

Batch Aqueous-Phase Reforming of Woody Biomass

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Aqueous-phase reforming (APR) is reported for the first time for the production of H₂ from actual biomass. The experiments are carried out in batch using a 100 mL Parr microreactor heated to 225 °C. In this one-pot, two-step process, acid hydrolysis is used to break down the polymeric constituents of biomass to smaller soluble molecules and these species are reformed using a Pt/Al₂O₃ catalyst. The experiments show that increasing the acid concentration from 1% to 5% causes more than a 12-fold increase in H₂ concentration, with hydrogen being a minor product accounting for 18% of the noncondensable gas phase and CO₂ as the major product. In the presence of the Pt/Al₂O₃ reforming catalyst, both the selectivity and yield of hydrogen in the gas phase increase. This is accompanied by a noticeable decrease in carbon monoxide production, which is attributed to the activation of the water gas shift reaction catalyzed by platinum. Comparison with other feeds such as glucose, wastepaper, and ethylene glycol showed that the amount of hydrogen produced from biomass is of a comparable magnitude per gram of feed, although biomass yields more hydrogen per gram of carbohydrate than either glucose or wastepaper. Baseline experiments with only the catalysts in the absence of any biomass show no increase in the reactor system pressure when only water and helium are present, indicating that the observed hydrogen produced is sourced from the biomass.

Introduction

Over the years, concerns about the steady decline of the available supply of petroleum in the face of ever-increasing demand for this valuable commodity have fueled researchers to look for possible alternative energy sources as well as chemical feedstock. One such resource is biomass. Biomass is a renewable, CO₂-neutral, and readily available source of energy. According to Oak Ridge National Laboratory estimates,¹ about 512 million dry tons of biomass per year can be initially available at less than \$50/dry ton delivered. This amount is equivalent to 8.09 Quads² of primary energy. Currently, only 72 million dry tons (1.2 Quads) are being used for fuel. This leaves quite a margin which can still be exploited for energy production. Putting this into perspective, 6.89 Quads is ~1.2 B barrels of oil—equivalent to ~27% of the U.S. net import of crude oil in 2004.³

Hydrogen has been identified as a very attractive energy carrier.⁴ Unfortunately, many technologies still rely on fossil fuel as the hydrogen source. Considering concerns about the future supply of petroleum, extensive research on alternative hydrogen generation technologies is currently underway. Several processes have been explored to produce hydrogen from biomass. One of the existing approaches involves the pyrolysis of biomass, followed by subsequent reforming of the bio-oil produced.^{5,6} Another technology is biomass gasification. How-

ever, these processes require very high temperatures (673–1100 K) even in the presence of catalysts and different gasification agents.^{4,5,7–9} Dalai et al. reported a yield of about 26 and 32 mmol/g of sawdust in the gasification of aspen and cedar wood, respectively, at 2.4 wt % impregnation with CaO.⁷ They reported that the presence of CaO caused a decrease in the temperature from ~850 to ~675 °C at which the hydrogen production rate was at a maximum.

Hydrothermal processing of biomass and related model compounds has also been reported in the literature as a possible technology for hydrogen production. Modell¹⁰ in 1985 reported the complete solubility of maple sawdust in supercritical water. Sinag and co-workers also studied hydrolysis of glucose in supercritical water.^{11,12} In the presence of K₂CO₃ at supercritical water conditions, they reported high yields of CO₂ and H₂ with low yields of CO. Degradation compounds identified in the liquid byproduct included furfural, phenols, and acids. The group of Antal et al. also studied the hydrothermal processing of wood, suggesting mechanisms for the formation of degradation products from wood carbohydrate constituents.^{13–15}

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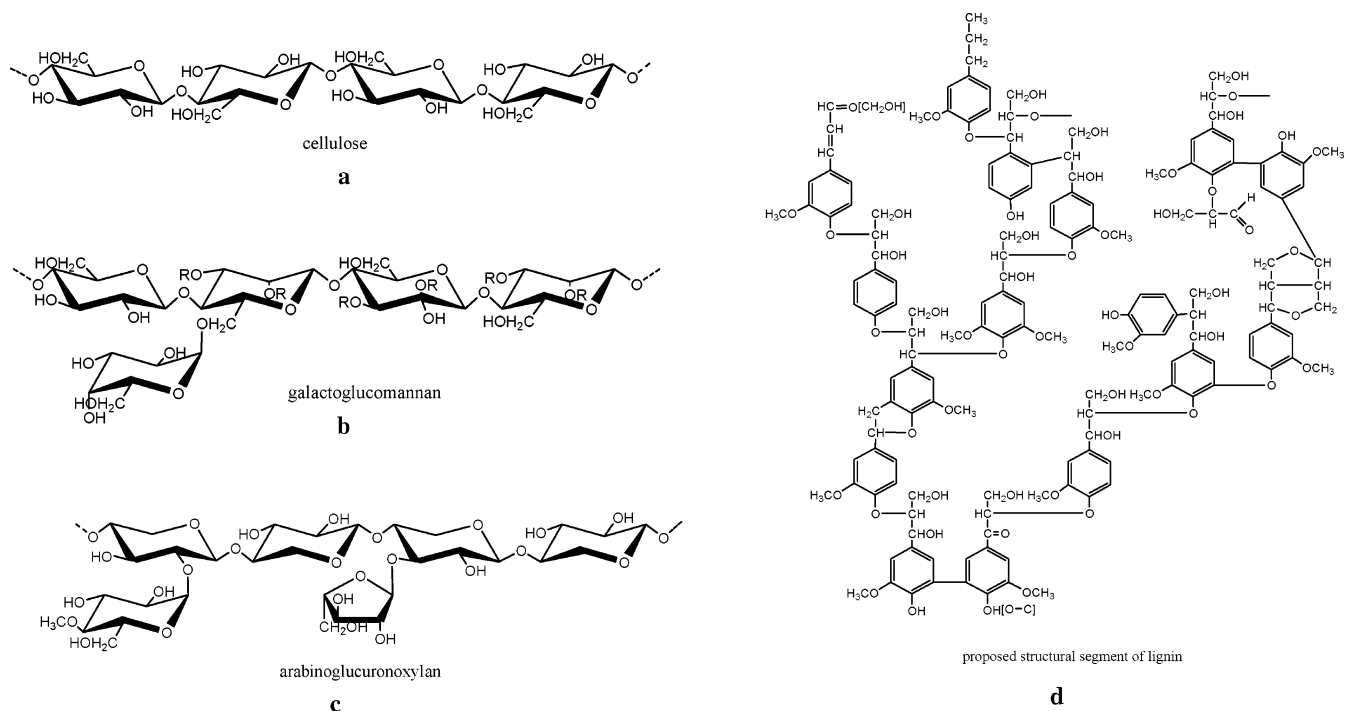
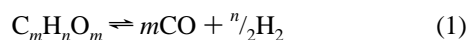
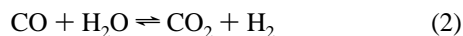


