BIOMASS TO HYDROGEN VIA PYROLYSIS AND REFORMING

M. Mann, E. Chornet, S. Czernik. and D. Wang
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado, 80401-3393

ABSTRACT
Pyrolysis of lignocellulosic biomass and reforming of the pyroligneous oils is being studied as a strategy for the production of hydrogen. New technologies for the rapid pyrolysis of biomass provide compact and efficient systems to transform biomass into vapors which are condensed to oils, with yields as high as 75-80% by weight of the anhydrous biomass. This "biocrude" is a mixture of aldehydes, alcohols, acids, oligomers from the constitutive carbohydrates and lignin, and some water produced during the dehydration reactions. Hydrogen can be produced by reforming the biocrude with steam. A process of this nature has the potential to be cost competitive with conventional means of hydrogen production.

The concept of hydrogen from biomass offers significant opportunities for novel research and development. The use of a renewable resource feedstock is an alternative to conventional means of hydrogen production from petroleum and natural gas. As a consequence, the environmental benefit of zero net carbon dioxide emissions facilitates the approach to a pollution-free energy system.

Two scenarios for the production of hydrogen from pyrolysis oil can be envisioned. One would involve a regionalized system of hydrogen production with small and medium-sized pyrolysis units (<500 Mg/day) providing biocrude to a centralized reforming unit. The alternative is to pyrolyze biomass in a large unit and feed the uncondensed vapors directly to the reforming unit. The first case has the advantage of the availability of cheaper feedstocks, perhaps biomass waste. In the integrated system, however, the costs of condensing the vapors to the oil and transporting them to the hydrogen facility are avoided. The reforming facility can be designed to handle alternate feedstocks, such as natural gas and naphtha, if necessary. Additionally, the biocrude can first be refined to yield valuable oxygenates so that only the residue is used for hydrogen production.

Thermodynamic modelling of the major constituents of the biocrude has shown that reforming is possible within a wide range of steam/compound ratios. Additionally, catalytic reforming of model compounds to hydrogen using a Ni-based catalyst has begun. Existing catalytic data on the reforming of oxygenates has been studied to guide catalyst selection. An initial process diagram for the pyrolysis and reforming operations has been devised, and economic boundary estimates have been calculated.

FAST PYROLYSIS: BIOCRUDE YIELDS AND COMPOSITION
Gasification of solid fuels to yield a mixture of H_2 and CO, followed by shift conversion to produce H_2 and CO_2, and steam reforming of hydrocarbons are well established processes. Economics of current processes favor the use of hydrocarbons (natural gas, C_2-C_5, and naphtha) and inexpensive coal as feedstocks. However, biomass is a potentially cost-competitive feedstock for gasification. An alternative approach to H_2 production begins with fast pyrolysis of biomass.

Recent advances in the understanding of pyrolytic mechanisms and in the technology needed to achieve high heat transfer rates to particles, while controlling secondary cracking reactions responsible for gas and char production, have led to the development of fast pyrolysis routes. These convert biomass materials in high yields ($\sim$ 75% wt of dry biomass) into a "pyrolytic oil," or "biocrude." Very little ash and char are present in the biocrude when appropriate filtration technology is used in the pyrolysis process. Results from fluid bed fast pyrolysis (Radlein et al., 1991) have shown that a 76% wt yield of biocrude can be obtained from poplar ($CH_{1.47}O_{0.67}$). The organic fraction of the biocrude represents 85% wt and its elemental composition is $CH_{1.33}O_{0.53}$. Table 1 shows the expected yields of hydrogen from two thermochemical routes (pyrolysis and gasification), compared to the theoretical yield of the reaction between wood and steam using externally supplied heat.

Process Routes	Yield of Hydrogen (% wt biomass)	Energy Content (HHV) of H₂ / Energy Content of Biomass
Pyrolysis + Catalytic Reforming	12.6	91%
Gasification + Shift Conversion	11.5	83%
Biomass + Steam + External Heat (Theoretical Maximum)	17.1	124%

Calculations were made using current yields for non-optimized fast pyrolysis (Radlein et al, 1991) and gasification (Probstein and Hicks, 1982) processes, and the theoretical maximum for the indirectly heated gasification process. The H_2 production potential for these two routes is similar. However, the pyrolysis process is less severe and does not require an oxygen supply as in gasification. Both options require steam for the reforming and shift conversion steps.

