

Hydrogen by Catalytic Steam Reforming of Liquid Byproducts from Biomass Thermoconversion Processes

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Biomass, a product of photosynthesis, is a renewable resource that can be used for sustainable production of hydrogen. We propose an approach that combines production of hydrogen with valuable coproducts and shows promising economics. The concept is based on a two-stage process: fast pyrolysis of biomass to generate bio-oil, followed by catalytic steam reforming of the bio-oil, or a fraction thereof, to produce hydrogen. The preferred option is separation of the bio-oil into a lignin-derived fraction, which could be used for producing phenolic resins or fuel-blending components, and a carbohydrate-derived material, which would be reformed to produce hydrogen. The coproduct strategy can also be applied to residual fractions derived from pulping operations or ethanol production and to effluents from other biomass conversion technologies such as transesterification of vegetable oils or food processing residues. In addition, all of the biomass-derived liquids can be coprocessed with natural gas to produce hydrogen from mixed fossil–biomass feedstocks, a strategy similar to cofiring biomass and coal for power generation. This work focuses on the second stage of the process: catalytic steam reforming of various biomass-derived liquids. We have used a commercial nickel-based naphtha reforming catalyst in a fluidized-bed reactor to produce hydrogen from the various biomass-derived liquids. Yields have approached or exceeded 80% of those theoretically possible for stoichiometric conversion.

Introduction

At present, hydrogen is produced almost entirely from fossil fuels such as natural gas, naphtha, and coal. In such cases, however, the same amount of carbon dioxide is released during the production of hydrogen as that formed by direct combustion of those fuels. Renewable biomass is an attractive alternative to fossil feedstocks because it has essentially zero CO₂ impact. However, the hydrogen content of lignocellulosic biomass is only 6–6.5 wt %, compared to almost 25 wt % in natural gas, and on a cost basis producing hydrogen by a direct conversion process such as gasification cannot compete with the well-developed technology for steam reforming natural gas. Vegetable oils have a better potential for producing hydrogen than lignocellulosic feedstocks, but their high costs make the process economics unfavorable. Only an integrated process, in which biomass is partly used to produce more valuable materials or chemicals, while the residual fractions are utilized for the generation of hydrogen, can be economically viable in today's energy market. The process concept for producing hydrogen from biomass is shown in Figure 1.

In earlier papers^{1–4} we proposed a method that combines two stages: fast pyrolysis of biomass to generate bio-oil and catalytic steam reforming of the bio-oil to hydrogen and carbon dioxide. This concept has several advantages over the traditional gasification technology. First, bio-oil is much easier to transport than solid biomass and, therefore, pyrolysis and reforming can be carried out at different locations to improve the economics. For instance, a series of small-size

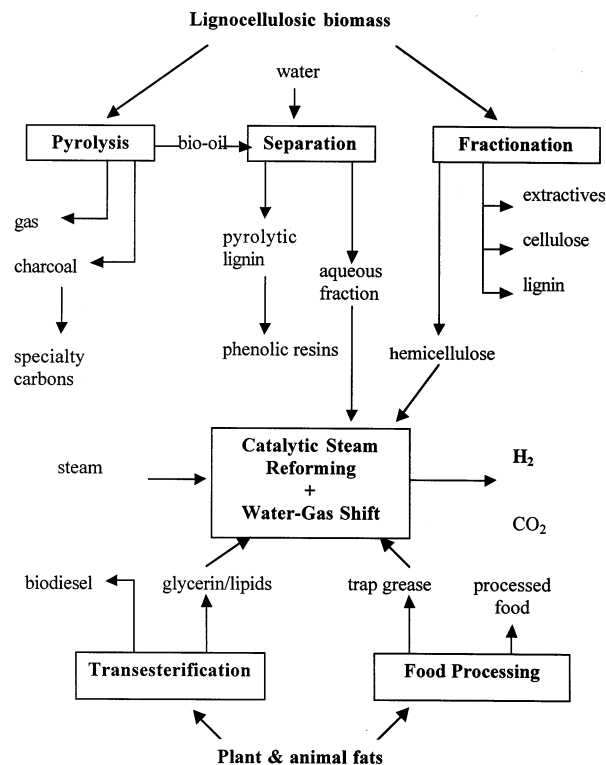


Figure 1. Biomass to hydrogen: process concept.

pyrolysis units could be constructed at sites where low-cost feedstocks are available. The bio-oil would be transported to a central reforming plant located at a site with existing hydrogen storage and distribution infrastructure. The second advantage is the potential for production and recovery of higher value coproducts from bio-oil that could significantly impact the economics of the entire process. The lignin-derived fraction can

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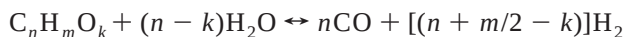
be separated from bio-oil and used as a phenol substitute in phenol–formaldehyde adhesives⁵ or converted to aromatic hydrocarbons and ethers for use as high-octane gasoline-blending components,⁶ while the carbohydrate-derived fraction is catalytically steam reformed to produce hydrogen.

