

Article

Dehydration Leads to Hydrocarbon Gas Formation in Thermal Degradation of Gas-Phase Polyalcohols

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Abstract: To understand the molecular mechanisms of hydrocarbon gas formation in biomass gasification, gasification of simple polyalcohols (glycerol, propylene glycol, and ethylene glycol) were studied at 400, 600, and 800 °C (residence times: 0.9–1.4 s) from the viewpoint of dehydration reactions that form aldehydes with various substituents as intermediates to produce hydrocarbon gases. The results were also compared with those of glyceraldehyde and dihydroxyacetone, which are reported to produce syngas (H_2 and CO) selectively. All polyalcohols became reactive at 600 °C to form condensable products in 15.7–24.7% yields (C-based), corresponding to 33.9–38.4% based on the amounts of reacted polyalcohols. These condensable products, mostly aldehydes, act as gas-forming intermediates, because the polyalcohols were completely gasified at 800 °C (hydrocarbon gas contents: 20.3–35.3%, C-based). Yields of the intermediates bearing alkyl groups at 600 °C were proportionally correlated to the yields of hydrocarbon gases at 800 °C, suggesting that the alkyl groups are further converted into hydrocarbon gases via the fragmentation of acyl radicals. Dehydration reactions were suggested to occur in both heterolytic and radical mechanisms by theoretical calculations. Glyceraldehyde tended to fragment directly into CO and H_2 , instead of forming a dehydration intermediate. These results are informative for controlling the product gas composition in biomass gasification.

Keywords: biomass gasification mechanism; polyalcohol; hydrocarbon gas; dehydration; density functional theory

1. Introduction

Biomass gasification, which produces oxygenated (OX) (carbon monoxide (CO) and carbon dioxide (CO_2)) and hydrocarbon (HC) (methane (CH_4), ethylene (C_2H_4) and acetylene (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 ($CO + H_2$). Contamination from hydrocarbon gases, however, should be eliminated for the Fischer–Tropsch process, because of the poisoning problem on the catalysts. Ethylene is an important industrial chemical currently produced from petroleum, and the improvement of the production in biomass gasification would promote replacing petroleum with biomass as the source of 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 [1,2] converts CO and H_2O into H_2 and CO_2 under steam gasification conditions. These processes increase the H_2 content instead of CO from biomass. However, reports are limited for the reactions that produce hydrocarbon gases from biomass gasification. However, molecular mechanisms that produce hydrocarbon gases in biomass components gasification have not been well clarified.

Stein et al. [3] reported the ethylene formation from acrolein, and they explained the formation via vinyl radical formed by the α -scission of the acrolein radical. Fukutome et al. [4] 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 [5]. Therefore, the gas composition from cellulose gasification varies depending on the chemical structure of the volatile intermediates during cellulose gasification.

Levoglucosan (1,6-anhydro- β -D-glucopyranose) is a major volatile intermediate in cellulose gasification, because of the large amounts (69.3% and 52.7%, C-based under nitrogen and 7% oxygen/nitrogen conditions, respectively) detected during the pyrolysis in a flow-type reactor [6]. The gaseous levoglucosan is stable up to around 500 °C and starts to fragment at 600 °C into smaller compounds and finally into non-condensable gases [7], although it readily degrades into polymerization and dehydration products, including coke, in the molten state by cooling [8]. High reactivity of the molten levoglucosan has been explained by the intermolecular hydrogen bonding acting as acid and base catalysts [9–11].

The kinetic analysis of the decomposition of gaseous levoglucosan indicated the radical chain reactions acting as the rate-determining step [12]. In analyzing the fragmentation pathways of the C- and O-centered radicals of levoglucosan from the perspective of organic reaction mechanisms, an interesting hypothesis has been proposed; hydrocarbon gases (methane, ethylene, and acetylene) are produced by the cleavage of the substituents of aldehydes, produced by the dehydration reactions from the levoglucosan radicals [12]. This hypothesis suggests that the hydrocarbon gas formation is directly related to the extent of the progression of dehydration reactions that can occur in both heterolysis and β -scission of radical intermediates. However, contributions of these mechanisms have not been fully clarified due to the complexity of the gasification reactions of levoglucosan as an intermediate from cellulose and hemicellulose in biomass gasification. Consequently, simple polyalcohols: glycerol (Gly), propylene glycol (PG), and ethylene glycol (EG) in Figure 1 were used in this study. It is easier to identify the intermediate products and to discuss their gas-forming reactions by effectively utilizing the theoretical calculation results obtained by using density functional theory (DFT) conducted at MP4(sdq)/Aug-cc-pVTZ//DFT(M06-2X)/6-31+G (p,d) levels. The results are also compared with those reported for Gald and DHA [5], which selectively produce synthesis gas (CO and H₂) instead of the hydrocarbon gases.

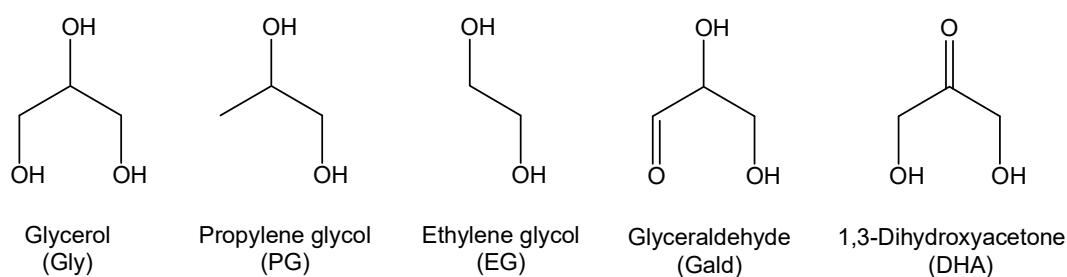


Figure 1. Polyalcohols used in the present investigation.

2. Materials and Methods

2.1. Materials

Ethylene glycol, propylene glycol, and glycerol, which were used for pyrolysis trials, were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). Table 1 summarizes some physicochemical data of these polyalcohols. These chemicals were used as received, without further purification.

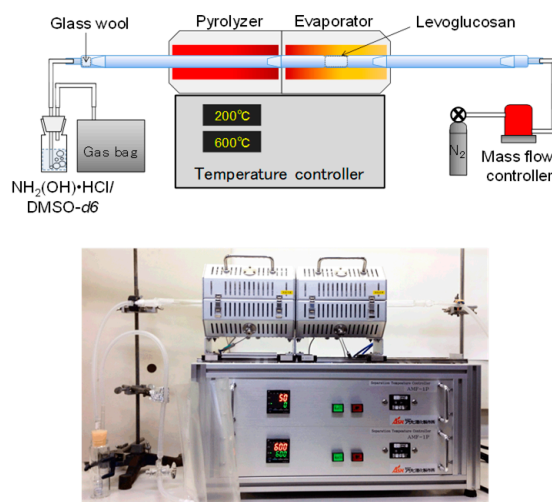
Table 1. Physicochemical data of polyalcohols.

	Molecular Weight (Da)	Density (g/cm ³)	Melting Point (°C)	Boiling Point (°C)
Glycerol	92.09	1.261	17.8	290
Propylene glycol	76.09	1.036	−59	188
Ethylene glycol	62.07	1.113	−12.9	197
Glyceraldehyde	90.08	1.455	145	228 *
1,3-Dihydroxyacetone	90.08	1.283	90	214 *

* predicted value in SciFinder.