Figure 1. Representative structures of the main polymeric components in lignocellulosic biomass: (a) cellulose; (b) galactoglucomannan; (c) arabinoglucuronoxylan; and (d) lignin.

In 2002, Dumesic and co-workers first reported aqueous-phase reforming (APR) of oxygenated compounds that were chosen as model biomass mimics.¹⁶ They demonstrated the capacity to produce hydrogen in a flow reactor at temperatures (~ 500 K) much lower than those required for either pyrolysis or gasification. They reported that APR of molecules more reduced than sugars (methanol and ethylene glycol) had the highest hydrogen selectivity.^{16–19} Dumesic's group considered two reactions to be of major importance for hydrogen evolution: the reforming reaction (C–C cleavage),



and the water gas shift (WGS) reaction,



Ideally, the metal catalyst used in the process should catalyze both of the aforementioned reactions. Studies with various supported metal catalysts showed platinum supported on alumina to be the most selective of the catalysts tested for hydrogen production by APR.^{18,19} In a system with heterogeneous Pt/Al₂O₃ as catalyst, it was proposed that adjacent Pt atoms act as sites for C–C, and C–O cleavage. Cleavage of the carbon–carbon bond is necessary to produce H₂—at the same time, this process gives rise to formation of CO and CO₂. On the other hand, C–O cleavage is unwanted, as this leads to the formation of alkanes, which depletes the potential pool of H₂. Another

reaction that was identified which lowers hydrogen yield is hydrogenation.¹⁹

Lignocellulosic biomass is chemically complex, consisting of cellulose, hemicellulose, lignin, extractives, and inorganic materials. The first three groups are the main constituents, comprising as high as 98% of the material by weight. Both cellulose and hemicellulose are polymeric carbohydrates. The former (Figure 1a) is a linear homopolymer of β -D-glucose linked by β -1 \rightarrow 4 glycosidic linkages with high degrees of polymerization (DP). Cotton fibers contain the purest naturally occurring cellulose—with DP reaching as high as 10000. The linearity of cellulose allows it to be compactly packed in crystalline regions in the cell wall. However, a small portion of the chains may become disordered and have a more random arrangement. These amorphous regions increase the susceptibility of cellulose to solvents and reagents.

The other carbohydrate group, collectively known as hemicelluloses, consists of heteropolysaccharides of glucose, galactose, mannose, xylose, and arabinose. Hemicelluloses are branched, with chains that are much shorter than cellulose (DP = 150–250). Because of this, they are more susceptible to chemical degradation. Aside from the sugar components, some hemicellulose fractions may also be in acetylated or in uronic acid forms.^{20,21} Figure 1 shows the two most abundant groups of hemicelluloses in plants. Mannans (Figure 1b) are the major component of softwoods, while xylans (Figure 1c shows a typical softwood xylan) are the main constituent of hardwoods.^{21,22} Lignin, on the other hand, is phenolic and structurally more complex than the other components (Figure 1d). To date, all studies of APR have focused on the use of model compounds that could be derived from biomass, such as sorbitol and glucose—no one has yet reported the APR of actual biomass for hydrogen production.

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Though biomass-derived energy is yet to be fully demonstrated as an economically viable alternative to fossil fuel, the application of this process directly to readily available biomass reserves may prove to be more attractive in the long run when petroleum becomes increasingly more scarce and expensive. So far, results of hydrogen production studies using APR on compounds such as ethylene glycol have been encouraging. However, because of its varied composition, we expect that APR of lignocellulosics would be more complicated than when using these representative compounds. The chemistries would certainly be different, with functionalities present in biomass that are absent in the model compounds. Reforming of biomass also introduces a solid phase into a previously completely aqueous-phase feed. We also anticipated that, unlike in the previous studies, breakdown of polymeric structures to simpler molecules would be necessary for platinum reforming to occur.

At typical APR temperatures, the preliminary breakdown of lignocellulosics could proceed through hydrolysis. Hydrolysis could be catalyzed in two ways: by presence of an acid or with a base. Acid hydrolysis causes the cleavage of the glycosidic bonds in carbohydrates to produce monomers. This process has been used to extract sugars from biomass for subsequent ethanol fermentation.²¹ Prolonged contact with acid at elevated temperatures (160 to 280 °C) can cause formation of degradation products such as 5-hydroxymethylfural (from hexoses) and 2-furaldehyde (from pentoses).²⁰ On the other hand, alkali, in general, causes only rearrangements of aldoses and ketoses. However, a strong concentration of base can catalyze what is known as the *peeling reaction* of holocellulose (a collective term for both cellulose and hemicelluloses together) in biomass.^{21,23} In this reaction, the monomeric units of the carbohydrate chains are cleaved one by one, starting from the reducing end, producing an isosaccharinic acid terminal group. After some time, the so-called *stopping reaction* might occur. This happens when a metasaccharinic acid end group or other functionality that cannot form a hemiacetal (i.e., nonreducing) is generated instead of the isosaccharinic form.²¹

In general, because of its branched structure and lower degree of polymerization, hemicelluloses are more susceptible to hydrolysis than cellulose.^{20,21,23–25} It is to be expected then that the hemicellulose fraction of biomass is degraded faster than the cellulose fraction. This was observed by Tran and Chambers²⁶ during mild sulfuric acid hydrolysis of southern red oak at 150 °C as well as in the hydrothermal processing of lignocellulosic materials between 150–230 °C in the study made by Garrote and others.²⁷ In a study reported by Karagoz et al.²⁸ on biomass liquefaction, it was shown that mainly phenolic compounds are found in the bio-oil of wood biomass when it is treated with different bases and their salts at 280 °C for 15 min. This might be attributed to the decomposition of lignin constituents which are generally more reactive under basic conditions than acidic ones. No appreciable increase in gas products was noted in any of their runs. Hydrogen was not

mentioned in their product gas mixture, which consisted mostly of CO₂ with CH₄, C₂H₄, C₂H₆, and C₃H₆.