Another option, also under development, employs steam–aqueous fractionation instead of pyrolysis as the first step for processing biomass. In the second step, hydrogen is produced by catalytic steam reforming of the lower-value hemicellulose-rich liquid byproduct, and cellulose and lignin are used for other applications.⁷ The process concept can be extended to other existing biomass conversion technologies.

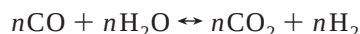
This research focuses on the second stage of the process: catalytic steam reforming of various biomass-derived liquids. In addition to lignocellulosic biomass-derived liquids generated by pyrolysis and by steam fractionation, we have also studied the catalytic steam reforming of “crude glycerin”, a byproduct from a vegetable oil based biodiesel plant, and “trap grease”, a widely available low-cost waste material recovered from restaurants, food processing plants, and water treatment facilities.

Steam Reforming of Biomass-Derived Liquids.

The steam reforming reaction of any oxygenated organic compound proceeds according to the following equation:



Because of the excess steam used in the process, carbon monoxide further undergoes the water gas shift reaction:



Thus, the stoichiometric maximum yield of hydrogen that can be obtained by reforming/water gas shift (corresponding to the complete conversion of organic carbon to CO₂) equals $2 + (m - 2k)/2n$ moles per mole of carbon in the feed material. In reality, this yield will always be lower because both the steam reforming and water gas shift reactions are reversible, resulting in the presence of some carbon monoxide and methane in the product gas. In addition, thermal cracking that occurs in parallel to reforming produces carbonaceous deposits, which are especially significant for thermally unstable compounds.

The basic assumption underlying this work is that the mechanism of metal-catalyzed reforming of oxygenated organic molecules ought to be similar to that proposed for hydrocarbons.⁸ Organic molecules dissociatively adsorb on metal (nickel) crystallite sites, while water molecules are adsorbed on the support (alumina) surface. Hydrogen is produced via (a) dehydrogenation of adsorbed organic molecules and (b) reaction of adsorbed organic fragments with hydroxyl groups, which migrate from the alumina support to the nickel crystallites/alumina interfaces. The second reaction also results in the formation of carbon oxides. The above chemical processes are accompanied by side reactions leading to the formation of carbon deposits on the catalyst surface. This unwanted effect is enhanced by higher nonsaturation, molecular weight, and aromaticity of the organic molecules.⁹ Biomass-derived liquids are more reactive than hydrocarbons because they already have some carbon–oxygen bonds. However, at elevated tempera-

tures, they also show a greater tendency to form carbon deposits because of the large size and thermal instability of constitutive molecules (carbohydrates, furans, and phenols). Therefore, reforming biomass-derived liquids will require process conditions that allow for a good contact of the organic molecules with the catalyst and that minimize formation, or facilitate removal by steam gasification, of carbon residues from the catalyst.

In previous years we demonstrated, initially through microscale tests¹ and then in bench-scale fixed-bed reactor experiments,² that bio-oil model compounds as well as the carbohydrate-derived fraction from bio-oil can be efficiently converted to hydrogen. Employing process conditions similar to those used for steam reforming of natural gas (fixed bed, commercial nickel catalysts, temperatures in the 800–850 °C range, and barometric pressure), we obtained hydrogen yields exceeding 80% of those theoretically possible. However, the formation of carbonaceous deposits, especially in the upper layer of the catalyst bed and in the reactor freeboard, limited the reforming time to 3–4 h, after which the catalyst required regeneration. The regeneration with steam or with CO₂ restored the catalyst activity but required 6–8 h. The limitations of the fixed-bed reactor were even more obvious for processing the whole bio-oil or the hemicellulose-rich solution from steam–aqueous fractionation. For example, the hydrogen yield obtained from the whole bio-oil was only 41% of that stoichiometrically possible; the reforming duration with a reasonable catalyst activity was less than 45 min, and the regeneration of the catalyst still required 8 h. Considering this, we concluded that a fixed bed was not an appropriate configuration for processing thermally nonstable biomass liquids, and it was replaced with a fluidized-bed reactor. An advantage of a fluidized bed is that, in a well-mixed regime, the feedstock is in contact with all of the catalyst particles, not only with its upper layer, as is the case in fixed-bed mode. Also, carbon deposits on the particles are better exposed to contact with steam and, therefore, can be gasified more quickly. Consequently, a fluidized-bed reactor should extend the duration of the reforming activity of the catalyst and shorten the regeneration cycle. In addition, if needed, the catalyst regeneration can be carried out continuously in a two-reactor system (circulating bed configuration or continuous withdrawal from a bubbling bed and transfer to the second reactor).