2.2. Pyrolysis

A flow-type two-stage tubular reactor (Figure 2) used in this study is fully described in our previous paper [5]. Sample (15 mg) put in a ceramic boat was placed at the center of the evaporator, and the air inside the reactor made of quartz glass tube was replaced with a nitrogen flow at 400 mL min^{−1}. The nitrogen flow was continuously supplied during the pyrolysis and for additional 2 min after the pyrolysis to recover the volatile products. After the pyrolyzer temperature was pre-set to 400, 600, or 800 °C, the evaporator was heated to 120 °C and held for 5 min, then further heated to 200 °C at 16 °C min^{−1} and held for 5 min. This process completely volatilized the sample and led it to the pyrolyzer. The residence times of gaseous sample in the pyrolyzer were 1.4 s (400 °C), 1.2 s (600), and 0.9 s (800 °C), which were settled to be near residence times of actual gasifications [13,14]. After the pyrolysis, the furnace cover was open and cooled by an air flow. The volatile products were passed through a gas washing bottle containing an oximation reagent (hydroxylammonium chloride (NH₂OH•HCl), 20 mg) in dimethylsulfoxide (DMSO)-d₆ (2.0 mL), where aldehydes and ketones were converted into the corresponding oxime derivatives. The non-condensable gases were recovered into a gas bag.

**Figure 2.** A flow-type two-stage tubular reactor consisting an evaporator connected to a pyrolyzer and product recovery unit.

2.3. Product Analysis

The condensed substance attached on the reactor tube was washed with the DMSO-*d*₆ solution in the gas washing bottle, and then the resulting solution was directly measured by proton (¹H) nuclear magnetic resonance (NMR) spectroscopy using a Bruker AC-400 (400 MHz) spectrometer. Yields of the products were determined by the comparison of the peak areas with those of the internal standard (2-furoic acid) which was added to the NMR sample solution.

Except for acetylene, non-condensable gases were determined by micro GC (Varian CP-4900) with the two columns system (MS5A (10 m) and PoraPLOT Q (10 m)). Acetylene was determined by

GC (Shimadzu GC-14B) with the column: RESTEC, Rt@-Alumina BOND/N₂SO₄ (30 m, 0.53 mm Ø). The details of the chromatographic conditions are described in our previous paper [5].

2.4. Computational Methods

Calculations were made with Gaussian 09 software package [15]. The geometry optimizations and vibrational frequency calculations were conducted with DFT (M06-2X) and 6-31+G(d,p) basis sets. The energies of optimized geometries were calculated with MP4(SDQ). Single point energy calculation to estimate bond dissociation energy (BDE) were conducted with the CCSD(T) method and the AUG-cc-pVTZ basis sets. Activation energy (E_a) and BDE include zero-point energies. In frequency analysis, one imaginary mode was observed for transition state, but no imaginary modes for the reactants, products, and precomplexes. The intrinsic reaction coordinate calculations were also conducted to ascertain the transition state connecting the reactant and product.

3. Results and Discussion

3.1. Experimental Study of Gas Formation via Fragmentation of Intermediates

Gly, PG, and EG were recovered almost quantitatively at 400 °C and became reactive at 600 °C, where 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 non-condensable gases. Because polyalcohols were completely converted into the non-condensable gases by increasing the temperature to 800 °C, these condensable products are the gas-forming intermediates from the polyalcohols. Therefore, a comparison of the chemical structures of condensable intermediates (600 °C) with the final gas composition (800 °C) would be valuable to understand the gasification pathways of polyalcohols.

The compositions of the non-condensable gases produced from Gly, PG, and EG at 800 °C are summarized in Figure 3, compared with those reported for Gald-DHA (61/36, mol/mol) and DHA [5]. The gas yields (82.2–97.4%, C-based) are also shown in the figure. Although the major gaseous products were syngas, the hydrocarbon gas yields were different depending on the chemical structure of the polyalcohol. Gald-DHA (61/36) and DHA produced syngas selectively with the limited amounts of HC gases (2.9–3.0%, C-based) and CO₂, 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.

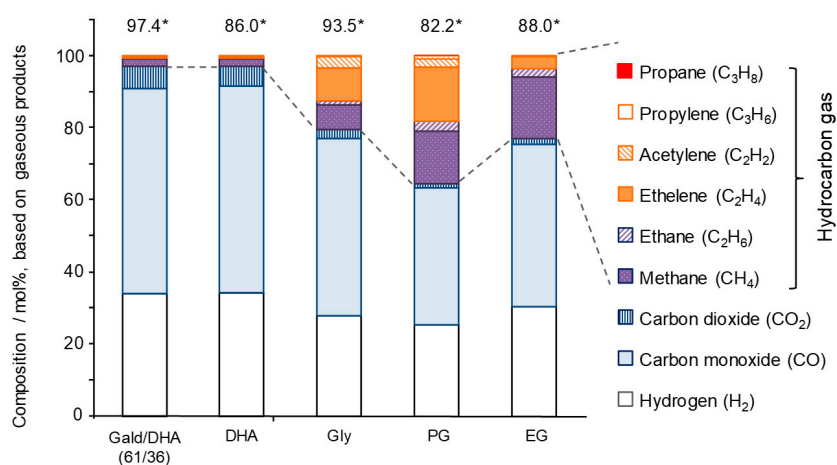


Figure 3. Composition (mol%) of non-condensable (gaseous) products from glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36, mol/mol), DHA, glycerol (Gly), propylene glycol (PG), and ethylene glycol (EG) at 800 °C (residence time of 0.9 s under N₂ flow of 400 mL min^{−1}). * Yield (% C-based) of the non-condensable product. The data of Gald/DHA, DHA and Gly are from literature [5].

Discussion of the non-condensable gas formation with the composition formulas of polyalcohols provides insight into the gas-forming reactions. As shown in Figure 4, the CHO ratio of Gald and DHA ($C_1H_2O_1$) is ideal for the production of equimolar amounts of CO and H_2 . However, PG ($C_1H_{2.7}O_{0.6}$) has insufficient oxygen for the production of oxygenated (OX) gases (CO and CO_2); therefore, PG produced larger amounts of HC gases (35.3%, C-based). Gly ($C_1H_{2.7}O_1$) and EG ($C_1H_3O_1$) 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 CO_2 were low from Gly and EG, some of the oxygen atoms must be lost as water from these polyalcohols. Consequently, gas composition is not merely determined by the elemental composition, indicating that the gas forming reactions are not equilibrated but controlled kinetically under the present experimental conditions. Dehydration may compete with the fragmentation reactions to form non-condensable gases.

	Molecular formula	Composition formula	
Glycolaldehyde (GA)	$C_2H_4O_2$	$\rightarrow C_1H_2O_1$	} Suitable for CO + H_2
Glyceraldehyde (Gald)	$C_3H_6O_3$	$\rightarrow C_1H_2O_1$	
Glycerol (Gly)	$C_3H_8O_3$	$\rightarrow C_1H_{2.7}O_1$	
Ethylene glycol (EG)	$C_2H_6O_2$	$\rightarrow C_1H_3O_1$	
Propylene glycol (PG)	$C_3H_8O_2$	$\rightarrow C_1H_{2.7}O_{0.67}$	Oxygen deficient for CO + H_2

Figure 4. Production of syngas (CO + H_2) from glyceraldehyde, 1,3-dihydroxyacetone, glycerol, ethylene glycol, and propylene glycol as discussed with the composition formula.