In this contribution, we report the first investigation of the use of woody biomass as a feedstock for aqueous-phase reforming. The use of much lower temperatures than pyrolysis and gasification, and the utilization of a directly available feed, make this process potentially attractive. We present here our initial efforts in characterizing this process. The breakdown of the polymeric biomass units to soluble compounds was achieved using aqueous sulfuric acid with simultaneous use of Pt/Al₂O₃ as the reforming catalyst. Thus, we report results obtained from the combined one-pot acid hydrolysis/APR of woody biomass for hydrogen production.

Experimental and Analytical Methods

Materials. The lignocellulosic material used in this study was Southern pine sawdust—obtained from Georgia Pacific as small chips, milled, and then passed through Tyler screens. The –35 +60 fraction (average aperture = 375 μm) was used in the experiments. Elemental and proximate analyses were done by outside laboratories: Desert Analytic Laboratory for the elemental analysis of the wood and the IPST Wood Chemistry Laboratory for its proximate analysis. For comparison, office wastepaper, D-glucose (anhydrous, Fisher), and ethylene glycol (Fisher) were also investigated. Catalysts used were 2 M sulfuric acid (diluted from concentrated stock, 36 M, Fisher), platinum on alumina (Pt/Al₂O₃) pellets (0.5 wt % Pt, Engelhard), and gamma-alumina (γ-Al₂O₃) powder (Strem Chemicals).

Apparatus. A 100-mL stainless steel Parr batch microreactor was used for all the runs in this study. It was outfitted with a gas collector at the outlet. The pressure of the collected product gas was allowed to equilibrate to atmospheric pressure in a balloon, and samples were taken using gastight syringes.

Procedure. In a typical experiment using sawdust, 5.54 g of biomass (10.63% moisture content via thermogravimetric analysis (TGA)) and 0.498 g Pt/Al₂O₃ pellets were put inside the reactor. The reactor configuration used did not allow for prereduction of the platinum catalyst before the reaction without exposure to ambient conditions. To obtain a liquid-to-wood ratio (L/W) of nine, 43.7 mL of water was added. Using a micropipet, 1.263 mL of 2M H₂SO₄ was transferred into the reactor for a 5% acid concentration run (wt % based on dry biomass). The pH of the resulting mixture was then recorded. After securing the reactor head, helium gas was allowed to flow through the reactor and to purge out air from the headspace. After ~1.5 min, the reactor was pressurized with 30 psig of He, sealed, and then heated to 225 °C (498 K). The temperature and pressure of the system were recorded every 5 min. For runs where wastepaper was used, an additional 30 min of soaking in water was performed before the addition of acid and platinum. This was done for the easy defiberization of the paper.

Several baseline experiments were carried out to probe the possibility that the catalysts (both H₂SO₄ and Pt/Al₂O₃ in concert or separately) could catalyze the production of hydrogen from water. In these runs, only water and the catalyst(s) in question were put inside the reactor. Before the system was heated to the target temperature (225 °C), the reactor was also pressurized with helium as mentioned above.

Analysis. The reaction was allowed to run for 3 h. Sampling of the gas phase was done after reaction. Two packed-column gas chromatography units were utilized for the gas analysis. The amount of hydrogen was analyzed using a Hewlett-Packard 6890 GC equipped with a thermal conductivity detector (TCD) and N₂ as carrier gas. Carbon dioxide was also quantifiable in

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Table 1. Chemical Composition of Southern Pine Sawdust Used in the Study

percentage of component based on dry weight of biomass (%)	
Elemental Analysis	
C	52.87
H	4.96
O	41.81
N	0.15
S	<0.06
ash	0.15
Proximate Analysis ^a	
carbohydrates	
arabinan	1.00
galactan	2.30
glucan	39.00
xylan	5.30
mannan	11.70
lignin	
acid insoluble	27.50
acid soluble	0.40
extractives	3.70
ash	0.30

^a Proximate analysis from IPST Wood Chemistry laboratory did not sum to 100%. This may be attributed to possible insufficient hydrolysis before carbohydrate determination (percentages of other wood constituents agree with given value ranges in the literature). The HPLC-pulsed amperometric determination (HPLC-PAD) method used was calibrated only to determine the listed monosaccharides. The presence of dimers or oligomers will not be accounted for because the program used was completed shortly after mannose eluted. This discrepancy was not encountered with the analyses of the solid residues (Table 2), most probably because the majority of the carbohydrates were degraded during the reaction.

the HP GC. Carbon monoxide, methane, and carbon dioxide were analyzed in a Buck Scientific 910 GC packed with Carboxen 1000. This GC also has TCD, with He as carrier gas. The GCs were calibrated using a standard mixture of gases (Airgas). Aside from the permanent gases H₂, CO, and CO₂, methane and ethane were included in anticipation of the possible presence of the alkanes, as reported in the literature.

The liquid and solid byproducts of the reaction were centrifuged for separation. The solid residue was then oven-dried to remove water, weighed, and stored. Some of the solid residues were analyzed for carbohydrate content, extractives, lignin, and ash at the IPST Wood Chemistry Laboratory. The liquid phase was also kept and stored for future analysis.