The most important parameters in the steam reforming process are temperature, steam-to-carbon (S/C) ratio, and catalyst-to-feed ratio. Steam reforming of natural gas is carried out at 800–900 °C, with a molar S/C ratio in the range of 3–5, and a space velocity, VHSV (volumetric flow rate of natural gas per unit volume of catalyst), of 1500–2000 h^{−1}. High temperature and excess steam favorably shift the equilibrium and increase the rate of reforming. Water gas shift to convert CO is carried out in a separate reactor operating at a lower temperature. Simple oxygenated organic compounds such as methanol or acetic acid are more reactive than hydrocarbons and can be reformed at lower temperatures.^{10,11} However, complex biomass-derived liquids that include large, thermally unstable molecules need high temperature and more steam to effectively gasify the carbonaceous deposits formed by thermal decomposition. In initial tests of reforming, the carbohydrate-derived biomass pyrolysis oil fraction at

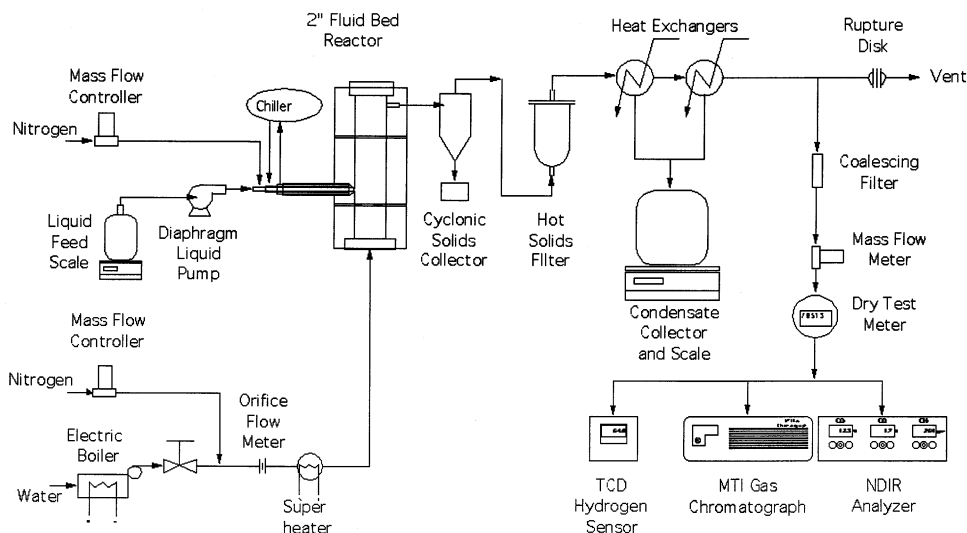


Figure 2. Fluidized-bed reformer system.

S/C = 5, significant catalyst deactivation, due to carbon deposits, was observed after only 3–4 h on stream. Considering this, the reforming of bio-oil and hemicellulose solutions was usually carried out at 800–850 °C with S/C > 7 (including water in the feed). Also, the methane-equivalent space velocity, $G_{CH_4}HSV$, defined as the volumetric gas flow that would be observed if all carbons in the feed were in the form of CH_4 per unit volume of catalyst, was in the range 800–1000 h^{-1} , which is less than that employed in commercial natural gas reforming installations. “Trap grease” and waste glycerin did not show a high tendency to coke and were processed using less excess steam. This paper reports the results of the catalytic steam reforming of four different types of biomass-based liquids to produce hydrogen as presented in the conceptual diagram in Figure 1.

Experimental Section

Materials. Bio-oil used for this study was generated from pine sawdust using the NREL fast pyrolysis vortex reactor system.¹² The oil comprised 47.7% carbon, 7.4% hydrogen, and 44.8% oxygen, with a water content of 26.7%. It was separated into aqueous (carbohydrate-derived) and organic (lignin-derived) fractions by adding water to the oil in a weight ratio of 2:1. The aqueous fraction (75% of the whole oil) contained 21.8% organics ($CH_{1.25}O_{0.55}$) and 78.2% water.

Steam–aqueous fractionation of poplar wood was performed at the University of Sherbrooke, Sherbrooke, Canada, using a continuous Stake II unit.¹³ This treatment led to solubilization, after washing, of 30% of the biomass into a hemicellulose-rich aqueous solution, which contained 32.1% solutes of the elemental formula $CH_{1.36}O_{0.67}$. These solutes were mostly oligomeric pentosans with a small amount of dissolved lignin.