Occurrence of dehydration reaction converts polyalcohols into enols, which are further rearranged into carbonyl compounds (Figure 5A). As summarized in Figure 6, carbonyl compounds, particularly aldehydes, are the major components of condensable products. These results support the occurrence of dehydration reactions during polyalcohol gasification, although the chemical compositions are different depending on the polyalcohol type. Gald-DHA (61/36, mol/mol) and DHA gave formaldehyde (FA), glycolaldehyde (GA), glyoxal (GO), and methylglyoxal (MeGO) as the major components. Gly and PG produced larger amounts of C_3 products, which include hydroxyacetone (HA) and acrolein (ACR) from Gly, and propionaldehyde (Pald) and allyl alcohol (AllyOH) from PG. EG, a C_2 polyalcohol, formed acetaldehyde (AA) and FA selectively.

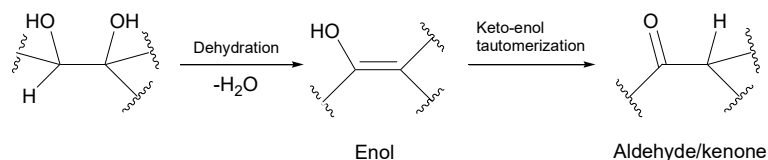
Aldehydes are known to fragment via acyl radicals (Figure 5B) [16]. Aldehydic hydrogens have been suggested as the predominant sites for hydrogen abstraction by $\bullet OH$, from experimental and theoretical investigations [17–19]. Pre-reactive complex formation between aldehyde and $\bullet OH$ has been proposed for this selective abstraction [19]. Although the reactivities of alkyl radicals such as $\bullet CH_3$ remain unclear, the resulting acyl radical ($\bullet CR(=O)$) is fragmented into CO and $\bullet R$ through the α -scission mechanism. Therefore, the final gas compositions vary depending on the chemical structure of $\bullet R$, which is stabilized as R-H by abstraction of hydrogen or degraded further (Figure 5C).

When $\bullet R$ is $\bullet H$ (case of FA), H_2 is produced through hydrogen abstraction reaction. As in the case of GO, the resulting $\bullet R$ ($\bullet CH=O$) fragments into CO and $\bullet H$ through similar β -scission reaction. When R is hydroxymethyl or hydroxymethyne group (case of GA and Gald), the resulting $\bullet C(R'')-OH$ would be converted into CO and H_2 via the aldehyde and enol intermediates. Accordingly, these intermediate aldehydes selectively produce syngas (CO and H_2). Selective syngas formation from Gald and DHA is explainable with these reactions, since DHA is suggested to be rearranged into Gald in the gas phase [5].

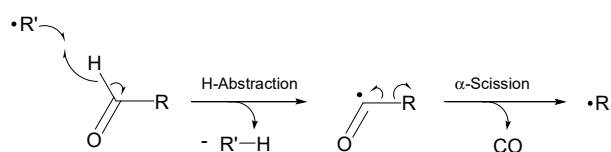
On the other hand, the acyl radicals with alkyl groups can form HC gases via the stabilization of the alkyl radical intermediates. Methyl radical ($\bullet CH_3$) formed from AA would produce methane,

and ethyl ($\bullet\text{CH}_3\text{--CH}_3$) and vinyl ($\bullet\text{CH}_2\text{=CH}_3$) radicals formed from Pald and ACR, respectively, can be converted into ethane and unsaturated hydrocarbons such as ethylene and acetylene.

(A) Aldehyde/ketone formation through dehydration of polyalcohol

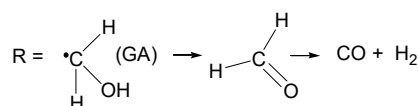
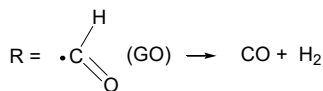
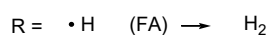


(B) Fragmentation of aldehyde



(C) Further conversion of $\bullet\text{R}$

to syngas



to hydrocarbon gas

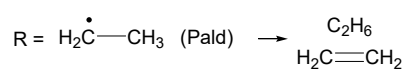
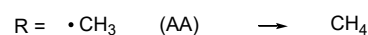


Figure 5. Gas-forming reactions considered for polyalcohols, including fragmentation of aldehyde intermediates into syngas and hydrocarbon gases.

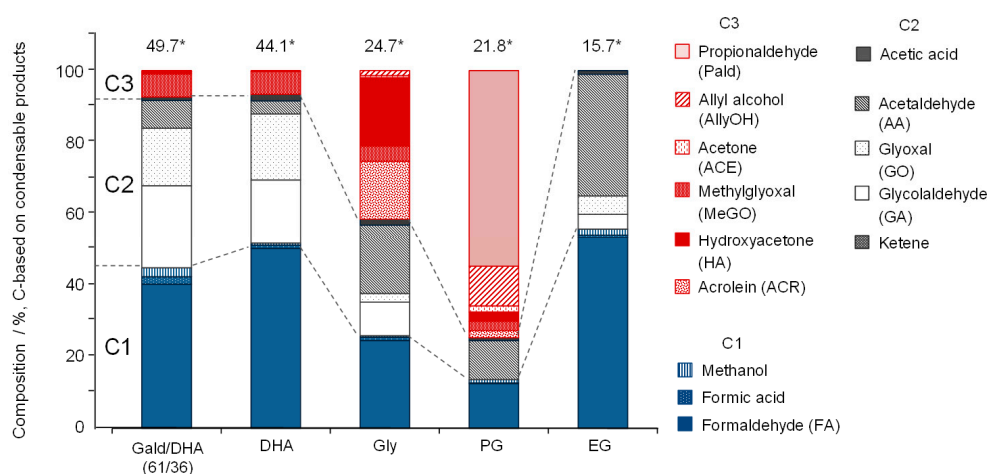


Figure 6. Composition (% C-based) of condensable products from glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36, mol/mol), DHA, glycerol (Gly), propylene glycol (PG), and ethylene glycol (EG) at 600 °C (residence time of 0.9 s under N_2 flow of 400 mL min^{-1}). * Yield (% C-based) of the condensable product. The data of Gald/DHA, DHA and Gly are from literature [5].

Alkyl groups attached on ketonic ($>C=O$) and carboxylic ($-COOH$) groups are also reported to produce HC gases [4]. Based on such information, acetone (ACE), MeGO, HA, acetic acid, AA, methanol, Pald, ACR, AllyOH and ketene are picked up as the intermediates bearing alkyl groups, and the yields of these compounds from polyalcohols (% C-based on the condensable products) are compared in Figure 7. 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%). It is noted that these yields are proportionally correlated to the contents of the HC gases in Figure 3, supporting the hypothesis; the intermediates bearing alkyl groups produce hydrocarbon gases. Many of such intermediates can be produced by dehydration reactions as discussed below.