Characterization of the Pt/Al₂O₃ catalyst was done through hydrogen chemisorption experiments as well as elemental analysis. A Micromeritics ASAP 2020 instrument was used for hydrogen chemisorption experiments of fresh, spent, and calcined spent Pt/Al₂O₃ at 308 K. Before the isotherms were recorded, samples were evacuated at 623 K followed by reduction in flowing H₂ at the same temperature. Elemental analyses of two samples (fresh and spent Pt/Al₂O₃) were completed by Galbraith Laboratories, Inc.

Results

Biomass. The elemental and proximate analysis of the wood sawdust used in the study is reported in Table 1. As expected, carbon was the most abundant element by weight, considering that it is the backbone of almost all constituents in the wood. Together with oxygen and hydrogen, these three elements comprise >99% of the sample—comparable to the model oxygenated compounds that the group of Dumesic used in their APR studies.

The proximate analysis shows the abundance of the different group constituents in the wood—cellulose, hemicellulose, lignin,

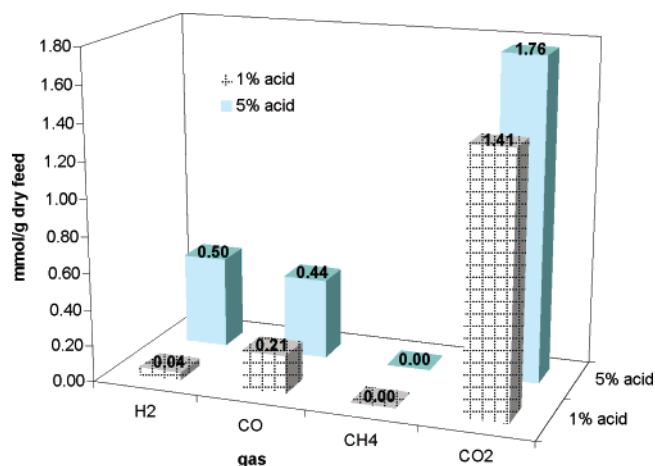


Figure 2. Gas production caused by acid hydrolysis of biomass in the absence of reforming catalyst.

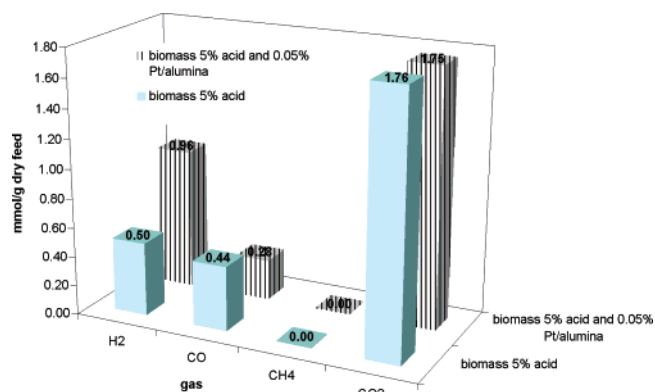


Figure 3. Comparison of gas production in the absence and presence of platinum using woody biomass as feed.

extractives, and ash. Cellulose and hemicellulose contents are reported in terms of their monosaccharide constituents. Together, they comprise ~60% of the dry feed weight. Lignin is ~28%, consisting of an acid-insoluble component and an almost negligible acid-soluble part. Extractives are nonstructural wood constituents that are necessary to maintain the diversified biological functions of the tree. Their composition and amount varies even in the different parts of the same tree.²¹ Together with the inorganic component of the wood dust, they account for 4% of the biomass weight.

Acid Hydrolysis. Figure 2 shows the amounts of gases produced after 3-h acid hydrolysis of biomass using 1% H₂SO₄ and 5% H₂SO₄ by dry weight of feed. As shown in the figure, an increase in the acid concentration caused an overall increase in the production of gases. There was more than an 11-fold increase in the amount of H₂ produced with 5% acid than with 1% H₂SO₄. As expected, no methane was formed, as there was no catalyst present in the system for its formation.

Aqueous-Phase Reforming with Platinum. The addition of platinum into the reaction resulted in about a 2-fold increase of hydrogen production, as shown in Figure 3. Carbon monoxide produced was lower than in the absence of platinum. Both these results might be considered indicators of the water gas shift reaction catalyzed by platinum. Surprisingly though, the amount of carbon dioxide, which is a product of WGS, did not show any change, hinting that other reactions were likely important.

Analysis of the Solid Residues Formed. The solid residue byproducts of both biomass hydrolysis with 5% H₂SO₄ and APR with the same amount of acid and Pt/Al₂O₃ were analyzed. The

Table 2. Proximate Analyses of Pine Saw Dust Solid Byproducts Due to Hydrolysis (5% H₂SO₄) and APR (5% H₂SO₄ + 10% Pt/Al₂O₃)

	hydrolysis residue ^a (wt % based on dry residual solid)	APR residue ^a (wt % based on dry residual solid)
carbohydrates		
glucan	4.30	1.80
xylan	nd ^b	nd
galactan	nd	nd
mannan	nd	nd
arabinan	nd	nd
lignin		
acid insoluble	82.90	86.60
acid soluble	0.70	0.70
extractives	6.70	4.40
ash	3.90	4.30
total carbon	64.70	63.30

^a Analyses samples taken from a single representative batch treatment.

^b nd = not detected.