“Crude glycerin” samples were obtained from the West Central Co-op biodiesel plant in Ralston, IA. The technology employed in this plant is based on the transesterification of vegetable oils with methanol, which produces a mixture of biodiesel (methyl esters of fatty acids) and glycerin. Glycerin settles at the bottom of a separation tank, and biodiesel forms the top layer. The “crude glycerin” obtained for testing was a very viscous liquid, only partially miscible with water. Its elemental composition, 54.7% carbon, 9.9% hydrogen,

and 35.5% oxygen, indicates that the liquid was a mixture of glycerin (55%) with methyl esters of fatty acids (45%).

Samples of “trap grease”, pretreated by filtration to remove solid impurities, were obtained from Pacific Biodiesel. The grease was a dark-colored liquid of very high viscosity at room temperature. The viscosity decreased to 80 mPa·s at 45 °C, which made the grease easy to pump after preheating. The grease mainly was comprised of fatty acids and their mono-, di-, and triglycerides. The overall elemental analysis of the grease showed 75.5% carbon, 11.8% hydrogen, and 12.7% oxygen.

At this time, no commercial fluidizable steam reforming catalyst is available because industrial reforming processes are carried out in fixed-bed reactors. For this series of experiments, C11-NK, a commercial nickel-based naphtha reforming catalyst that was obtained from Süd-Chemie in the form of large rings, was selected. The rings were ground, and the particles with diameters in the range of 300–500 μm were used in the fluidized-bed reactor. Particles in this size range fluidized uniformly in a cold model with no visible entrainment at the flow rates used in the process.

Fluidized-Bed Reformer. The bench-scale bubbling fluidized-bed reactor is shown in Figure 2. The 2-in.-diameter Inconel 625 reactor supplied with a porous metal distribution plate was placed inside a three-zone electric furnace. The reactor contained 200–250 g of commercial nickel-based catalyst ground to a particle size of 300–500 μm . Superheated steam at a pressure slightly above barometric was used as a fluidizing gas as well as a reactant in the reforming process. Steam was generated in a boiler and superheated to 750 °C before entering the reactor at a flow rate of 120–240 g/h. The reactor was operated in the temperature range of 800–850 °C, which is similar to that for reforming natural gas and which was also found suitable for processing biomass-derived liquids.¹ The liquids were fed at a rate of 120–300 g/h using a diaphragm pump. A water-cooled injection nozzle was used to spray liquids into the catalyst bed. The temperature in the injector was maintained below the feed boiling point to prevent evaporation of volatile components and deposition of nonvolatile components in the tip. The product gas passed through a cyclone and hot-gas filter, which

Table 1. Hydrogen Yields from the Steam Reforming of Biomass-Derived Liquids

feedstock	temp, °C	S/C, mol/mol	G _{C1} HSV, h ⁻¹	yield of H ₂ , g of H ₂ /100 g of feed	yield of H ₂ , % stoichiometry
wood pyrolysis liquids (aqueous extract)	800	7.0	770	2.6	77
	850	8.6	820	2.7	77
	850	9.0	830	3.0	89
	850	7.1	1000	3.3	78 ^a
hemicellulose (aqueous solution)	850	9.0	800	2.0	66
	850	14.1	1000	2.3	77
crude glycerin	850	2.1	1400	17.6	74
	850	2.6	1440	17.0	72
trap grease	600	2.7	950	18.8	53
	700	3.1	1000	21.2	60
	850	5.0	1100	29.0	82

^a Different batch (composition) of pyrolysis liquids than in the three other experiments.

captured fine catalyst particles and carbonaceous solids generated in the reactor, and then through two heat exchangers, which removed excess steam. The condensate was collected in a vessel in which the weight was continuously monitored. The outlet gas flow rate was monitored by a mass flowmeter and measured by a dry test meter. The concentrations of CO₂, CO, and methane in the product gas were monitored by a nondispersive infrared analyzer (NDIR model 300 from California Analytical Instruments); the hydrogen concentration was tracked by a thermal conductivity monitor TCM4. In addition, the gas was analyzed every 5 min by an online MTI gas chromatograph, which provided concentrations of hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, and nitrogen. The temperatures in the system, as well as the flows, were recorded and controlled by the OPTO data acquisition and control system. Based on the flows and composition of the process streams, global and elemental mass balances and the yield of hydrogen generated from the feed were calculated.

