

# Mechanistic Roles of Hydroxyl Group in the Supercritical Water Reaction of Polyhydric Alcohols

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**Abstract:** Hydroxyl functional groups present in oxygenated hydrocarbons play an important role in determining the mechanistic routes and the extent of reaction of supercritical water decomposition. To examine the effect hydroxyl groups have on supercritical water reactions, kinetic experiments were performed using isopropanol, propylene glycol, and glycerin; e.g., monohydric, dihydric, and trihydric alcohols of C<sub>3</sub> hydrocarbons. The experiments used a Haynes® Alloy 282 reactor system and were conducted at temperatures from 550°C to 650°C at a pressure of 24.13 MPa and reactor space time of 45 seconds. Based on a thorough analysis of carbon gasification, gaseous effluent compositions, and liquid effluent compositions, the mechanisms for supercritical water decomposition and the impact of hydroxyl groups on those reaction mechanisms were elucidated.

**Keywords:** Supercritical water, gasification, hydrogen, hydroxyl functional group

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## 1 Introduction

When water enters the supercritical region, it becomes a highly energetic reaction medium that is miscible with a variety of nonpolar molecules. This unique property allows water to act as a very effective solvent for gasification of hydrocarbons. Decomposition and reformation of hydrocarbons in supercritical water are versatile and non-catalytic processes used to produce hydrogen-rich synthesis gas (syngas), and a variety of hydrocarbon feedstocks can be used in these processes, such as jet fuel, sucrose, ethanol, methanol, and glycerin [1–6]. Even with the wide variety of hydrocarbon fuels, the primary gaseous products are always hydrogen,

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carbon monoxide, methane, and carbon dioxide. Ethylene, ethane, propane, and propylene can also be formed from feedstocks containing larger hydrocarbon molecules.

While all hydrocarbon fuels break down to make hydrogen-rich syngas, each reacts differently with supercritical water. Some fuels undergo supercritical water reformation, wherein they directly react with the water and produce hydrogen and carbon monoxide. Other fuels do not react with the supercritical water, and instead use it as a medium for decomposition. The presence of hydroxyl functional groups in the hydrocarbon feedstock can have a direct effect on the role supercritical water plays during the production of syngas. This study attempts to elucidate those effects by comparatively examining the reactions of isopropanol, propylene glycol, and glycerin in supercritical water at 550°C, 600°C, and 650°C. Each compound represents a C<sub>3</sub> hydrocarbon with a differing number of hydroxyl functional groups: 1, 2, and 3 for isopropanol, propylene glycol, and glycerin, respectively. The critical points and other physical properties of isopropanol, propylene glycol, glycerin, and water are shown in Table 1.

In the presence of supercritical water, glycerin undergoes decomposition, as opposed to reacting directly with supercritical water for reformation [7]. During glycerin decomposition, the first step is dehydration into either hydroxyacetone or 3-hydroxypropanal. Both of these intermediates can decompose into formaldehyde and acetaldehyde [8–10]. Formaldehyde decomposes readily into carbon monoxide and hydrogen, while acetaldehyde decomposes into methane and carbon monoxide [7, 11, 12]. 3-Hydroxypropanal can also undergo dehydration to form acrolein, which can then decompose into carbon monoxide and ethylene [13, 14]. Ethylene can then undergo hydrogenation to produce ethane.

Like glycerin, propylene glycol has multiple decomposition mechanisms in the presence of supercritical water. One pathway for propylene glycol decomposition

**Table 1** Physical properties of glycerin, propylene glycol, isopropanol, and water.

Property	Glycerin	Propylene Glycol	Isopropanol	Water
Molecular Weight (g/mol)	92.09	76.09	60.09	18.02
Density at 25°C and 1 bar (g/cm <sup>3</sup> )	1.26	1.032	0.786	0.99
Melting Point (°C)	17	-60	-88	0
Boiling Point (°C)	287	189	82	100
Critical Temperature (°C)	577	353	236	375
Critical Pressure (atm)	74.02	60.2	48.35	217.7

is dehydrogenation to hydroxyacetone, which can then decompose further as explained above [15]. Another mechanism of propylene glycol decomposition is dehydration to propionaldehyde, which subsequently decomposes to ethane and carbon monoxide [16, 17].

There are many decomposition pathways that isopropanol can go through before forming gaseous products. Isopropanol can first decompose by dehydrogenation into acetone [18, 19]. Acetone may undergo free radical decomposition by dissociation to methyl and acetyl radicals [20]. Another possible mechanism for isopropanol decomposition starts with dehydration to become propylene [21, 22]. Propylene can then undergo a series of free radical decomposition reactions, which produce primarily methane, ethylene, and hydrogen, with small quantities of higher hydrocarbons [23].