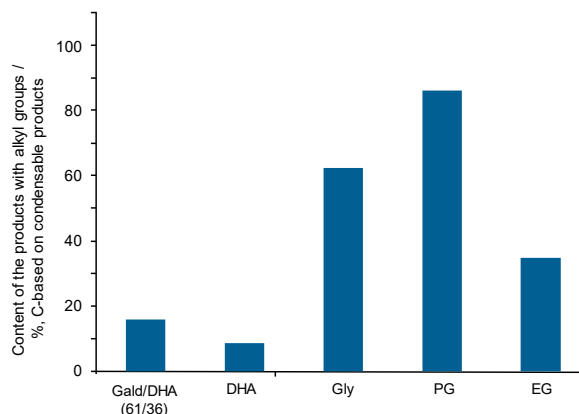


Figure 7. Contents (% C-based) of the products with saturated and unsaturated alkyl groups in condensable products obtained from glyceraldehyde (Gald)/1,3-dihydroxyacetone (DHA) (61/36, mol/mol), DHA, glycerol (Gly), propylene glycol (PG), and ethylene glycol (EG) at 600 °C. The data of Gald/DHA, DHA and Gly are from literature [5].

Comparatively large amount of methane formation from EG is explainable with the higher yield of AA, and the greater yields of ethylene from PG and Gly are coincide with the greater yields of Pald and ACR, respectively. Although the HC gas yields are quite small from Gald and DHA, high contributions of methane in HC gas are explainable with the AA and MeGO formation.

Gald is reactive for gasification and directly converted into CO and H_2 with a smaller contribution of dehydration reaction to form MeGO leading to the methane production. Ethane would be produced through coupling of two $\bullet CH_3$.

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

3.2. Theoretical Study of Intermediate Formation

Dehydration of the alcohols could proceed in the gas phase through heterolytic dehydration, homolysis of the C–OH bond, and β -scission of C-centered radicals as illustrated in Figure 8. However, very high bond dissociation energies of the C–OH bonds in polyalcohols (93.5–95.6 kcal mol^{−1} for Gly [5]) 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 [20].

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 [21]. Various radical species such as $\bullet OH$ and $\bullet CH_3$ existing in the pyrolysis environment can abstract these hydrogens [22].

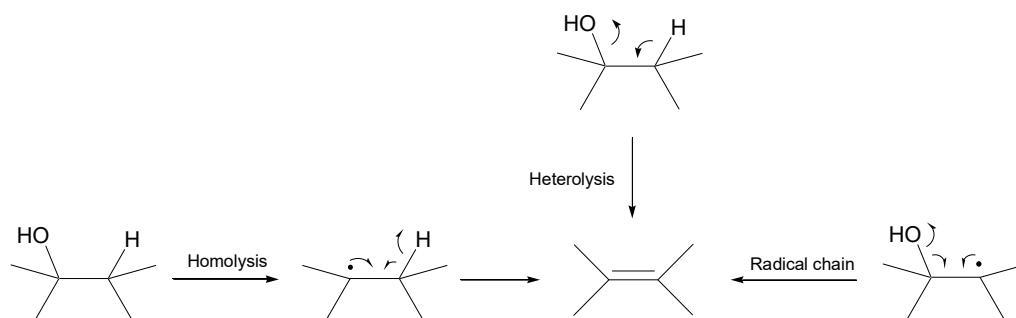


Figure 8. Three possible dehydration pathways for polyalcohols.

In this section, heterolytic dehydration reactions were theoretically evaluated and discussed with the pyrolysis products obtained at 600 °C. Then, the products that could not be explained with the heterolytic reactions are discussed with the radical pathways that are reasonably drawn from the C- and O-centered radicals.

Bimolecular reactions are also considered, since bimolecular keto–enol tautomerization have been suggested for $\text{DHA} \leftrightarrow \text{enol} \leftrightarrow \text{Gald}$ in our previous paper [5]. In this paper, pyrolytic degradation of Gald into $\text{MeGO} + \text{AA}$ and $\text{GA} + \text{FA}$ at 400 °C were explained with the unimolecular reactions, that is, dehydration via the six-membered cyclic TS of enol intermediate of Gald (E_a 35.5 kcal mol^{−1}) and retro-aldol fragmentation of Gald (E_a 40.9 kcal mol^{−1}), respectively. DHA was suggested to degrade via the enol and Gald. However, the values of E_a of the enolization steps of Gald and DHA were calculated to be too high (E_a 72.5 and 69.3 kcal mol^{−1}, respectively) to explain why these steps proceed at such a low temperature of 400 °C. In explaining the contradiction between experimental and theoretical calculation results, bimolecular mechanisms have been proposed for decreasing the values of E_a to 46.4 and 48.7 kcal mol^{−1}, respectively.

Nevertheless, bimolecular mechanism should be treated carefully, because the meeting of two molecules are necessary in the gas phase, which is not effective due to the increasing entropy. Accordingly, to conclude the bimolecular mechanisms, more systematic studies should be necessary. However, we consider that the bimolecular reactions would be possible under some special conditions such as in cluster and a product–water complex formed just after the dehydration reaction even in the gas phase.

Some molecules such as carboxylic acids and alcohols, both of which have the ability of the hydrogen-bonded complex formation, are known to exist as a cluster in the gas phase. For example, it is suggested that methanol exists as dimers, trimers, and oligomers in addition to the monomer in the gas phase [23–29].

3.2.1. Ethylene Glycol (EG)

EG produced AA and FA as the major condensable products. As shown in Figure 9, both direct dehydration (E-i, E_a 74.1 kcal mol^{−1}) and pinacol rearrangement (E-iii, E_a 73.0 kcal mol^{−1}) pathways can explain the formation of AA from EG, although the energy barriers are not small. The E_a (74.1 kcal mol^{−1}) of the unimolecular dehydration decreased to 64.0 kcal mol^{−1} by assuming the bimolecular mechanism involving two EG molecules.

To understand the natures of the bimolecular mechanisms in direct dehydration (E-i), the $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values were calculated for EG (unimolecular), EG-EG, and EG-H₂O at 25, 400, and 600 °C (Table 2), and compared with those calculated for the keto–enol tautomerization of DHA (unimolecular), DHA-DHA, and DHA-H₂O (Table 3). The $\Delta G^\ddagger$ of the enolization 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 due to the significant decrease in the $\Delta H^\ddagger$ values (65.5–65.7 to 42.3–46.6 kcal mol^{−1}). 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.

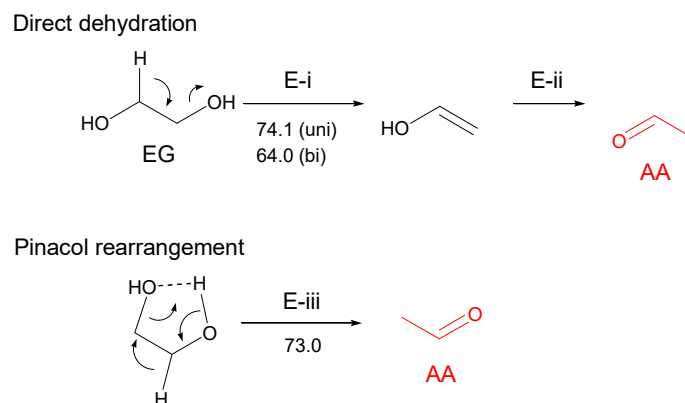


Figure 9. Possible heterolytic dehydration pathways for ethylene glycol (EG). The values next to the arrows represent the activation energies (kcal mol^{-1}), as calculated at the MP4(SDQ)//DFT(M06-2X) level. AA, acetaldehyde; uni, unimolecular mechanism; and bi, bimolecular mechanism (EG-EG).