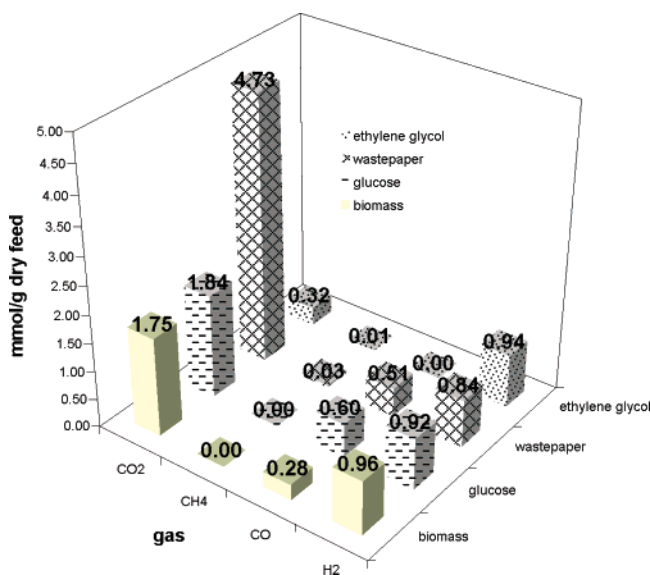


Figure 4. Comparison of APR gas production using different feed sources in the presence of both acid and reforming catalysts.

weights of residues recovered were less than the feed dry weight, indicating degradation of the pine sawdust. The results are summarized in Table 2. Acid hydrolysis caused the complete degradation of hemicellulose, as evidenced by the absence of monosaccharides other than glucose in the residue. Lignin was the main component, followed by the extractives (solvent used = dichloromethane). This result can be also used as an indicator of which wood constituent underwent degradation, i.e., from which component the gaseous product was sourced.

Proximate analysis of the residue obtained after APR indicated this residue is similar to the residue obtained after hydrolysis. Lignin was also the main component of the residue, followed by the extractives component. Though there was a further decrease in the weight percent of the glucan fraction, there was not much difference in the amount of carbon in the residue. Thus, the role of APR was expected to be in the formation of gaseous products from the hydrolyzed biomass in the aqueous phase.

Comparison of Biomass APR with Other Feeds. Figure 4 summarizes the gas yields of biomass, waste paper, and glucose. From the figure, it was shown that for 3-h batch APR containing 5% H₂SO₄ and Pt/Al₂O₃, the hydrogen productions in all of the runs were about the same. Biomass surprisingly gave the highest hydrogen yield as well as percentage in the gas phase.

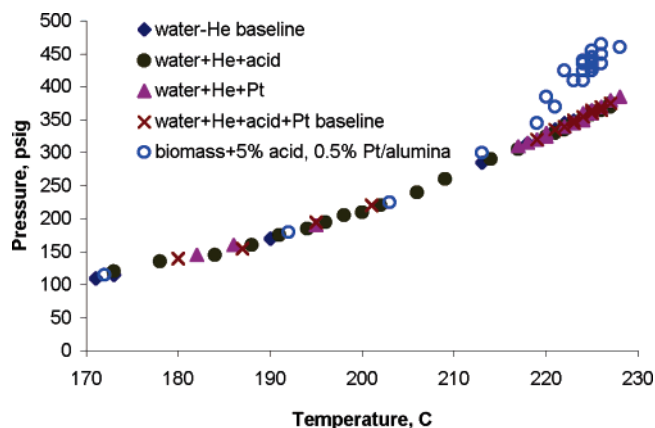


Figure 5. Increase in system pressure due to evolution of gases. Pressure profiles: water–He baseline (◆); water–He–acid (●); water–He–Pt (▲); water–He–Pt–acid (×); biomass with both 5% acid and Pt/Al₂O₃ (○).

More carbon monoxide as well as carbon dioxide was produced from feeds other than biomass. Noteworthy was the almost 3-fold increase in CO₂ production during the APR of wastepaper.

Baseline Reactions. Several experiments were done to confirm that the hydrogen being produced was because of the APR of the biomass and not because of the action of either or both catalysts on water at high temperatures. As in normal APR runs, the increase in system pressure over the vapor pressure of water at a given temperature was used as an indicator for the evolution of gases. Figure 5 summarizes the pressure–temperature profile for the evolution of gases. Figure 5 summarizes the pressure–temperature profiles for all four runs coincide on the same baseline. This establishes that any deviation (i.e., increased pressure) from this baseline in the presence of biomass can be attributed solely to the gaseous products formed during acid hydrolysis and/or APR. As seen in Figure 5, when biomass is present together with acid and Pt/Al₂O₃ (open circles), a deviation from the baseline exists.

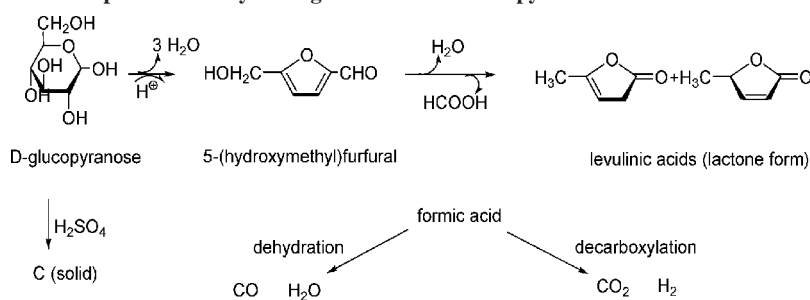
Discussion

Acid Hydrolysis. The difference between the susceptibility of hemicelluloses and cellulose was shown in the analysis of the hydrolysis residue (Table 2). No monosaccharide other than glucose was found to be present in the residue. This glucose was expected to have come from the more recalcitrant crystalline region of cellulose. Previous studies in different operating conditions also reported the same trend.^{20,24,27,29}

On the other hand, lignin was not solubilized in dilute acid to any significant degree. Though some small fraction was acid-soluble, this was almost negligible compared to the acid-insoluble part (Table 1). Indeed, the lignin fraction in the solid residue increased after subjecting the pine to hydrolysis conditions in this study (operating temperature ~498 K). Depolymerization of lignin occurs to a limited extent during the initial stages of hydrolysis because of the presence of some acid-labile bonds that are readily hydrolyzed, especially splitting of α - and β -ether or ester linkages.^{30–32} However, the liberated fragments are quite reactive and tend to form insoluble condensation

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Scheme 1. Proposed Pathway of Degradation of D-Glucopyranose in the Presence of Acid^{21,25}

products of high molecular weights with longer contact with acid.^{21,23,31} For softwoods, Matsushita and Yasuda reported that the condensation of gymnosperm lignin in acidic conditions is due to the intermolecular dehydrations between benzylic carbons and the guaiacyl aromatic ring.³³ In another study, Hasegawa et al. reported the cross-linking effect of sulfuric acid on lignin, thus producing ligneous polymeric products with higher molecular weights.³⁴