Any carbon monoxide produced during decomposition or reformation in supercritical water may then undergo a forward water gas shift reaction to produce carbon dioxide and hydrogen. While the reaction is of a reversible kind, the forward reaction is thermodynamically favored at temperatures below 815°C, where  $K_p > 1$  [24]. In this study, all carbon dioxide detected in the gaseous effluent is assumed to originate solely from the forward water gas shift reaction.

## 2 Experimental

### 2.1 Materials

The chemicals used for these experiments were deionized water, 99.7% pure glycerin from the chemistrystore.com, 99% extra pure propylene glycol from Acros Organics, and 70% isopropanol and 30% water solution from Fisher Scientific. Glycerin above 80% purity by weight is hygroscopic and will absorb atmospheric water. To prevent unknown quantities of water from diluting the glycerin and confounding the experimental results, freshly unsealed containers were pre-diluted with water to 75% purity. The solutions for these experiments were mixed so there was a water-to-fuel molar ratio of eight. The molar and weight compositions of these solutions are shown in Table 2.

**Table 2** Weight and mole % of water/fuel solutions.

Fuel	Solution Type Water/fuel ratio	Weight %		Mole %	
		Water%	Fuel%	Water%	Fuel%
Glycerin	8.00	61.03	38.97	88.89	11.11
Propylene Glycol	8.00	65.45	34.55	88.89	11.11
Isopropanol	8.00	70.58	29.42	88.89	11.11

## 2.2 Reactor System

These experiments were performed on a custom-designed supercritical water reaction system of Ohio University's Sustainable Energy and Advanced Materials (SEAM) Laboratory. The experimental system is a fully continuous mini-pilot scale supercritical water reaction system consisting of a metered solution feed system, a preheating system, a superalloy (Haynes® 282) reactor with a four-zone heater, a liquid effluent collection/analysis system and a gas sampling/analysis system. The entire process system and its operation is controlled using Labview® data acquisition and control software.

## 2.3 Analysis

The analysis of the gas samples for these experiments was performed on an HP 5890 Series A gas chromatograph with a thermal conductivity detector. Argon was used as a carrier gas for the gas samples, and the column was calibrated with a standard gas mixture from Praxair to quantify hydrogen, carbon monoxide, methane, carbon dioxide, ethylene, ethane, propylene, and propane. Samples of the liquid effluent were collected and stored in seal-tight bottles. The samples were then analyzed using a Thermo Scientific ISQ gas chromatograph/mass spectrometer. Before analysis, each sample was diluted using methanol to a 1/5 sample-to-methanol solution to aid in separation and reduce noise peaks in the sample.

## 2.4 Procedure

The reactor was heated and pressurized to the pre-determined experimental conditions using deionized water. Once process conditions stabilized, the system feed was switched to the reactant solution. Each experiment was conducted until steady state conditions were achieved. An experiment was considered to have reached steady state when two gas samples showed matching percentages of all effluent gases. During the same time period, there also needed to be no significant changes in the volumetric flow rate of the gas or any process variables. Table 3 shows a summary of the experiments conducted for this investigation.

## 2.5 Definitions

The reactor space time given for each experimental run was calculated using the internal volume of the Haynes® Alloy 282 reactor and the estimated volumetric flow rate of the solution at the nominal reactor conditions. The volumetric flow rate inside the reactor was calculated at the reactor temperature and pressure with Aspen®-Plus simulation software using the Peng-Robinson equation of state with Wong-Sandler mixing rules. This ensured that a uniform volumetric flow rate entered the reactor and that all experiments maintained the same reactor space time of 45 seconds, regardless of temperature and pressure changes that affect the fluid density.