Results and Discussion

Representative results of the yields of hydrogen produced by steam reforming of four different biomass-derived liquids are presented in Table 1. The duration of the experiments ranged from 4 to 90 h. Global mass balance closures for these tests were 95–99%, and carbon to gas conversion was in the range 91–100%. In all of the experiments entrainment of the catalyst particles from the reactor occurred at a rate of about 5%/day. This entrainment was caused by attrition of the particles that were obtained by grinding large rings designed for use in fixed-bed reactors. After grinding, the catalyst particles did not have the strength needed in the fluidized beds. To eliminate or, at least, significantly reduce the catalyst losses, an attempt to develop a fluidizable catalyst that will combine both high reforming activity and resistance to attrition will be undertaken. The work on catalyst development will be presented in a separate paper; below, the performance of the steam reforming process, which varied depending on the feedstock and process conditions, is discussed.

Biomass Pyrolysis Oil–Aqueous Fraction. The steam reforming tests of the aqueous extract of pine bio-oil were carried out at temperatures of 800 and 850 °C. The S/C ratio was in the range of 7–9, and G_{C1}HSV was 700–1000 h⁻¹. During the experiments at 800 °C, a slow decrease in the concentrations of hydrogen and carbon dioxide and an increase in carbon monoxide and methane in the product gas were observed. These changes resulted from a gradual loss of the catalyst activity,

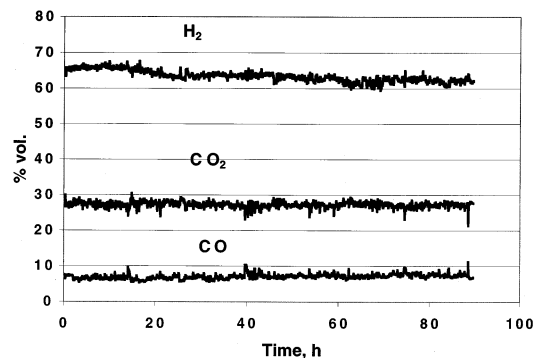


Figure 3. Gas composition from reforming of aqueous extract of bio-oil: $t = 850$ °C, $S/C = 7$, $G_{C1}HSV = 1000$ h⁻¹.

probably because of coke deposits. As a consequence, the yield of hydrogen produced from the bio-oil fraction decreased from the initial value of 85% to 77% of the stoichiometric potential (3.24 g of hydrogen from 100 g of liquid feed) after 12 h on stream.

At 850 °C, either the formation of char and coke was much lower or their gasification by steam was more efficient than at 800 °C. During over 90 h of uninterrupted reforming, the product gas composition remained almost constant and only a small decrease in the concentration of hydrogen was observed, as presented in Figure 3.

In addition to hydrogen, CO, and CO₂, small amounts of methane and ethylene were also present in the product gas. The hydrocarbons were most likely formed by the thermal cracking of organic vapors, which always accompanies the catalytic reforming. Over the run time, the concentration of methane increased and then stabilized at 2.5%. This indicates that the catalyst was slowly losing activity (decreasing the rate of reforming relative to thermal cracking), which eventually leveled off. The yield of hydrogen produced from the bio-oil fraction was around 80% of the stoichiometric potential (Figure 4). It would be greater than 90% if CO underwent the complete shift reaction with steam. About 95% of the carbon from the feed was converted to gas. Only a small amount of char was collected in the cyclone and in the filter, and little or no coke was deposited on the catalyst. Very little organic matter (total organic carbon of 2–5 mg/L) was found in the condensate.

Co-reforming of Bio-oil and Natural Gas. At present, the amount of biomass-derived liquids available for reforming is rather limited. A viable way to increase the production of hydrogen in a biomass-based plant could be co-reforming pyrolysis liquids and natural gas. If successful, this approach, similar to cofiring of biomass with coal for power generation, would improve

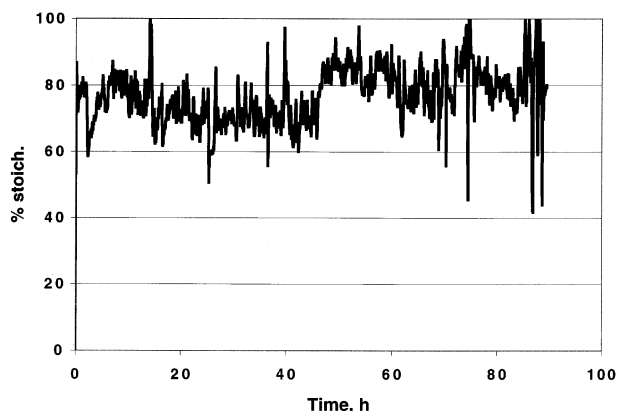


Figure 4. Yield of hydrogen from reforming of aqueous extract of bio-oil: $t = 850\text{ }^{\circ}\text{C}$, $S/C = 7$, $G_{\text{CHSV}} = 1000\text{ h}^{-1}$.

feedstock flexibility for producing hydrogen and add environmental benefits to the traditionally fossil-based technology. Therefore, a series of co-reforming tests was performed to investigate the technical feasibility of the process.