Table 2. The $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values (kcal mol^{-1}) calculated for the dehydration of ethylene glycol (EG) by assuming the unimolecular (uni) and bimolecular (bi, EG-EG, and EG-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.

		kcal mol^{-1}			
		$\Delta G^\ddagger$	$\Delta H^\ddagger$	$T\Delta S^\ddagger$	
EG (uni)	25 °C	71.3	71.6	0.3	 EG (uni)
	400 °C	70.7	72.1	1.4	
	600 °C	70.3	72.2	1.9	
EG-EG (bi)	25 °C	61.0	59.3	−0.7	 EG-EG (bi)
	400 °C	63.1	59.3	−2.8	
	600 °C	64.3	59.4	−3.9	
EG + H ₂ O (bi)	25 °C	66.5	65.3	−1.2	 EG + H ₂ O (bi)
	400 °C	68.2	65.1	−3.1	
	600 °C	69.1	65.2	−3.9	

Table 3. The $\Delta G^\ddagger$, $\Delta H^\ddagger$, and $T\Delta S^\ddagger$ values (kcal mol^{-1}) calculated for the keto–enol tautomerization of 1,3-dihydroxyacetone (DHA) by assuming the unimolecular (uni) and bimolecular (bi, 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.

		kcal mol^{-1}			
		$\Delta G^\ddagger$	$\Delta H^\ddagger$	$T\Delta S^\ddagger$	
DHA (uni)	25 °C	66.4	65.7	−0.7	 DHA (uni)
	400 °C	67.2	65.6	−1.6	
	600 °C	67.8	65.5	−2.3	
DHA-DHA (bi)	25 °C	45.4	43.3	−2.1	 DHA-DHA (bi)
	400 °C	48.4	42.6	−5.8	
	600 °C	50.2	42.4	−7.8	
DHA + H ₂ O (bi)	25 °C	48.9	46.6	−2.3	 DHA + H ₂ O (bi)
	400 °C	52.3	45.6	−6.7	
	600 °C	54.3	45.4	−8.9	

The influences of the bimolecular mechanisms on the dehydration reaction were much lower, because of the smaller reduction of the $\Delta H^\ddagger$ values (71.6–72.2 to 59.3–65.3 kcal mol^{-1}); 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.

Formation of FA and other minor products, that is, GA, GO, and MeOH, cannot be explained with the heterolysis reactions, but with the radical pathways from the C- and O-centered radicals of EG as illustrated in Figure 10. FA and MeOH can form via the β -scission of the O-centered radical of EG (E-e). The formations of GA and GO are possible by the radical pathways E-a, E-d, and E-f and pathway E-g, respectively. Thus, radical pathways are necessary to explain the product formation from EG. AA can also form by pathway E-b.

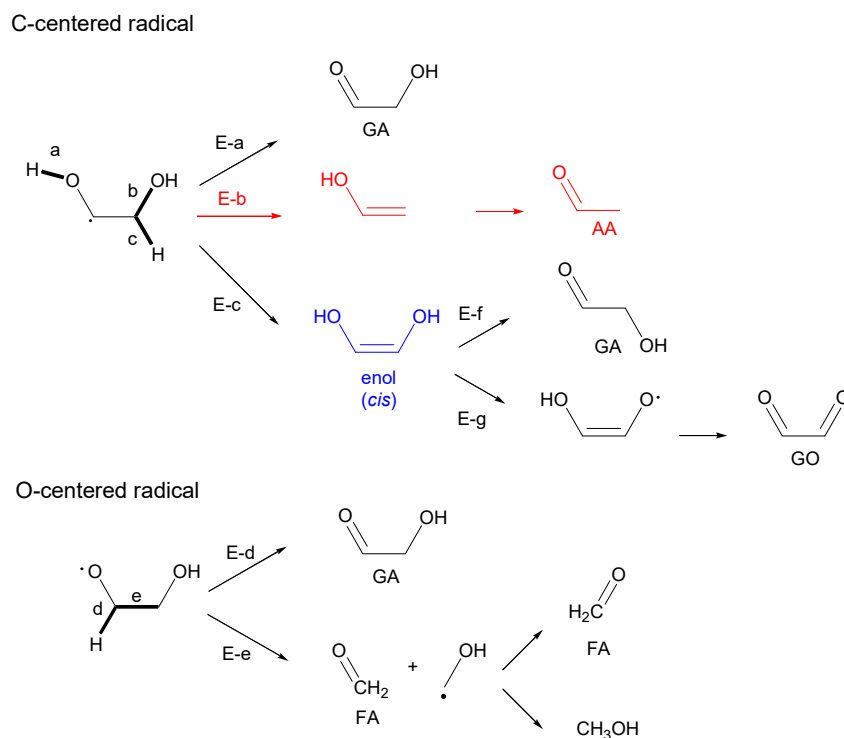


Figure 10. Possible radical chain pathways from the C- and O-centered radicals of ethylene glycol (EG). The bond with a bold line, which is located at the β -position to the radical, is expected to be cleaved through β -scission reaction. GA, glycolaldehyde; GO, glyoxal; AA, acetaldehyde; and FA, formaldehyde.

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 [30]. This pathway leads to the stereoselective formation of *cis* enol from EG (reaction E-c in Figure 10). Therefore, the influences of these stereoisomers during the keto–enol tautomerization were studied further (Figure 11). 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, $\text{O}-\text{H}$ would 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. Consequently, pathway E-f would compete with the hydrogen abstraction pathway E-g reading to the formation of GO. The intramolecular hydrogen bonding lowers the BDE of the $\text{O}-\text{H}$ bond in the *cis* isomer to 70.6 kcal mol^{−1}. The *trans* enol, which is not formed from the radical reactions of EG, may be transformed to GA through the unimolecular keto–enol tautomerization, because of the low E_a of 58.6 kcal mol^{−1}.

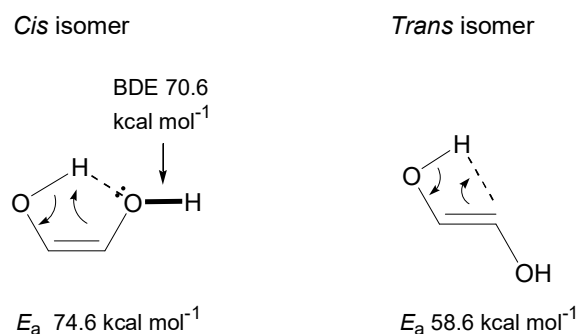


Figure 11. Influences of the stereochemistry of *cis/trans* enol on activation energy (E_a , kcal mol⁻¹) of keto–enol tautomerization by assuming the unimolecular mechanisms, as calculated at the MP4(SDQ)//DFT(M06-2X) level. BDE: bond dissociation energy.

Based on the above discussion, both heterolysis and radical chain pathways are suggested to be involved in the gas-phase pyrolytic conversion of EG into gasifying intermediates.