Early researchers had recognized that breakdown of hemicelluloses and cellulose in the presence of acid will produce sugars that are subject to further degradation upon continued exposure to acid.³⁵ Monosaccharides undergo dehydration reactions in acidic conditions, giving rise to formation of what was previously referred to as "humic substances of indefinite composition",³⁵ the furfurals: 5-hydroxymethyl-2-furaldehyde (HMF) (from hexoses) and 2-furaldehyde (from pentoses and hexuronic acids) as well as some low molecular weight organic compounds.^{21,23,31} Some of the earliest studies of the mechanism for this degradation were by Feather and Harris.^{36–38} However, their suggested mechanism for HMF formation from fructose was later refuted by Antal et al.^{13–15} Antal et al. further reported the presence of other degradation products such as levulinic acids. A path has been established between HMF and the formation of levulinic acid, which involves formation of formic acid through decarboxylation.^{21,25} Scheme 1 summarizes a possible pathway of degradation from glucose.

It has been suggested that the decomposition of formic acid results in the formation of H₂ in the processing of carbohydrates.^{11,12} Parallel pathways for formic acid decomposition have been reported in the literature: (1) *decarboxylation*, to CO₂ and H₂ and (2) *dehydration*, to form CO and H₂O. Several studies on gaseous formic acid decomposition^{39–41} showed that production of CO was favored over that of CO₂. On the other hand, it was noted that decarboxylation was preferred in aqueous-phase

conditions.^{42–44} At subcritical and supercritical conditions, Yu and Savage⁴⁴ found that formation of CO₂ and H₂ was favored over that of CO and H₂O. Corollary to these findings, computational studies showed a lower energy barrier for decarboxylation in the presence of water than for dehydration.^{41,42,45,46}

Considering the mechanism suggested by Sinag and co-workers,^{11,12} it could be said that the increase in acid concentration caused an increase in the degradation of the biomass, producing more degradation products (i.e., formic acid) and, thus, producing more hydrogen in the process. However, it must be noted that production of hydrogen through formic acid degradation is not the only possible mechanism operating in our reaction conditions. This is illustrated by the nonstoichiometric increase of H₂ and CO₂ from 1% acid to 5% acid concentration. Further study is required to elucidate the mechanism of the reactions.

The relationship between hydrogen evolution and acid concentration agrees with observations from a study done by Parajo et al.²⁹ In that work, they monitored the amount of xylose (derived from the hemicellulose fraction) produced in the prehydrolysis of *Eucalyptus* wood with sulfuric acid at much lower temperatures of 113 and 130 °C. In their study, they found that, at short times (0.25–1 h), there was a significant increase in xylose concentration with increasing acid concentration from 2% to 6%. Increasing the reaction temperature also improved xylose yield. However, by increasing reaction times (up to 6 h), the amount of xylose produced decreased, starting with an acid concentration of 4% acid at 113 °C. Under harsher conditions at 130 °C, a decrease of xylose occurred even with just 3% of acid. They attributed these to degradation reactions that consumed the monosaccharide. These reactions, as mentioned earlier, could result in the formation of H₂, among other byproducts.

Effect of Addition of Platinum. Platinum on alumina was identified by Dumesic and co-workers as a very selective catalyst for the production of hydrogen.^{18,19} As previously mentioned, platinum could catalyze both the C–C bond and C–O bond cleavage, generating species such as H₂, CO₂, CO, methane, and other alkanes through reforming, dehydrogenation, and hydrogenation reactions. Also, it could catalyze the water gas shift reaction, which produces H₂ and CO₂ from CO and H₂O.

In our experiments, the addition of platinum resulted in an increase in both the total amount of gaseous products formed as well as hydrogen volumetric percentage in the gas produced.

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In the presence of only 5% H₂SO₄, the gas-phase products contained 18.5% H₂ (by volume), whereas in the presence of 5% H₂SO₄ and Pt/Al₂O₃, the gas phase contained 33.4% H₂. On the other hand, both CO₂ and CO percentages decreased, from 65% to 57% and from 16.3% to 9.5%, respectively. It must be noted, though, that the amount of CO₂ produced remained almost the same while the CO yield decreased with APR—from 0.44 to 0.28 mmol/g of dry feed. This might be attributed to the presence of water gas shift reaction catalyzed by Pt. However, other liquid-phase reactions probably occurred concurrently with the reforming, water gas shift, and hydrolysis reactions. These reactions may have produced liquid-phase compounds, which cannot be quantified through gas sampling and analysis. Liquid-phase analysis could give indicators of some of these reactions. However, a comprehensive survey of aqueous products is required in order to get meaningful mechanistic information, considering the chemical complexity of the feed.

Catalyst stability is an important consideration in any reaction requiring a catalyst—especially those utilizing expensive noble metals. H₂ chemisorption of the fresh Pt/Al₂O₃ catalyst showed Pt dispersion of ~26% with a metallic surface area 0.325 m²/g of catalyst and a crystallite size of ~4.4 nm. In contrast, chemisorption measurements of the spent catalysts after use in the APR reaction of biomass with exposure to sulfuric acid, water, and biomass showed no measurable H₂ chemisorption. We initially hypothesized that this could be due to either (i) loss of Pt from the catalyst pellets due to solubilization at reaction conditions; (ii) Pt poisoning due to interaction with sulfur species; and/or (iii) formation of carbonaceous deposits on the catalyst that make the Pt unavailable for chemisorption.