**Table 3** Summary of experimental conditions.

Experiment	Temperature (°C)	Pressure (psig)	Water (g/min)	Fuel	Fuel Concentration (wt%)	Water/Fuel ratio (mol/mol)
1	549	3498	17.1	Glycerin	38.97	8
2	599	3485	14.4	Glycerin	38.97	8
3	648	3452	13.0	Glycerin	38.97	8
4	549	3510	13.5	Propylene Glycol	34.55	8
5	599	3480	12.2	Propylene Glycol	34.55	8
6	648	3456	11.2	Propylene Glycol	34.55	8
7	549	3501	12.3	Isopropanol	29.42	8
8	598	3485	11.1	Isopropanol	29.42	8
9	649	3499	10.6	Isopropanol	29.42	8

The carbon gasification for each of the experiments is defined as the moles of carbon exiting in the gaseous effluent divided by the total moles of carbon entering the reactor. The gas composition results shown in Table 4 are based on the moles of gaseous species per mole of carbon entering the reaction system. These results show overall amounts of each gaseous species being produced at the different conditions, but it is difficult to tell what is happening with regard to reaction selectivity because the amount of all gaseous species tends to increase with increasing carbon gasification. The gas results can also be represented as the amount of gaseous species per mole of gaseous carbon exiting the reactor. Normalizing all experiments this way better displays trends in the selectivity of gaseous products, rather than using the actual amount being produced.

### 3 Results and Discussion

The results of each hydrocarbon species with increasing temperature will be examined first, followed by the effect of increasing the amount of hydroxyl groups at a given temperature. The primary gases produced in these experiments were hydrogen, carbon monoxide, methane, carbon dioxide, ethane, and ethylene. No detectable quantities of propane or propylene were produced. The results of all the experiments can be found in Table 4.

**Table 4** Summary of experimental results.

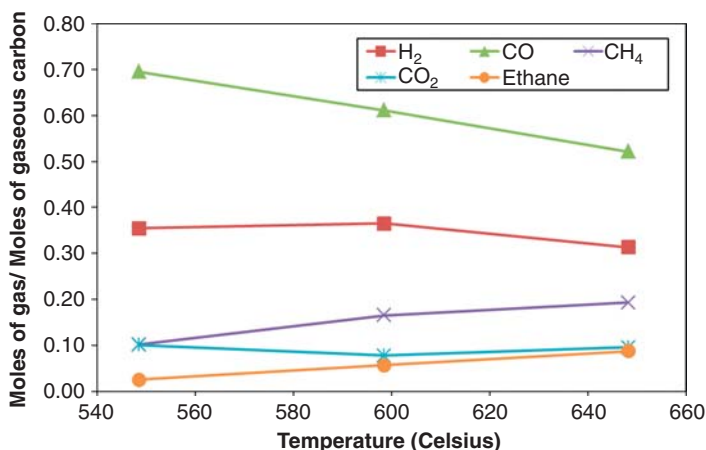
Experiment	Product Gas Flow (L/min)	Gas Yield (mol gas/mol carbon fed)						Carbon Gasification
		H <sub>2</sub>	CO	CH <sub>4</sub>	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	
1	1.48	0.08	0.15	0.02	0.02	0.00	0.01	21.4%
2	3.21	0.20	0.34	0.09	0.04	0.00	0.03	55.8%
3	4.46	0.29	0.48	0.18	0.09	0.00	0.08	91.2%
4	0.50	0.06	0.02	0.01	0.02	0.00	0.01	5.5%
5	3.09	0.25	0.19	0.11	0.11	0.01	0.09	61.4%
6	3.65	0.23	0.25	0.25	0.12	0.00	0.13	89.5%
7	0.64	0.11	0.00	0.02	0.01	0.00	0.00	3.3%
8	1.89	0.27	0.02	0.12	0.04	0.00	0.01	22.9%
9	3.52	0.17	0.08	0.41	0.12	0.05	0.09	91.1%

### 3.1 Glycerin

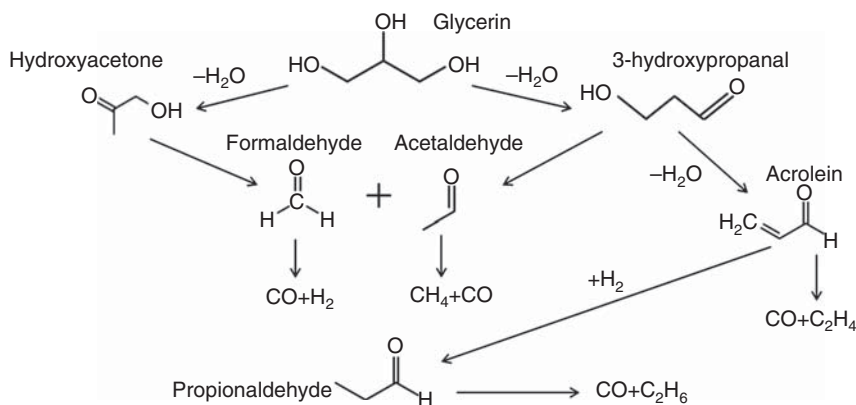
With increasing temperature, the amount of gasification of carbon in a glycerin solution increases, starting at 22% at 550°C and reaching 91% at 650°C. Likewise, the number of moles of each gaseous species being produced per mole of carbon fed increase with increasing temperature. The results using a basis of moles of gaseous carbon exiting the reactor are shown in Figure 1. Carbon dioxide stays approximately constant, indicating little increase in the water gas shift reaction with temperature at these conditions. Hydrogen also stays relatively constant, while carbon monoxide decreases and ethane and methane increase.