In this series of tests, the reactor was operated at $850\text{ }^{\circ}\text{C}$. Natural gas was compressed and fed to the fluidized-bed reformer at the rate of $45\text{ L}_{\text{STP}}/\text{h}$, while the pyrolysis liquid feed rate was 120 g/h . During a 56-h-long test, the mode of operation alternated between co-reforming and reforming the bio-oil fraction only. In the co-reforming mode, G_{CHSV} was approximately 1000 h^{-1} and the S/C equaled 4.6. Cofeeding natural gas helped maintain and restore the catalyst activity. At the beginning of cofeeding phase, the concentration of methane in the product gas was 3 times greater than that observed for reforming of the bio-oil fraction. However, this concentration decreased by a factor of 2 and stabilized at this level within the first 20–30 min of co-reforming. We believe that during reforming of the bio-oil fraction only, the catalyst partly oxidized because of the large steam excess in the process ($S/C = 13$) and the relatively low concentration of hydrogen in contact with the catalyst. Consequently, the catalyst was losing activity, which was restored to a large extent during the co-reforming mode, when nickel was stabilized, probably by efficient reduction due to a greater concentration of hydrogen in the reactor. The gas composition was almost constant during the respective modes of reforming bio-oil only and co-reforming, though a decrease in the hydrogen concentration from 73% to 70% and an increase in methane from 1.5% to 4.5% were observed. Methane conversion, calculated assuming that the difference in the CH_4 content in the product gas between co-reforming and reforming bio-oil only corresponded to nonreacted natural gas, was initially 92.5% but decreased to 80% by the end of the test. The hydrogen yield was initially 80% and then decreased to 75% of the stoichiometric potential as shown in Figure 5. A total of 3.8–4.3 times more hydrogen was produced when the bio-oil fraction was co-reformed with natural gas than during the reforming phase. Thus, apparently, 23–26% of the hydrogen was generated from bio-oil and 73%–77% from natural gas.

Hemicellulose-Rich Aqueous Solution. The steam reforming experiments were carried out at temperatures of $800\text{--}850\text{ }^{\circ}\text{C}$ with hemicellulose solution feed rates of $240\text{--}300\text{ g/h}$ and steam flows of $140\text{--}180\text{ g/h}$. This corresponds to a G_{CHSV} of about 1000 h^{-1} and a molar S/C ratio of 9.5–14. For over 5 h the product gas

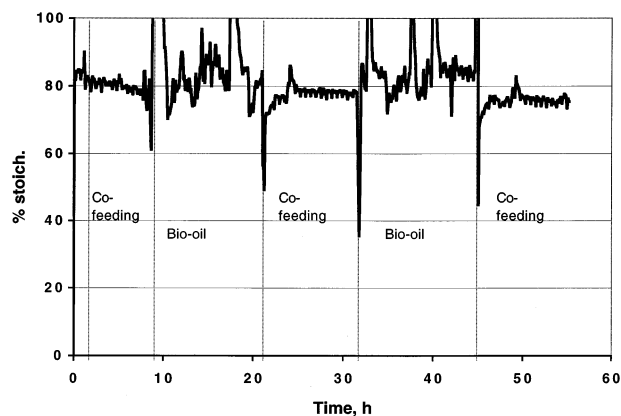


Figure 5. Yield of hydrogen from co-reforming of bio-oil fraction with natural gas: $t = 850\text{ }^{\circ}\text{C}$, $S/C = 4.6$, $G_{\text{CHSV}} = 1000\text{ h}^{-1}$.

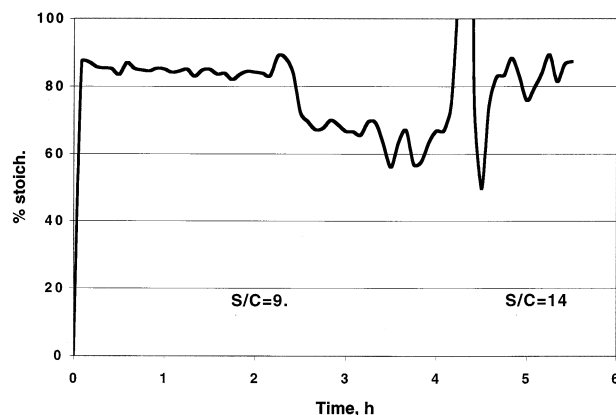


Figure 6. Yield of hydrogen from steam reforming of aqueous hemicellulose solution: $t = 800\text{--}850\text{ }^{\circ}\text{C}$, $S/C = 9\text{--}14$, $G_{\text{CHSV}} = 1000\text{ h}^{-1}$.

