reactions.

In *Section 4.3*, thermal stability of LG vapor has been compared with those of methyl α -glucoside and methyl β -glucoside vapors to study whether the vapor-phase stability is characteristic to LG. As a result, methyl glucosides were found to become more reactive in the vapor-phase and gave LG selectively at 200 and 300°C . This is an opposite trend to that observed for LG vapor. Fragmentation reactions of methyl glucosides were also found to proceed at a lower temperature of 400°C than those of LG vapor. The greater transglycosylation reactivity of methyl glucosides has been explained with the concerted heterolysis mechanisms, which reduce the energy barriers significantly. Reduced radical chain reactivity arising from the steric bicyclic ring system of LG has been proposed as a mechanism that stabilizes LG vapor against fragmentation. Consequently, LG is a special carbohydrate which is stabilized in the vapor-phase, and this is a reason why large amount of LG is produced from the pyrolysis of cellulose and other glucose-based carbohydrates.

In *Section 4.4*, thermal degradation kinetics of LG vapor has been studied, and the degradation mechanism has been proposed with reference to the model compound data along with the theoretical calculation results. The obtained kinetics did not follow heterolysis and homolysis mechanisms, and radical chain mechanisms have been suggested to play more important roles particularly at high temperatures. The radical chain pathways were discussed for various C- and O-centered radicals which are formed through hydrogen abstraction from LG. As a result, formation of unsaturated groups such as vinyl ether and conjugated C=O was suggested to form weak vinyl ether C–O and allylic C–C bonds that are readily cleaved homolytically at such high temperatures >600°C. This has been proposed as a mechanism explaining why benzenes and furans are not produced from the LG vapor.

In addition, reactivities of three types of concerted heterolysis reactions (direct dehydration, cyclic Grob fragmentation, and Pinacol rearrangement) were compared between LG and glycerol, a model free of bicyclic ring system, by theoretical calculations [6]. As a result, LG was found to be stabilized against Pinacol rearrangement and two of the three cyclic Grob reactions due to the steric effects of the bicyclic ring of LG, which increase the activation energies. Contrary to this, only one type of the cyclic Grob reactions, which cleaves both cyclic rings in LG, rather reduced the activation energy to 57.4 kcal/mol. The involvement of this heterolysis reaction as a radical initiation reaction was suggested by the product composition from the pyrolysis of LG vapor at a relatively low pyrolysis temperature of 500°C.

In *Chapter 5*, cellulose gasification as conducted with the similar experimental set up has been compared with the results obtained for the LG vapor, in order to understand the role of pyrolysis of LG vapor in cellulose gasification [7]. As a result, most of the reactions in cellulose gasification were found to be explained by vapor-phase reactions of LG, except for aromatization including benzenes, furans, and coke formation, all of which originates from the liquid-phase reactions. Influences of the addition of oxygen to cellulose and LG gasification have also been reported in this chapter.

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

References

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