Results from the liquid analysis show the primary intermediates produced were hydroxyacetone, acetic acid, propanoic acid, and methyl propionate. Minor products include 2-butanone, 1-propanol, allyl alcohol, phenol, and 2-methyl phenol. Acetaldehyde and propionaldehyde oxidize to acetic acid and propanoic acid, respectively, when exposed to atmospheric air, which explains their absence in the liquid sample [25]. Methyl propionate is the product of propionic acid reacting with the methanol solution used to dilute the liquid samples.

While the final products of glycerin decomposition in supercritical water are gaseous, a mechanistic reaction pathway can be elucidated based on the species found in the liquid effluent and their subsequent atmospheric derivatives, because these intermediate species found in the liquid show a snapshot of the mechanism before decomposition is complete. Based on the most prominent species observed in the liquid analysis, a mechanism of glycerin decomposition was elucidated that involves two preferred reaction pathways for glycerin



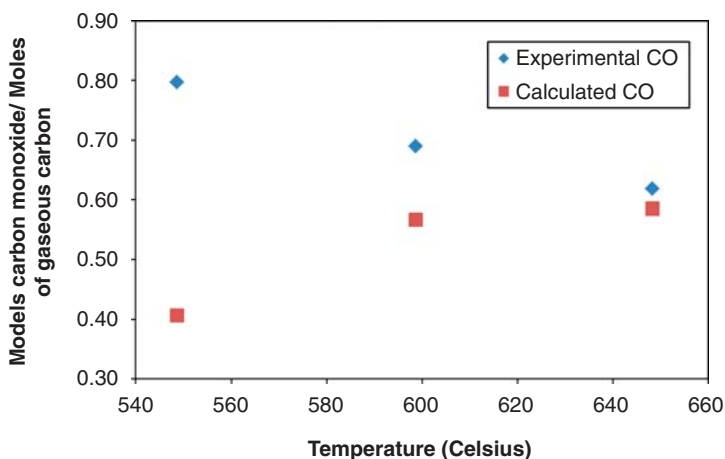
**Figure 1** Effect of temperature on the gas composition of glycerin decomposition in supercritical water.



**Figure 2** Preferred reaction pathways of glycerin decomposition in supercritical water.

decomposition to gaseous products. The first pathway involves dehydration of a primary hydroxyl group of glycerin to produce hydroxyacetone (Pathway A), and the second pathway involves the dehydration of a secondary hydroxyl group to produce 3-hydroxypropanol followed by the dehydration of a primary hydroxyl group to yield acrolein (Pathway B). These reaction pathways are shown in Figure 2.

These two preferred reaction pathways for glycerin decomposition were then analyzed. This was accomplished by comparing the amount of carbon monoxide



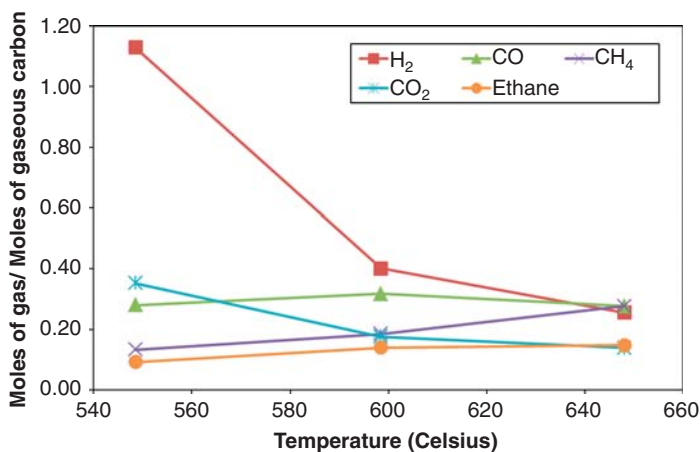
**Figure 3** Effect of temperature on the accuracy of the proposed glycerin decomposition mechanism.