Elemental analysis of the spent Pt/Al₂O₃ catalyst showed a relatively unchanged Pt/Al ratio compared to that of the fresh catalyst. We eliminate, therefore, the first of the probable causes given above for the absence of chemisorption capacity on the spent catalyst. This leaves us with the possibility of poisoning—either by sulfates, other sulfur species or by coke. Elemental analysis of the spent catalyst also revealed a significant sulfur content due to exposure to sulfuric acid. Indeed, the S/Pt elemental ratio was 24.3, showing that there is likely enough sulfur present to potentially allow a complete poisoning of all Pt atoms. Though the presence of carbonaceous deposits on Pt/Al₂O₃ would also be expected to decrease the catalyst activity,⁴⁷ we expect that calcination at 400 °C in air should be sufficient to burn off the carbonaceous deposits and restore some chemisorption capacity back to the catalyst. Hydrogen chemisorption after calcination of the spent catalyst also revealed little or no chemisorption capacity, indicating that sulfur poisoning is the most likely cause for the loss in capacity. Certainly, the interaction of sulfur with the platinum could contribute to the low hydrogen yields observed in this process via catalyst poisoning.

APR of Different Substrates. As mentioned earlier, previous studies on aqueous-phase reforming in the literature dealt with flow reactor studies of representative model molecules that can be derived from biomass. Ethylene glycol (C₂H₆O₂) was found to be a good molecule for APR with reported selectivities⁴⁸ as high as 96% with Pt/Al₂O₃¹⁶ and 95% with Sn-modified nickel

catalyst⁴⁹ in a continuous mode. APR of other compounds with lower H/C ratios was found to be less selective to hydrogen production. Sorbitol (H/C ratio = 2.3) had a selectivity of 66%, while glucose (H/C ratio = 2) was reported to have ~50% selectivity.

This varied response to APR depending on the feed source became the impetus to study the use of actual biomass for hydrogen production via APR. It is important to note that a direct comparison between the current work and Dumesic's previous work with regard to hydrogen selectivity and yield is hampered by the huge influence of reactor configuration on the results (flow vs batch, vide infra). Thus, we compared the lignocellulosic APR results with other feeds to have an idea of how this reactor performs compared to feeds that have already been studied. Glucose was chosen as a representative compound. Waste paper was considered as another viable, alternative source. Ethylene glycol was also used as a feed, but the acid catalyst was not included during its APR. This is because acid hydrolysis was deemed unnecessary, since this feed has only two carbons in its backbone. The results of the study are summarized in Figure 4.

As shown in Figure 4, the gases produced in APR were mainly H₂, CO, and CO₂. In some runs, trace peaks of CH₄ were detected by the GCs, but the amount of methane produced was too small to be quantifiable. For ethylene glycol, C₂H₆ was detected, but its amount was also negligible. In all the runs, the CO yield was found to be smaller compared to the H₂ yield, which could be attributed to the water gas shift reaction, as mentioned before. Hydrogen production showed no dependence on the type of feed used in the system. The woody biomass produced the same amount of H₂ per dry gram of feed as the other compounds. It should be noted, though, that lignocellulosic materials contain lignin, and our proximate analysis indicates that, for the most part, it is not degraded to produce the permanent gases under our process conditions. If we consider the yield of biomass to be based only on its carbohydrate content, there would be an increase of hydrogen yield to 1.41 mmol H₂ per gram of dissolved feed for pine sawdust. Similarly, waste paper gives a yield of 1.05 mmol H₂ per gram of carbohydrate. Thus, in this context, biomass gives a 50% higher hydrogen yield than glucose under these conditions.

It was initially expected that glucose and ethylene glycol would have produced more H₂, because these molecules are more readily accessible to the platinum for both the reforming and the WGS reactions to proceed. Both form a homogeneous liquid phase with water at the beginning of the reaction. However, their chemistries were quite different—as suggested by the difference in their product distribution. APR of ethylene glycol showed almost zero production of carbon monoxide. A possible reason, aside from a possibly very efficient WGS, is the presence of reactions that have gone undetected here with products that are soluble in the aqueous phase. Ethylene glycol is the only feed molecule whose product contained hydrogen as the major product rather than carbon dioxide.

Another difference between glucose and ethylene glycol APR was that the former produced a black solid residue at the end of the reaction while APR of ethylene glycol did not. The production of the black solid residue in glucose APR may be explained by the acid-catalyzed complete dehydration of sugar, which leads to the production of solid carbon.⁵⁰ This did not

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occur when using ethylene glycol because of the different solution chemistry of the ethylene glycol system and is not simply a consequence of the lack of sulfuric acid in these runs, because when acid was used (data not shown), all byproducts remained a homogeneous liquid as well. Dumesic and co-workers also noted the difference between APR behavior of ethylene glycol and glucose.¹⁶ They attributed this to further degradation reactions of glucose in the liquid phase that ethylene glycol did not undergo. By virtue of its smaller size and perhaps the absence of the carbonyl functionality, ethylene glycol may undergo fewer reactions than glucose.

The APR of wastepaper showed a very high amount of CO₂ produced. This can be attributed to the presence of fillers and additives that go into the production of paper. CaCO₃-based fillers eventually produce CO₂ upon decomposition. However, it must be noted that CaCO₃ decomposition itself occurs at very high temperatures. For ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) (two forms that are usually used as fillers in the paper manufacturing industry), thermal decomposition occurs from 1150 K.⁵¹ It is then proposed that formation of CO₂ in the process could have been brought about by two pathways: (a) the reaction of the acid and CaCO₃, which directly liberates CO₂, and (b) formation of carbonic acid from the dissociation of calcium carbonate to Ca²⁺ and CO₃²⁻, which then undergoes water-catalyzed decomposition to produce CO₂.⁵²

Baseline Reactions. Experiments showed that baseline reactions (water–He and acid; water–He and Pt/Al₂O₃; and water–He, acid, and Pt/Al₂O₃) did not register any increase in the total system pressure of runs with only water and pressurized with He. As such, evolution of gases other than steam was considered absent, even in the presence of platinum.