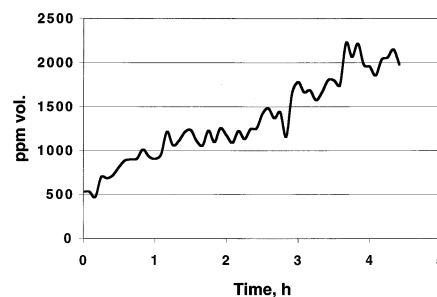


Figure 7. Concentration of methane during steam reforming of "crude glycerin": $t = 850\text{ }^{\circ}\text{C}$, $S/C = 2.6$, $G_{\text{CHSV}} = 1400\text{ h}^{-1}$.

composition was almost constant with the hydrogen concentration of about 65%, CO_2 30%, and CO 5%. However, after 2.5 h on stream at $800\text{ }^{\circ}\text{C}$, the amount of gas generated at a constant feed rate started to decline. Consequently, the hydrogen yield, which at the beginning reached 85% of the stoichiometric potential, decreased to 55% (Figure 6). Increasing the temperature to $850\text{ }^{\circ}\text{C}$ and the steam flow (to achieve $S/C = 14.2$) resulted in an improvement of the process performance. Mass balances indicated that 85% of carbon from hemicellulose was converted to CO_2 and CO in the first phase of the experiments. The remaining 15% of the carbon probably formed char, entrained from the system, and coke deposits on the catalyst surface, which would explain the loss of its activity. The activity of the catalyst used for reforming was restored by steam gasification of the deposits; the catalyst was reused in the next experiments and showed somewhat lower

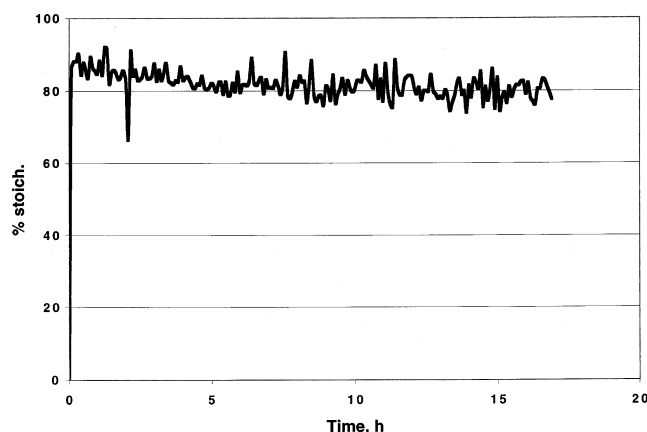


Figure 8. Yield of hydrogen from steam reforming of "trap grease": $t = 850\text{ }^{\circ}\text{C}$, $S/C = 5$, $G_{C1}HSV = 1100\text{ h}^{-1}$.

efficiency. Though the carbon to gas conversion again reached 85%, the hydrogen yield was in the range of 75–80% (85% initially) of the theoretical potential, and more methane was observed in the product gas than during the tests using fresh catalyst. This indicates some permanent loss of catalyst activity. At this point, the cause of the permanent loss in activity and why it was more visible during reforming hemicellulose-rich liquids than during reforming of the bio-oil carbohydrate-derived fraction has not been identified.

In summary, hemicellulose-rich liquids were more difficult to reform than an aqueous extract of bio-oil, probably because of a higher content of oligomeric material that tends to carbonize during the process. Therefore, it required a higher S/C ratio to remove carbon deposits from the catalyst.

"Crude Glycerin" from Biodiesel Production.

"Crude glycerin" was received as a high-viscosity liquid that had to be preheated to facilitate pumping and atomizing (the whole feeding line was maintained at 60–80 $^{\circ}\text{C}$). The liquid was fed at a rate of 78 g/h ($G_{C1}HSV = 1400\text{ h}^{-1}$) and steam at a rate of 145 g/h ($S/C = 2.6$). The experiments at 850 $^{\circ}\text{C}$ proceeded very smoothly with only occasional fluctuations in the liquid feed rate, which were attributed to nonhomogeneity of the feed. The concentration of the major gas products was constant during the run, but a gradual increase in methane production was noticed (Figure 7). The process performance did not decrease significantly during several hours on stream. The hydrogen yield was around 77% of the stoichiometric potential, which equaled 23.6 g/100 g of feed. The total conversion of CO in the gas through water gas shift would increase the hydrogen yield to 95% of that theoretically possible. These promising results suggest that a low-value byproduct from biodiesel production could be a viable renewable raw material for producing hydrogen. An integration of transesterification and reforming technologies could be beneficial for the economics of both processes.