experimentally observed to the amount of carbon monoxide that should be produced based on the proposed mechanism. Given the values of all other gaseous species (hydrogen, carbon dioxide, methane, and ethane) exiting the reaction system, the mechanism can be used to calculate the corresponding amount of carbon monoxide that should be released. This calculated carbon monoxide value was then compared to the value that was observed experimentally and the results are shown in Figure 3. At lower temperatures, the mechanism does not match the experimental data well, while the values are approximately the same at 650°C when there is almost complete carbon gasification. The discrepancy at lower temperatures is believed to be the result of hydrogenation of liquid intermediates containing double bonds such as acrolein, and therefore hydrogen being depleted from the gaseous effluent. When carbon gasification is close to completion and there are very few liquid intermediates remaining, the predictability of the glycerin decomposition mechanism improves.

### 3.2 Propylene Glycol

The extent of propylene glycol gasification increases with increasing temperature, with very little carbon gasified at 550°C and almost 90% conversion achieved at 650°C. Looking at the gas composition in moles of gaseous species per mole of gaseous carbon exiting the reactor, as shown in Figure 4, increasing temperature resulted in decreasing amounts of hydrogen and carbon dioxide. Carbon dioxide is only produced as a product of the water gas shift reaction, indicating a decrease in the relative extent of that reaction. The methane and ethane produced increased with increasing temperature.

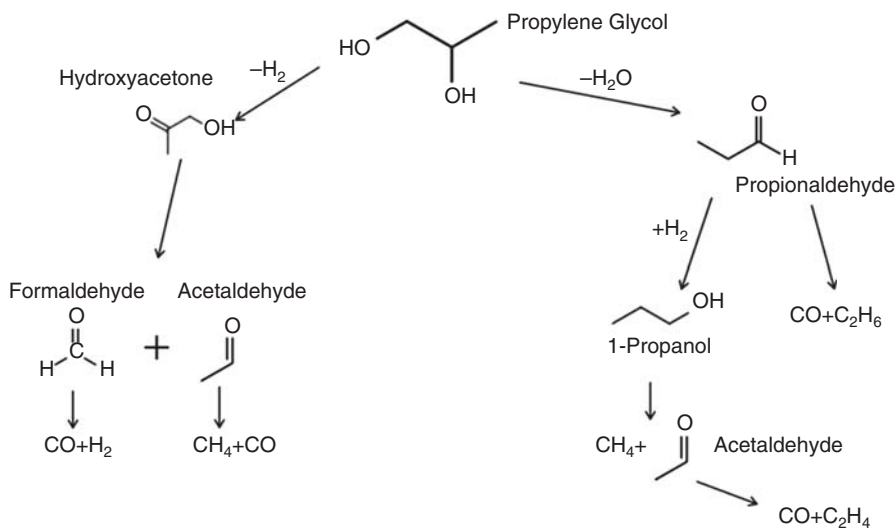




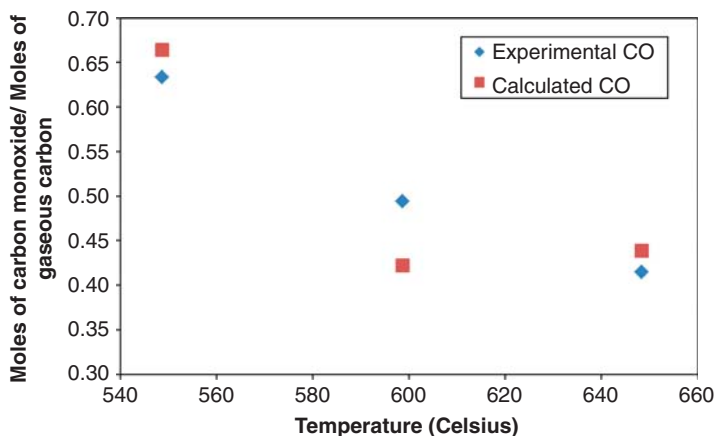
**Figure 4** Effect of temperature on the gas composition of propylene glycol decomposition in supercritical water.