3.2.2. Propylene Glycol (PG)

Pald represents 54.8% of the condensable products from PG, followed by AllyOH, AA, FA, and other minor products (ACE, MeGO, and ACR) at 600 °C. Heterolysis and radical pathways, which were considered for the pyrolysis of PG, are summarized in Figures 12 and 13, respectively.

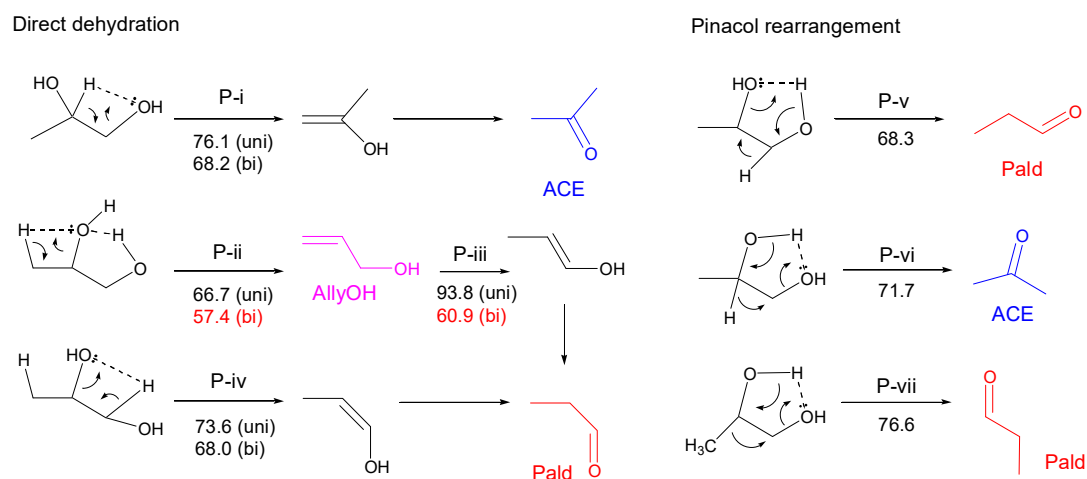


Figure 12. Possible heterolytic dehydration pathways for propylene glycol (PG). The values next to the arrows represent the activation energies (kcal mol⁻¹), as calculated at the MP4(SDQ)//DFT(M06-2X) level. Pald, propionaldehyde; AllyOH, allyl alcohol; ACE, acetone; uni, unimolecular mechanism; and bi, bimolecular mechanism.

For unimolecular heterolysis reactions, Pald can form from three pathways, P-iv, P-v, and P-vii, with the values of E_a of 73.6, 68.3, and 76.6 kcal mol⁻¹, respectively. Pathway P-ii (E_a , 66.7 kcal mol⁻¹) and pathways P-i (E_a , 76.1 kcal mol⁻¹) and P-vi (71.7 kcal mol⁻¹) can produce AllyOH and ACE, respectively. The lower values of E_a of 68.3 (P-v) and 66.7 kcal mol⁻¹ (P-ii) are reasonable to explain why Pald and AllyOH are produced as the major products. The reactions forming ACE as a minor product (1.7%, C-based) have the greater values of E_a of 76.1 (P-i) and 71.7 kcal mol⁻¹ (P-vi).

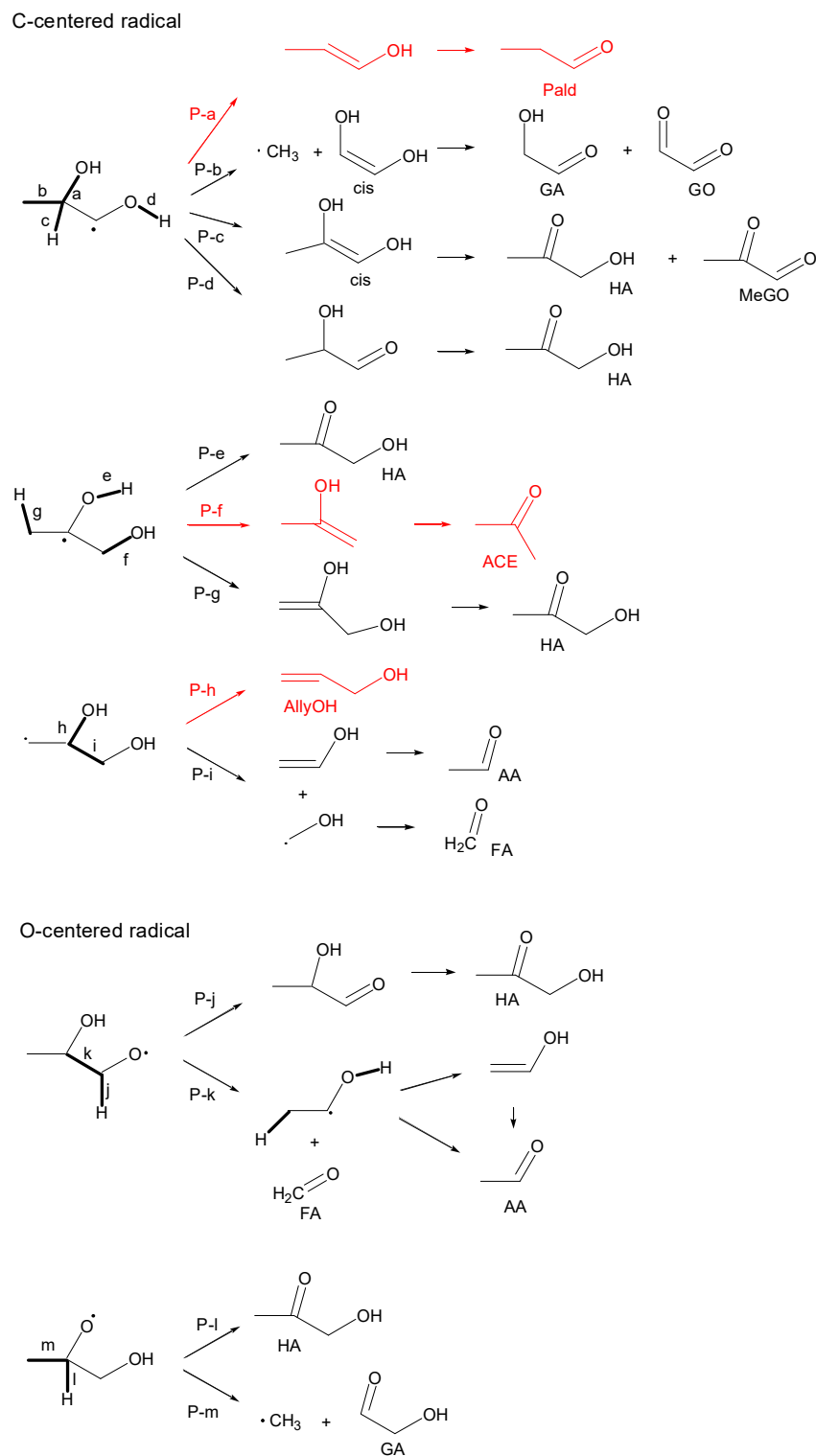
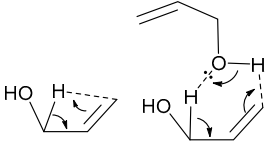


Figure 13. Possible radical chain pathways from the C- and O-centered radicals of propylene glycol (PG). The bond with a bold line, which is located at the β -position to the radical, is expected to be cleaved through a β -scission reaction. Pald, propionaldehyde; AllyOH, allyl alcohol; MeGO, methylglyoxal; HA, hydroxyacetone; ACE, acetone; GA, glycolaldehyde; GO, glyoxal; AA, acetaldehyde; and FA, formaldehyde.