"Trap Grease". "Trap grease" was fed to the reactor operated at approximately 850 $^{\circ}\text{C}$ at a nominal rate of 50 g/h, resulting in a $G_{C1}HSV$ of 1100 h^{-1} . As with glycerin, the feed container and the feeding lines had to be maintained at 60–80 $^{\circ}\text{C}$ to facilitate the liquid flow. With a steam flow rate of 250 g/h, the molar S/C ratio was about 5. The concentration of the major gas products was constant during the whole run time of 17 h. However, the concentrations of minor components, methane and ethylene, were increasing during the first

10 h of the experiment, which indicates a decrease in catalyst activity. Eventually, they leveled off in the second half of the reforming test. The hydrogen yield that was initially 31.1 g/100 g of "trap grease" decreased to 28.7 g after 17 h of operation. This corresponds, respectively, to 88% and 81% of the stoichiometric potential (Figure 8). These yields could be 10% higher if the reforming was followed by water gas shift to convert CO to CO_2 . During the reforming operation, no carbon deposits were formed on the catalyst; all of the carbon from "trap grease" was completely converted to gaseous product.

Conclusions

Biomass can be an important and economically viable renewable resource for producing hydrogen if used in an integrated process that also generates other marketable coproducts. Following this concept, we demonstrated the following process options: fast pyrolysis of lignocellulosic biomass followed by steam reforming of the carbohydrate fraction of bio-oil; steam–aqueous fractionation of biomass followed by steam reforming of the hemicellulose-rich solution; transesterification of vegetable oils followed by steam reforming of glycerin residue; and steam reforming of waste grease residue from the food processing sector. All of the biomass-derived liquids can also be co-reformed with natural gas to increase feedstock flexibility and to add environmental benefits to the fossil-based production of hydrogen.

The fixed-bed reactor configuration, traditionally employed for reforming natural gas and naphtha, is not suitable for processing thermally unstable complex liquids obtained from lignocellulosic biomass, because of their tendency to decompose thermally and form carbon deposits in the upper layer of the catalyst and in the reactor freeboard. However, reforming of these complex liquids can be efficiently carried out in a fluidized-bed reactor using commercial nickel catalysts. The C11-NK catalyst showed good activity in processing biomass-derived liquids and was readily regenerated (20 min to 2 h) by steam or CO_2 gasification after deactivation, which occurred during reforming. As expected, higher process temperature, lower space velocity, and higher S/C ratio extended the catalyst time on stream before regeneration was needed.

The hydrogen yield obtained in a fluidized-bed reactor from the carbohydrate-derived fraction of wood pyrolysis oil was about 80% of theoretical, which corresponds to approximately 6 kg of hydrogen from 100 kg of wood used for pyrolysis. This fraction of bio-oil was also co-reformed with natural gas. The hydrogen yield from the co-reforming was about 80% of stoichiometric. This yield would increase to 90% if the CO present in the gas were further converted by water gas shift. It appears that about 75% of the hydrogen was obtained from natural gas, while 25% was from the bio-oil fraction.

The hydrogen yield from the hemicellulose solution obtained by steam–water fractionation of a lignocellulosic biomass was about 70% of that for stoichiometric conversion. A lower performance than that observed for other biomass-derived liquids was probably due to the higher content of oligomeric material, which is more difficult to reform and has a greater tendency to form carbon deposits on the catalyst.

Lipids and lipid-derived liquids are easier to reform than the lignocellulosic-based liquids and can produce higher yields of hydrogen; almost 18 g of hydrogen was

produced from 100 g of "crude glycerin", which is 76% of the theoretical maximum. "Trap grease" yielded approximately 29 g of hydrogen/100 g of the feed, which is about 82% of the stoichiometric yield, during 17 h of catalyst time on stream. Water gas shift following the reforming could further increase the hydrogen yield from both feedstocks to above 90% of the theoretical value.

These preliminary results look very promising even though the reforming process needs to be optimized to determine conditions that provide the maximum yield of hydrogen and minimum coke formation. In the case of waste glycerin and grease, inorganic impurities may impair the long-term catalyst performance. Also, the catalyst particles, ground from commercial catalysts, which were designed for the fixed-bed applications, were susceptible to attrition when used in the fluidized-bed application. Consequently, they were entrained from the fluidized-bed reactor at a rate of 5%/day. To reduce the losses of catalyst due to attrition, the development of a fluidizable catalyst, which will have both high activity and mechanical strength at the conditions of the steam reforming process, is needed and is being pursued by NREL.

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