The liquid analysis of the propylene glycol experiments was very similar to those of glycerin, with hydroxyacetone being one of the primary products. Therefore, one of the primary pathways is the dehydrogenation of propylene glycol to hydroxyacetone, which is followed by the formation of acetaldehyde and formaldehyde and their respective gaseous products [7, 15]. Another pathway involves the dehydration of propylene glycol to propionaldehyde, which is subsequently broken down into carbon monoxide and ethane [17]. Additionally, the increased presence of 1-propanol in the liquid analysis of propylene glycol experiments indicates more hydrogenation of propionaldehyde than was present in the glycerin experiments. 1-Propanol can decompose to produce acetaldehyde and methane [26]. Two compounds detected in the liquid effluent, 2-ethyl-4-methyl-1,3-dioxolane and 2-methyl-1,3-dioxane, are the likely condensation products of propylene glycol and propionaldehyde, and propylene glycol with acetaldehyde, respectively [27]. These larger molecules are not believed to contribute significantly to the gaseous products, and are therefore not included in the analysis of a primary decomposition reaction mechanism. Figure 5 shows the hypothesized propylene glycol decomposition mechanism.

The proposed decomposition pathways were checked against the experimental results. Figure 6 shows the calculated carbon monoxide produced using the mechanism plotted against the experimentally determined carbon monoxide. This decomposition mechanism appears to be consistent with the observed data at all temperatures, so hydrogen reacting with intermediates is at a minimum. This is because the propylene glycol decomposition mechanism does not involve any carbon-carbon double bond to be hydrogenated, while in glycerin decomposition the carbon-carbon double bond in acrolein is present.



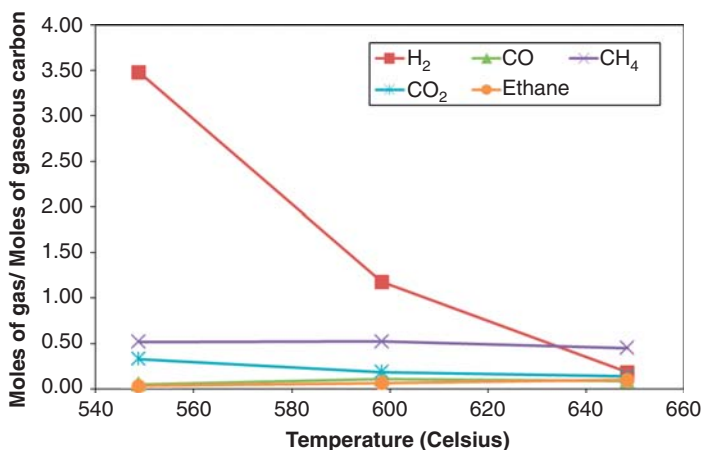
**Figure 5** Preferred reaction pathway of propylene glycol decomposition in supercritical water.



**Figure 6** Effect of temperature on the accuracy of the proposed propylene glycol decomposition mechanism.

### 3.3 Isopropanol

With increasing temperature, carbon gasification of isopropanol increases, reaching over 90% conversion at 650°C. The gaseous product composition for the isopropanol runs based on moles of gas species per mole of gaseous carbon is shown in Figure 7.



**Figure 7** Effect of temperature on the gas composition of isopropanol decomposition in supercritical water.

In Figure 7 the moles of hydrogen produced per moles of carbon coming out in the gaseous effluent is very high at low temperatures, at almost 3.5 hydrogen molecules per carbon at 550°C. This is indicative of isopropanol dehydrogenation to produce acetone occurring substantially at lower temperatures, with the subsequent decomposition reactions of acetone not occurring as readily. This leads to a small amount of carbon-containing molecules being present in the gaseous effluent. At higher temperatures where more carbon is gasified, the amount of hydrogen per gaseous carbon is much smaller. The relative amount of carbon dioxide produced decreases with increasing temperature, meaning less water gas shift reaction is occurring per carbon atom. The amounts of ethane, ethylene, and carbon monoxide increase with increasing temperature, while methane decreases by a small margin.

In the liquid analysis of the isopropanol experiments, the species with the highest relative abundance was reactant isopropanol, indicating a lack of its reactive conversion at the given temperature. Other liquid species were 2-butanone, 2-pentanone, 2-hexanone, acetic acid, methyl isobutyl ketone, and 2,5-hexanedione. Due to the amount of hydrogen produced at such low carbon gasification, one would expect to find acetone as the result of isopropanol dehydrogenation [19]. The lack of acetone in this liquid sample obtained at 650°C could be the result of acetone being a short-lived intermediate species in supercritical water.