Bimolecular mechanisms lower the values of E_a of direct dehydration reactions P-i, P-ii, and P-iv. As a result, the E_a of reaction P-ii forming AllyOH as the second greatest product decreased to the level

of 57.4 kcal mol^{−1}. Furthermore, the isomerization from AllyOH to enol, which exhibited extremely high E_a (93.8 kcal mol^{−1}) via a unimolecular mechanism (reaction P-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. The $\Delta G^\ddagger$ at 600 °C decreased from 95.7 (unimolecular) to 63.2 kcal mol^{−1} (bimolecular) due to the stabilization of the TS with a six-membered ring. Consequently, the preferential formation of Pald and AllyOH from PG is explainable with the pathways P-ii + P-iii followed by the keto–enol tautomerization, by assuming the bimolecular mechanisms. When the product water formed from reaction P-ii can be used for the bimolecular reaction P-iii before leaving the product AllyOH, the biomolecular reaction would proceed smoothly.

Table 4. 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.

		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	

As discussed in the case of EG, the formations of AA, FA, and other minor products (HA, MeGO and ACR) cannot be explained with the heterolysis pathways. These products would produce through radical pathways (Figure 13). AA and FA would form via the pathways P-i and P-k. The formations of other minor products are also explained with the pathways P-c, P-d, P-g, P-j, and P-l for HA and P-c for MeGO. ACR may form through oxidation of AllyOH. Pald, ACE and AllyOH would also form through P-a, P-f, and P-h, respectively. Therefore, radical pathways are also expected to contribute to the degradation of PG.

3.2.3. Glycerol (Gly)

Gly formed HA, ACR, AA, GA, and FA, along with other minor products at 600 °C. The postulated heterolysis pathways as summarized in Figure 14 explain the formation of the major components except for GA. The pathway with the lowest E_a (66.7 kcal mol^{−1}) with unimolecular mechanism is the pinacol rearrangement (G-v) giving FA and AA via the retro-aldol fragmentation (G-vi, E_a 41.7 kcal mol^{−1}). Cyclic Grob fragmentation (G-i, E_a 68.8 kcal mol^{−1}), which is a characteristic reaction of Gly, also forms AA and FA.

By assuming the bimolecular reactions, direct dehydration reactions G-ii (66.6 kcal mol^{−1}) and G-iii (63.4 kcal mol^{−1}) become more reactive to explain the formation of HA and ACR, respectively, more reasonably as the other major products.

All of the dehydration products listed in Figure 14 can be produced through radical reactions illustrated in Figure 15. Many of the radical reactions explain the formation of GA, a major product which is not expected to form by heterolysis reactions. Other minor condensable intermediates (MeGO and GO) can also be produced by the radical pathways.

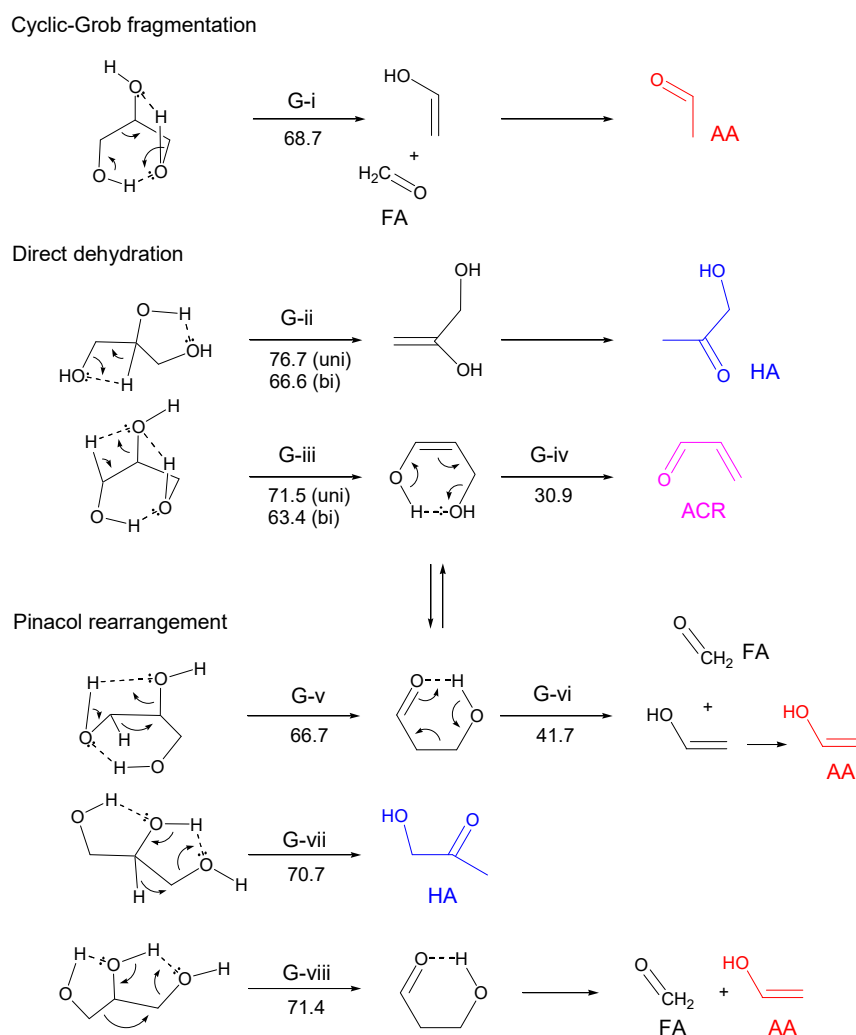
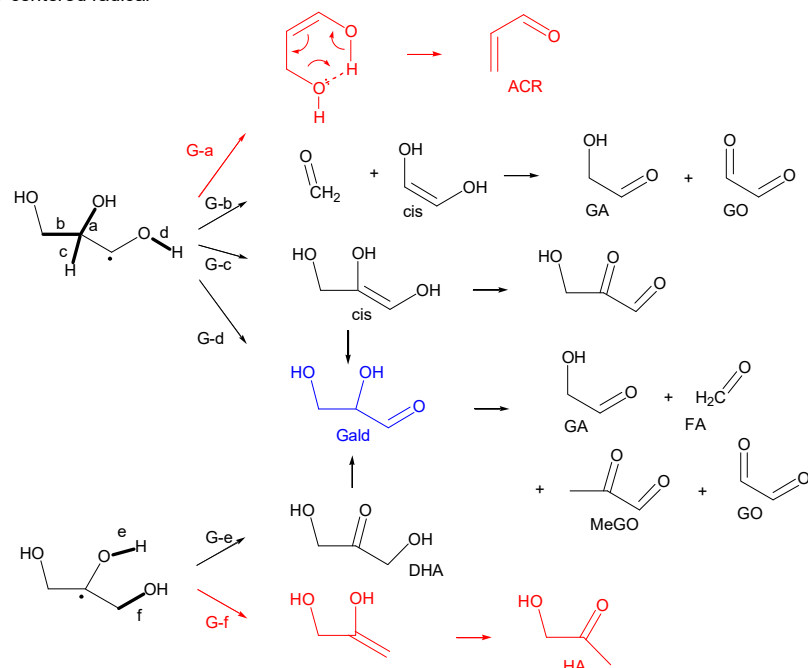


Figure 14. Possible heterolytic dehydration pathways for glycerol (Gly). The values next to the arrows represent the activation energies (kcal mol^{-1}), as calculated at the MP4(SDQ)//DFT(M06-2X) level. ACR, acrolein; HA, hydroxyacetone; AA, acetaldehyde; FA, formaldehyde; uni, unimolecular mechanism; and bi, bimolecular mechanism.