Three technologies appear to be capable of achieving high yields of biocrude:
- Fluid beds (Piskorz et al, 1988): 450°C-550°C, < 0.5s
- Entrained beds (Graham and Freel, 1988): ~650°C, < 1.0s
- Ablative reactors, i.e. vortex (Diebold and Scahill, 1988): 450°C-625°C, < 1.0s

In these technologies, 55-70% wt of mf biomass is the organic fraction of the biocrude, and 5-15% wt is water. A fourth, vacuum pyrolysis, has also demonstrated the ability to produce high biocrude yields (Roy et al, 1990); the organic fraction represents 50-60% wt of mf biomass and water 13-16% wt. Reliable values of oil, water, char and gas yields are difficult to obtain because of unclosed and/or unreported material balances. The composition of typical oils from poplar has only been reported in quantitative detail by the University of Waterloo, Canada (Piskorz et al, 1988), and is shown in table 2.

Table 2: Pyrolytic Oil Composition Derived from Poplar (Radlein et al, 1991)

wt % mf wood

Oil*	65.8	Oil + Water = Biocrude
Water*	12.2	
Char	7.7	
Gas	10.8	
Unaccounted	3.5	

Composition of the Oil		
Acetic Acid	5.4	
Formic Acid	3.1	
Hydroxyacetaldehyde	10.0	
Glyoxal	2.2	
Methylglyoxal	0.65	
Formaldehyde	1.2	
Acetol	1.4	
Ethylene Glycol	1.05	
Levoglucosan	3.0	
1,6-Anhydroglucofuranose	2.4	
Fructose	1.3	
Glucose	0.4	
Cellobiosan	1.3	
Oligosaccharides	0.7	
Pyrolytic Lignin	16.2	Material precipitated by addition of water
Unidentified	15.5	

Variations in the composition of pyrolysis oil should be expected as a function of raw material, pyrolysis conditions (T, t, and dT/dt), and the use of catalysts during the pyrolytic step. However, the biocrude is essentially a mixture of two major acids, aldehydes and alcohols plus a significant fraction of lignin. Based on the works of Antal (1982), Shafizadeh (1982), and Richards (1987), the unidentified compounds should contain a large number of

carbohydrate-derived components. Monomeric lignin-derived products having alcohol characteristics should also be present (Elliott, 1988).

THERMODYNAMICS
Thermodynamic simulations of the reforming reaction were performed in order to guide experimental design and determine equilibrium constraints. These simulations were performed on ASPEN Plus using a mixture of compounds with the following composition, based on the results obtained by the University of Waterloo and from the vortex reactor at NREL.
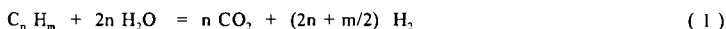
Table 3: Mixture Composition for Thermodynamic Simulations

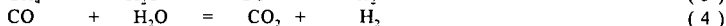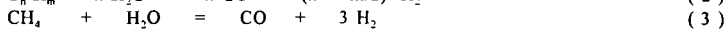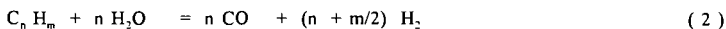| Compound	Molar Percent	Weight Percent
hydroxyacetaldehyde	38%	33%
acetic acid	27%	23%
acetol	9.3%	9.8%
guaiacol	3.7%	6.6%
syringol	1.4%	3.3%
formic acid	7.5%	4.8%
coniferol	2.6%	6.6%
phenol	2.4%	3.3%
benzene	2.9%	3.3%
toluene	2.5%	3.3%
furfural	2.4%	3.3%

The plots of hydrogen production versus temperature and the molar ratio of steam to carbon content (S/C_1), were very similar for all compounds and the mixture. Because pyrolysis oil vapors are produced at approximately 450 - 600 °C, a practical temperature for the reforming reaction is 500 °C. Figure 1 shows the approach of many of the model compounds and the mixture of compounds to maximum stoichiometric yields of hydrogen as a function of (S/C_1). The necessary steam is dependent only on the carbon content of the compound. Therefore, regardless of the compounds in the oil, the appropriate amount of steam for high hydrogen yields can be estimated solely from the empirical formula.

CATALYTIC REFORMING OF OXYGENATES
Steam reforming of hydrocarbons (C_1-C_5, naphtha and gas oils) is well understood and proceeds readily at steam to carbon ratios (S/C_1) between 3.5 and 5.0, and temperatures up to 775°C. When the objective is to maximize the production of H_2, the stoichiometry describing the overall process is:

$$C_n H_m + 2n H_2O = n CO_2 + (2n + m/2) H_2 \qquad (1)$$

However, in a hydrocarbon reformer, the following reactions take place concurrently:

$$C_n H_m + n H_2O = n CO + (n + m/2) H_2 \qquad (2)$$
$$CH_4 + H_2O = CO + 3 H_2 \qquad (3)$$
$$CO + H_2O = CO_2 + H_2 \qquad (4)$$

Reforming of higher hydrocarbons (Equation 2) is irreversible (Tottrup and Nielsen, 1982), whereas the methane reforming reaction (Equation 3) and the shift conversion reaction (Equation 4) approach equilibrium. A large molar ratio of steam to hydrocarbon will ensure that the equilibrium for reactions (3) and (4) is shifted towards H_2 production.