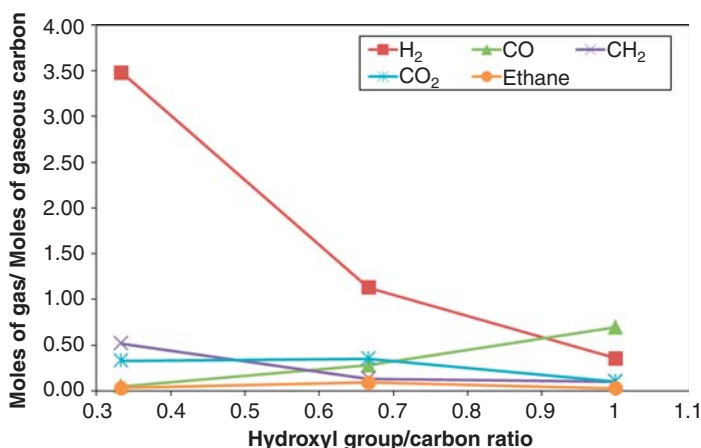
These liquid species are indicative of isopropanol dehydrogenating to acetone, and then undergoing a series of free radical reactions. The first step involves acetone dissociating to a methyl radical and acetyl radical [20]. The methyl radical can then react with other acetone molecules to produce 2-butanone and a hydrogen radical. Methyl radicals can continue to chain to produce 2-pentanone, methyl isobutyl ketone, and 2-hexanone. Methyl radicals may also react with

hydrogen radicals to produce methane, which appears in a significant amount in the gaseous effluent. If an acetone loses two methyl radicals then a carbon monoxide is produced, while two methyl radicals can react together to produce ethane. The hydrogen radicals can react with the acetyl radicals to produce acetaldehyde. Two acetone molecules can also react to produce 2,5-hexanedione and hydrogen gas. Due to the wide variety of reactions that can possibly occur with free radical isopropanol decomposition, a stoichiometric evaluation of the mechanistic pathway could not be performed.

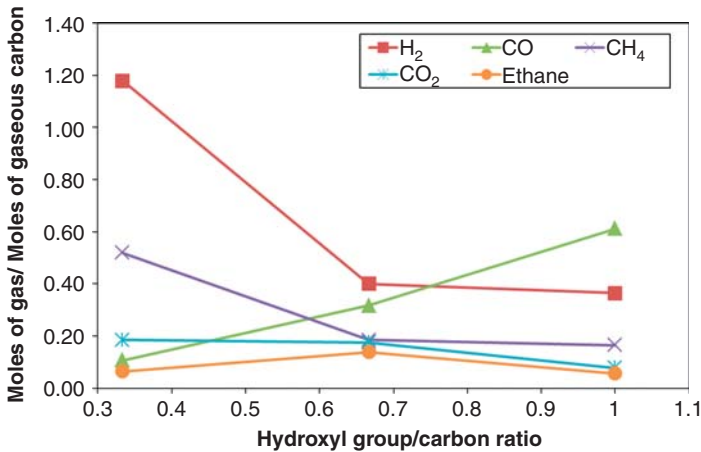
### 3.4 Role of Hydroxyl Groups

The effect of increasing number of hydroxyl groups on the different  $C_3$  hydrocarbon molecules was analyzed. Figures 8–10 show the trends in carbon gasification as well as gas composition at 550°C, 600°C, and 650°C. Data points with hydroxyl group to carbon ratios of 0.33, 0.66, and 1.00 correspond to isopropanol, propylene glycol, and glycerin, respectively.

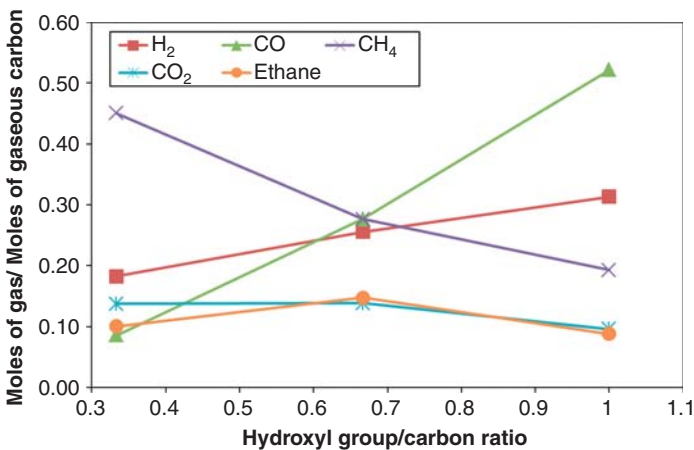
The gasification results at 550°C in Table 4 show that increasing the number of hydroxyl functional groups increases carbon gasification extent as well as carbon monoxide produced, which may be attributed to the fact that there are more hydroxylated carbons present. In other words, more hydroxyl groups in the hydrocarbon molecules make the chemical species much easier to decompose. To see a clearer view of the selectivity of different gaseous products, Figure 8 shows the results of the gas composition per mole of gaseous carbon. With an increasing ratio of hydroxyl groups to carbon atoms, the amount of carbon monoxide produced steadily rises while methane decreases. This result is expected as molecules



**Figure 8** Effect of increasing hydroxyl-to-carbon ratio on the gas composition of supercritical water treatment of  $C_3$  hydrocarbons at 550°C.