Mechanisms leading to hydrogen evolution from water on the surface of platinum have been suggested in the literature.^{53,54} However, these published papers also indicate that, although the release of two hydride species from the platinum site to form H₂ is favorable (k is in the order of $\sim 10^{13}$), the initial reaction where water binds to an available platinum site ($k \approx 10^{-1}$) is much slower compared to the reverse reaction ($k \approx 10^{13}$). Indeed, a literature search shows platinum-catalyzed production of hydrogen from water occurs only in photocatalytic reactions.⁵⁵

An experiment with biomass with no catalysts was also performed. Even in the absence of acid, traces of hydrogen were generated. This minimal hydrogen production may be attributed to the hydrolysis due to the autoionization of water at elevated temperatures.^{12,28} Hydrolysis due to the release of acetic acid from acetylated hemicellulose groups was considered to be of a lower extent compared to the water autoionization effect.²⁷

Figure 5 shows that the total system pressure of biomass APR became higher than the saturated vapor pressure of water at temperatures > 210 °C. We attribute this to the onset of the reforming and/or WGS reactions that are favorable at these temperatures.⁵⁶ In our system, the operating temperature of 225 °C was usually attained at ~ 45 min. A noticeable steady increase in system pressure was noted up to ~ 1.5 – 2 h, after which

Table 3. H₂ Turnover Frequency (TOF) of APR of Different Substrates

feed	TOF, min ⁻¹	
	(Dumesic et al.)	
pine saw dust	2.0	
glucose	1.3	0.5 ^a
ethylene glycol	8.0	7, ^a 6.72 ^b

^a See ref 16. ^b See ref 58.

pressure was more stable (i.e., rate of pressure increase was usually much slower).

Last, the importance of the platinum in the production of hydrogen in the gas phase was probed with runs having γ -alumina and sulfuric acid acting as catalysts in the reaction. Results of these tests showed that hydrogen production was only $\sim 5\%$ of the total amount of hydrogen produced in the presence of Pt/Al₂O₃ and sulfuric acid. This clearly points to the role of platinum in hydrogen production.

On Comparison between Batch and Continuous Mode.

In this paper, we have applied modified APR to actual biomass using a batch reactor. As a proof of concept, we have shown that hydrogen can be produced from pine saw dust at a much lower temperature than traditional gasification or pyrolysis processes by using a combination of two processes: acid hydrolysis and platinum-catalyzed reforming. APR of other substrates such as glucose and ethylene glycol, using the same batch Parr reactor, showed comparable hydrogen yields. This creates the hypothesis that biomass could perform as well as ethylene glycol in a continuous reactor—if acid hydrolysis for biomass is integrated into the process.

Two parameters may be considered important in evaluating APR: turnover frequency (TOF) and selectivity. We compute TOF by considering only the H₂ production attributed to platinum reforming by subtracting the amount of hydrogen produced when only 5% acid is reacted with the feed. Table 3 presents the summary of these values. It also shows a comparison of our data from the batch reactor with the TOF values of previous studies with platinum as catalyst in a flow system.^{16,57,58} Interestingly, the TOFs observed in our batch system are quite similar to those observed in the previous studies of Dumesic and co-workers. The values given are calculated considering the whole 3-h batch run. On the other hand, if the heating time to 498 K is discounted (the first 45 min where no increase in system pressure is observed over the vapor pressure of water), TOFs for pine sawdust, glucose, and ethylene glycol (without acid) are 2.6, 1.7, and 11 min⁻¹, respectively—showing higher H₂ production per surface Pt atom per minute. With respect to H₂ selectivity, use of ethylene glycol in our system gave a value of 110%. This is higher compared to the previously reported ethylene glycol selectivity when Pt/Al₂O₃ was used as the catalyst.¹⁶ In another study using Co as catalyst, Huber et al.⁵⁸ reported a selectivity of 128.9% for ethylene glycol at a conversion of 1%. A possible reason for this is the conversion of ethylene glycol into dehydrated species that are in the liquid phase and are, thus, not accounted for in the total C atoms in the gas phase. However, our system suffers from a lower selectivity for glucose APR—20% as opposed to a reported 50% by Cortright et al.¹⁶ This might be due to large void spaces that are unavoidable in a batch system (vide infra).

(57) Catalysts other than platinum have already been used. A recent study using supported bimetallic Pd (Pd₁Fe₉/Al₂O₃) has demonstrated this catalyst to be 40 times more active than Pd/Al₂O₃. (See ref 58.)

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Previous studies done by Dumesic and co-workers used continuous reactors for APR studies of ethylene glycol as well as other model compounds.^{16–19,49,58–64} They have noted the adverse effect of void space⁶⁴ on hydrogen production, especially for feeds such as glucose and sorbitol. Void space here was defined as portions of the reactor that do not contain solid catalyst. According to their reports, void spaces caused homogeneous liquid reactions that culminate in the production of acids, aldehydes, and other liquid products.^{65–67} These reactions compete with APR—thus, hydrogen selectivity, as well as hydrogen yield, were reduced. The presence of void space is essentially unavoidable in our batch system. Thus, lower hydrogen yields are to be expected. Considering this, a continuous system would be an improvement in the reported batch process. However, because of a solid feed as well as production of a solid residue in biomass APR, design of a continuous process is expected to be more challenging than for the APR of model compounds.

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Summary and Conclusion

The aqueous-phase reforming (APR) of real biomass is first reported in this contribution. Studies indicate that breakdown of the polymeric lignocellulosic components allows for the formation of hydrogen at temperatures much lower than those currently used in gasification and pyrolysis processes. Increasing acid concentration hastens the breakdown of these components. Addition of a reforming catalyst such as Pt/Al₂O₃ facilitates the formation of more hydrogen in the reaction product gas. Comparisons between APR of different feeds (biomass, glucose, ethylene glycol, and wastepaper) showed effectively no difference in the amount of hydrogen produced per gram of feed. However, the hydrogen yields per gram of carbohydrate were different, with biomass giving the highest yield. Additionally, differences in component gas proportions hinted at different solution chemistries for each feed molecule that are beyond the scope of this initial study. Further study and complementary liquid analyses are expected to improve the understanding of the reactions in this system. It must be noted that the process reported in this paper was not completely optimized, e.g., variations in metal catalyst type, metal catalyst concentration, and temperature were not explored. Additionally, the use of a continuous reactor such as a fixed-bed system for the APR of biomass, as reported by Dumesic and co-workers, may significantly increase hydrogen yields because of minimization of void spaces. Such void space is significantly increased and is unavoidable in our batch system.

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