The most commonly used catalyst is Ni on alumina. Ca, K and Mg are often used with the alumina to enhance water adsorption, lower the acidity and favor mobility of the OH species on the surface (Rostrup-Nielsen, 1984). Alternate Ni-based catalyst formulations with mixtures of rare earth oxides and a refractory support, have been developed (Patil, 1987) to increase the resistance of the catalyst to poisoning, particularly by sulfur.

Methanol is readily steam reformed at low temperatures (< 300°C). Cu-based catalysts and recently developed Pd/ZnO preparations are extremely selective towards the formation of CO_2 and H_2 via the formate ester mechanism (Takahasi, 1982). Ethanol requires higher reforming temperatures than methanol. The mechanism proceeds through acetaldehyde and ethylacetate

intermediates on the same Cu-based catalysts (Iwasa-Takezawa, 1991). The existing data on oxygenated aromatic compounds, i.e. cresols, suggest that they can be steam reformed using Pd, Rh or Ni on alumina, silica or chromia-alumina. Little is known, however, about optimum experimental conditions that will result in long-term catalyst activity. The challenge lies in finding a catalyst that can reform both the complex fraction (pyrolytic lignin) as well as the carbohydrate-derived fractions (monomeric sugars, anhydrosugars, and oligomers) while limiting undesirable side reactions which will lower the yields of H_2.

If the oxygen in the aldehydes, alcohols and acids could be removed as CO_2, via ester intermediates as in methanol reforming, the production of H_2 would be maximized. This could be done by separating a low molecular weight fraction of the biocrude from a high molecular weight fraction during the condensation of the pyrolytic vapors. An alternate approach is to conduct the steam reforming of the entire biocrude near equilibrium conditions. This may be possible by choosing a stable Ni-based catalyst operating in the 700°-800°C range. A favored formulation could be: NiO (20-30 wt%), MgO (10-15 wt%), Al_2O_3 (50-65 wt%), rare earth oxides (5-15 wt%), and a promoter like Cr_2O_3, V_2O_5, or WO_3 (5-10 wt%).

PROCESS DESIGN
Unlike other reforming processes, steam reforming pyrolysis oil to produce hydrogen involves very few unit operations, which should increase its economic feasibility. Because of the low sulfur content of biomass, a sulfur removal system is not likely to be required, while one is always used in petroleum and methane reforming. Also, according to current experimental results, only one medium temperature catalytic reformer is required; conventional methane reforming uses a furnace-like converter followed by a high temperature reformer and a low temperature reformer. Since the overall reaction of pyrolysis oil to H_2 is endothermic, the char produced in the pyrolysis of the biomass will be burned to produce heat and steam. Preliminary energy balances indicate that a fraction of the oil may also be used as a source of heat, especially in the centralized reformer supplied by satellite pyrolysis units. In the base-case design, a pressure swing adsorption unit will be used to purify the H_2 produced.

ECONOMICS
Preliminary calculations were performed in order to determine the boundaries of economic feasibility of the process. To examine these boundaries before plant costs can be figured, the ratio of the current market selling price of H_2 to the pyrolysis oil production cost was calculated. If the ratio is greater than one, the process has the potential to be economically feasible. This method assumes that the process to produce H_2 is completely free of capital and operating costs, and therefore sets the minimum limits on the recovery of theoretical hydrogen and product selling price.

The maximum stoichiometric amount of H_2 was calculated as that obtained by reforming all of the carbon in the oil with steam plus the hydrogen in the oil; the oil was defined to have the formula $CH_{1.33}O_{0.53}$, as described earlier. The current selling price of H_2 in industry is between $5.00/MM Btu and $15.00/MM Btu, depending on the size of the production facility.

For these calculations, the feedstock was considered pyrolysis oil rather than biomass, in order to take into account the cost of the pyrolysis process. The cost of the oil is $0.141/kg, as calculated in an NREL report by C. Gregoire, on producing pyrolysis oil from biomass for power generation. This study used a biomass cost of $2.50/MMBtu, which is equivalent to $42/dry ton. If 70% hydrogen recovery can be achieved, the selling price must be at least $7.50/MM Btu. If the selling price is $8.80/MM Btu, 60% of the H_2 that is available from reforming pyrolysis oil must be recovered to reclaim the cost of the feedstock. Again, these results do not include capital and operating expenses.