**Figure 9** Effect of increasing hydroxyl-to-carbon ratio on the gas composition of supercritical water treatment of C<sub>3</sub> hydrocarbons at 600°C.



**Figure 10** Effect of increasing hydroxyl-to-carbon ratio on the gas composition of supercritical water treatment of C<sub>3</sub> hydrocarbons at 650°C.

with more hydroxylated carbons will be more prone to producing carbon monoxide, while molecules with fewer hydroxylated carbons are more likely to produce methane. The amount of hydrogen being produced per gaseous carbon is very high for isopropanol and propylene glycol. This is due to dehydrogenation reactions occurring that produce gaseous hydrogen, but very little gaseous carbon species. With increasing number of hydroxyl groups in a molecule there is also a decrease in carbon dioxide, likely due to a decrease in the water gas shift

reaction. Additionally, ethane production reaches a maximum with propylene glycol decomposition as the result of propylene glycol producing ethane directly through propionaldehyde decomposition.

Table 4 shows that for an increasing number of hydroxyl groups at 600°C, the carbon gasification percentage increases substantially going from isopropanol to propylene glycol, but then seems to level off going to glycerin. This means the addition of a third hydroxyl group has little effect on additional carbon conversion at 600°C. To find out how reaction selectivity is changing with the number of hydroxyl groups, Figure 9 shows the gas composition per gaseous carbon. The trends for each gaseous species in Figure 9 appear similar to trends found in Figure 8. At 650°C, Table 4 shows that all of the hydrocarbon starting materials have a uniform carbon conversion of around 90%, meaning that at 650°C the ratio of number of hydroxyl groups to carbon in the molecule has little effect on the extent of gasification. Figure 10 shows the effect of increasing hydroxyl groups on the gas composition per gaseous carbon at 650°C. The trends with increasing the number of hydroxyl groups are similar to the previous temperatures, with increasing carbon monoxide, decreasing methane, decreasing carbon dioxide, and ethane having a maximum with propylene glycol. The only difference is that hydrogen is increasing with increasing number of hydroxyl groups. This is due to two factors. The first is an increase in isopropanol decomposing via dehydration to propylene rather than dehydrogenation to acetone, and therefore more of the hydrogen atoms in the isopropanol molecule are becoming water instead of becoming hydrogen gas. The second factor is increased hydrogen production from glycerin due to very little hydrogen reacting with liquid intermediates because gasification is almost complete.

## 4 Conclusion

By increasing the number of hydroxyl functional groups on the molecule, an increase in gasification was found at each temperature investigated, except at 650°C where the carbon conversion was approximately 90% for each fuel. The reason increasingly hydroxylated hydrocarbons decompose and gasify more readily is due to the presence of additional carbon-oxygen bonds, which have a mean bond energy of 360 kJ/mol. These bonds break much more readily than carbon-carbon bonds, which have a mean bond energy of 412 kJ/mol.

With an increasing number of hydroxyl groups in the hydrocarbon molecule, the relative amount of carbon monoxide produced increased, while the amounts of carbon dioxide and methane decreased. Hydrogen production decreased with increasing hydroxyl-to-carbon ratio at lower temperatures, but increased at 650°C. This was due to the isopropanol decomposition favoring dehydration to produce propylene at higher temperatures rather than the dehydrogenation to produce acetone, which occurs at lower temperatures. Also more hydrogen is produced from glycerin decomposition at higher temperatures due to the presence of fewer liquid intermediates with which the hydrogen can react.

Mechanisms for glycerin and propylene glycol decomposition were evaluated. The proposed glycerin decomposition mechanism had good predictability with more carbon gasification, but at lower temperatures the carbon monoxide values that were calculated based on the proposed mechanism were much lower than the actual experimental values. This is due to some of the hydrogen produced at lower temperatures reacting with liquid intermediates and not coming out in the gaseous effluent. The proposed propylene glycol mechanism was found to correlate well for all temperatures. A mechanism was proposed for isopropanol decomposition as well, but due to the complexity of the free radical reactions involved, it could not be evaluated like the glycerin and propylene glycol mechanism.

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