3.3. Discussion for Syngas and Hydrocarbon Gas Production from Polyalcohol

Gas-forming pathways suggested from the results of the present investigation are summarized in Figure 16. Several heterolysis pathways are suggested to explain the formation of dehydration products from polyalcohols along with the radical chain pathways, where C–OH bonds are cleaved by the β -scission type reactions occurring for the C-centered radicals. On the other hand, many of the radical chain pathways particularly from the O-centered radicals give aldehydes/ketones that bear the hydroxymethyl and hydroxymethyne groups such as glyceraldehyde and glycolaldehyde, leading to the syngas production. Accordingly, relative efficiency of hydrogen abstractions from C–H and O–H bonds may affect the relative composition of syngas and hydrocarbon gas in addition to the occurrence of heterolytic dehydration reactions. The higher concentration of syngas in the gaseous products from polyalcohol gasification would be due to the greater contribution of the radical chain fragmentations via the O-centered radicals, although further systematic study is needed to conclude it.

C-centered radical



O-centered radical

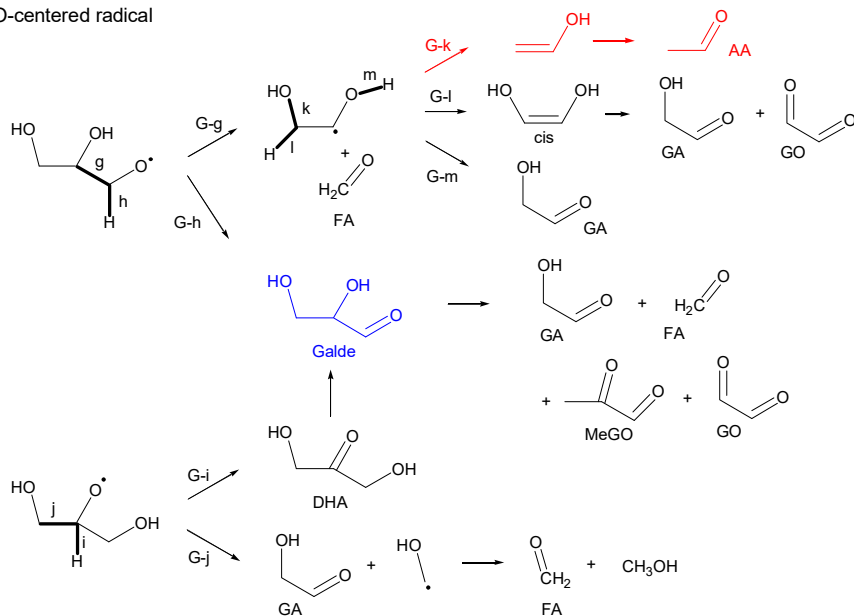


Figure 15. Possible radical chain pathways from the C- and O-centered radicals of glycerol (Gly). The bond with a bold line, which is located at the β -position to the radical, is expected to be cleaved through β -scission reaction. ACR, acrolein; MeGO, methylglyoxal; Gald, glyceraldehyde; DHA, 1,3-dihydroxyacetone; HA, hydroxyacetone; GA, glycolaldehyde; GO, glyoxal; AA, acetaldehyde; FA, formaldehyde.

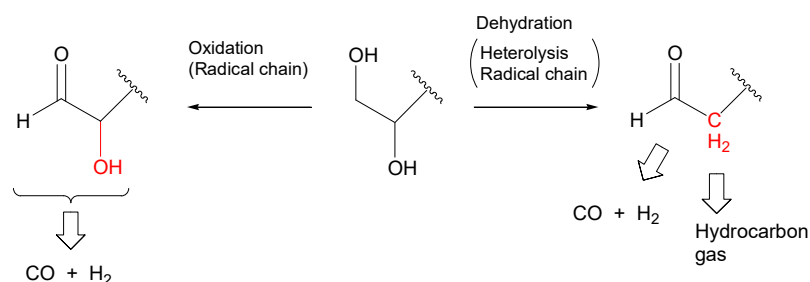


Figure 16. Syngas and hydrocarbon gas formation pathways from polyalcohol.

4. Conclusions

Thermal degradation of gas-phase simple polyalcohols (glycerol, propylene glycol, and ethylene glycol) was studied experimentally and theoretically, focusing on the formation and roles of condensable gas-forming intermediates at 400, 600, and 800 °C under nitrogen flow (residence times: 0.9–1.4 s), and the results were compared with those of glyceraldehyde. The following conclusions are obtained:

1. All polyalcohols become reactive at 600 °C and produce condensable products in 15.7–24.7% yields (C-based), corresponding to 33.9–38.4% based on the amounts of reacted polyalcohols. Because the polyalcohols are completely converted into non-condensable gases at 800 °C, the condensable products observed at 600 °C act as gas-forming intermediates.
2. Most of the condensable products are aldehydes, which can be formed from by dehydration and the following keto–enol tautomerization. Loss of some oxygen atoms as water is also suggested by the elemental compositions of gas and gas-forming intermediates.
3. Yields of gas-forming intermediates (600 °C, mostly aldehydes) bearing alkyl groups are proportionally correlated to the yields of hydrocarbon gases (800 °C), suggesting the alkyl groups being converted into hydrocarbon gases.
4. Fragmentation pathways of aldehydes via acyl radicals can explain the formation of characteristic hydrocarbons from polyalcohols (methane from ethylene glycol, ethylene and acetylene from glycerol and propylene glycol).
5. Glyceraldehyde directly fragments into CO and H₂ with a smaller contribution of dehydration reaction to form methyl glyoxal leading to the methane production, which explains why glyceraldehyde produces syngas selectively.
6. Theoretical calculations indicate heterolysis mechanisms for polyalcohol dehydration along with the contribution of radical chain mechanisms.
7. By assuming the bimolecular mechanisms for heterolytic dehydration reactions, the formations of gas-forming intermediates are explainable more reasonably.
8. 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.

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Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

Gly	glycerol
Gald	glyceraldehyde
HC	hydrocarbon
GA	glycolaldehyde
MeGO	methylglyoxal
HA	hydroxyacetone
BDE	bond dissociation energy
PG	propylene glycol
DHA	1,3-dihydroxyacetone
FA	formaldehyde
Pald	propionaldehyde
ACR	acrolein
AllyOH	allyl alcohol
Uni	unimolecular
EG	ethylene glycol
OX	oxygenated
AA	acetaldehyde
GO	glyoxal
ACE	acetone
E_a	activation energy
bi	bimolecular

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