Figure 2 shows the combinations of H_2 selling price and feedstock cost that will result in a ratio greater than one. Hydrogen from pyrolysis oil has the potential to be economically feasible if costs fall within the shaded region. This graph assumes that 70% of the maximum stoichiometric H_2 will be recovered. The pyrolysis oil cost will depend heavily on the cost of the biomass; a regionalized system to produce oil for a central hydrogen facility could utilize waste biomass which would bring down the cost of the oil considerably.

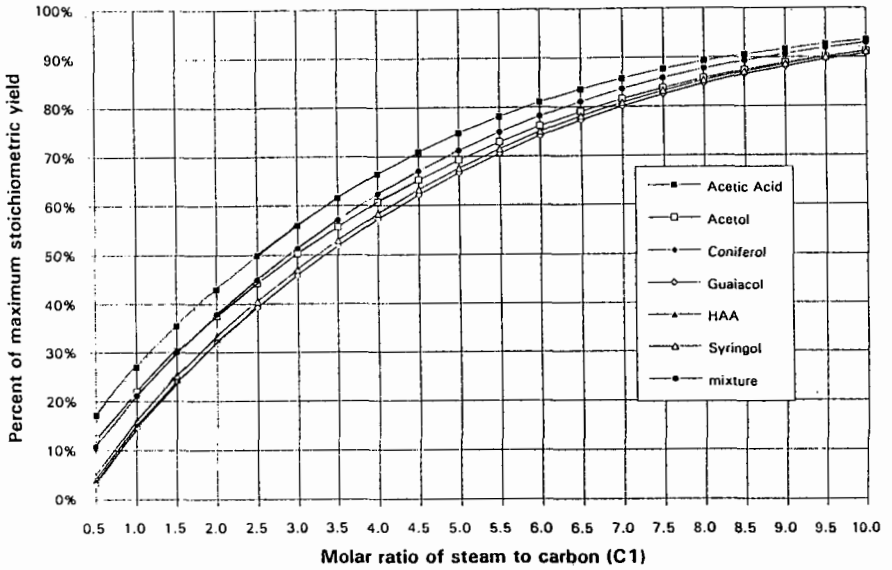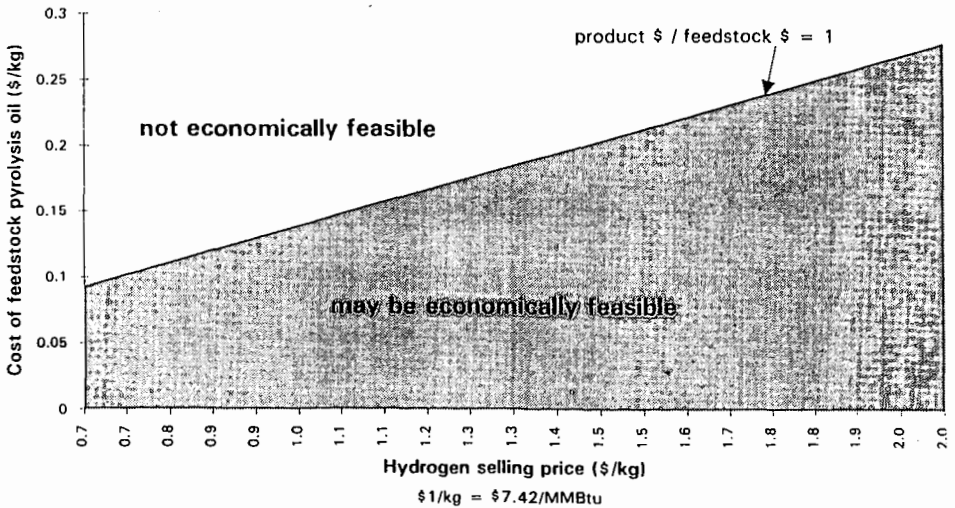# Figure 1: Approach to Maximum Stoichiometric Yield of Hydrogen at 500 °C

Figure 1: Approach to Maximum Stoichiometric Yield of Hydrogen at 500 °C

Legend: Acetic Acid, Acetol, Coniferol, Guaiacol, HAA, Syringol, mixture

X-axis: Molar ratio of steam to carbon (C1)
Y-axis: Percent of maximum stoichiometric yield

Figure 2: Limit on Potential Economic Feasibility of Hydrogen from Pyrolysis Oil at 70% Stoichiometric Maximum

Figure 2: Limit on Potential Economic Feasibility of Hydrogen from Pyrolysis Oil at 70% Stoichiometric Maximum

product $ / feedstock $ = 1

not economically feasible

may be economically feasible

X-axis: Hydrogen selling price ($/kg)
Y-axis: Cost of feedstock pyrolysis oil ($/kg)

$1/kg = $7.42/MMBtu

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