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HYDROGEN FROM BIOMASS VIA FAST PYROLYSIS

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ABSTRACT

The pyrolysis of biomass and steam reforming of the resultant oils is being studied as a strategy for producing hydrogen. New technologies for the rapid pyrolysis of biomass provide compact and efficient systems to transform biomass into vapors that are condensed to oils, with yields as high as 75%-80% by weight of the anhydrous biomass. A process of this nature is potentially cost competitive with conventional means of hydrogen production. Fast pyrolysis of biomass results in a pyrolytic oil that is a mixture of (a) carbohydrate-derived acids, aldehydes and polyols, (b) lignin-derived substituted phenolics, and (c) extractives-derived terpenoids and fatty acids. The conversion of this pyrolysis oil into H_2 and CO_2 is thermodynamically favored under appropriate steam reforming conditions.

Experimental work on this project has revolved around studying model compounds present within the oil. This approach was chosen to understand the chemistry of the operation so that catalysis and reforming conditions could be optimized early on. Microreactor screening results have proven that many of the compounds present in pyrolysis oils can be steam reformed using commercially available Ni-based catalysts. A mechanistic study of the catalysis has shown that the reforming process involves gas-phase thermal decomposition of the oxygenates followed by steam reforming of the intermediate compounds. Initial experiments have shown that coke formation on the catalyst is difficult to control even with careful choice of temperature profiles and steam-to-carbon ratios. Recycling the CO_2 from the PSA unit has been found to shift the equilibrium away from coke to produce CO and H_2 , thus offering the possibility of regenerating the catalyst in-situ.

The technical and economic feasibility of producing hydrogen from biomass by fast pyrolysis and steam reforming has been studied in parallel with the laboratory work. Because all necessary experimental data on the process have not been obtained, the economic assessment performed was preliminary. For many positive biomass feedstock costs, the selling price of hydrogen produced by reforming the entire biomass pyrolysis oil falls within the current market price of hydrogen. The economic position of this process depends on whether the pyrolysis oil can be produced in-house or must be purchased. If an adhesives coproduct can be made, the necessary hydrogen selling price is competitive with hydrogen produced from conventional processes and is lower than when no coproduct is produced. Because biomass pyrolysis oil is similar to petroleum crude oil in that many fuels and chemicals can be derived from it, further coproduct options will be studied according to current economic and market conditions. The coproduct option was not studied to economically justify producing hydrogen from a pyrolysis-based process, but is meant to be an example of the opportunities available from biomass pyrolysis oil once a system of coproducts is developed.

INTRODUCTION

The gasification of carbonaceous materials to yield syngas, followed by shift conversion to convert the CO into H₂ and CO₂, is a well established process. Currently, hydrogen is commercially produced by catalytically steam reforming hydrocarbons, particularly natural gas, liquefied petroleum gas, and naphthas. Recent advances in fast pyrolysis of biomass have prompted us to examine this route as an alternative to gasification and the conventional hydrogen production routes. The interest lies in converting residual or dedicated biomass to oil in several small pyrolysis units and transporting the resultant "biocrude" to a large centralized steam reformer to produce hydrogen.

Pyrolysis differs from gasification in that it is a thermal decomposition process as opposed to a partial oxidation process. Pyrolysis occurs at high temperatures in an inert atmosphere, and the resultant oil can be steam reformed to produce hydrogen. Fast pyrolysis has not yet been developed to the same stage of commercial demonstration as gasification, though several pilot plant units have been constructed and operated in recent years (Ensyn-Red Arrow, Union Fenosa). Pyrolysis is more complex than gasification because it generates a more diversified product and requires an external heat supply. However, it also has several important advantages. Potentially it can yield more hydrogen per unit of biomass than a gasification-based process, and fast pyrolysis is carried out at lower temperatures (450-550°C) than gasification. Further, because pyrolysis oils are easily transportable, the pyrolysis and catalytic reforming operations can be carried out independently at different locations to minimize feedstock costs, transportation, and hydrogen distribution. Pyrolysis can also be carried out at a high temperature (750-850°C), and if steam is added to the reaction chamber, most of the biomass is directly converted to gases containing a substantial amount of hydrogen. However, as in gasification, this approach also generates highly refractory polycyclic aromatic tars. Because of that, we favor a two-step approach with pyrolysis conditions optimized to generate oils free of polycyclic aromatic tars. The second step is the catalytic steam reforming of the oils to hydrogen.

The oil produced by fast pyrolysis of biomass is comprised of about 85 wt% oxygenated organic compounds and 15 wt% water dispersed in the organic medium (Elliott, 1988). The organic fraction is a mixture of acids, aldehydes, alcohols, ketones, furans, substituted phenolics, and oligomers derived from the carbohydrate and lignin fractions of the biomass. Very little ash and residual carbon (i.e., char) are present in the oil when the appropriate filtration technology is used. Fluid bed fast pyrolysis of poplar can result in a 76 wt% yield of oil (Piskorz *et al*, 1988; Radlein *et al*, 1991). Given that the organic fraction (~85 wt% of the oil) has an elemental composition of CH_{1.33}O_{0.53}, the theoretical maximum yield of hydrogen from pyrolysis oil is 12.6 wt% of the initial biomass. To address the technical feasibility of converting pyrolysis oil into H₂ and CO₂ via catalytic steam reforming, we have initiated a research project with the following objectives:

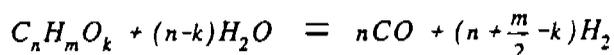
- Determine, using thermodynamic simulations, the conditions under which the components of the pyrolytic oils can be steam reformed to H₂ and CO₂
- Select suitable catalysts to convert the oxygen rich pyrolytic oil into H₂ and CO₂
- Assess, via bench scale experiments, the yields of H₂ (and CO₂) as a function of treatment severity, catalyst type and catalyst time-on-stream
- Develop a process flow diagram based on the results obtained and carry out economic forecasts as a function of feedstocks costs, plant configuration, and plant capacity.

In the first year of the project, FY 1994, we addressed the first two objectives (Chornet, *et al*, 1994). This report covers the work conducted in FY 1995 and is centered on the mechanistic aspects of the second objective and the results obtained in the newly constructed bench scale catalytic system. The fourth and fifth objectives are covered

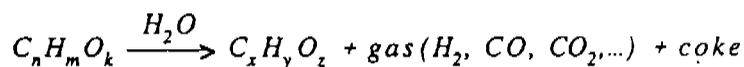
as part of a separate effort reported as a distinct paper (Mann, 1995, 1) and summarized here. Further detail on experimental efforts can be found in a paper by Chomet (1995).

The literature on steam reforming oxygenates is limited to that of simple alcohols (methanol and ethanol) and oxygenated aromatic compounds (cresols). The extensive literature on steam reforming methane and heavier hydrocarbon feedstocks suggests that pyrolysis oil, even though a complex mixture, can be steam reformed using known catalyst preparations. Little is known, however, about the optimal experimental conditions that will lead to long-term catalyst activity. To address these issues, we need a better understanding of mechanisms of both the thermal decomposition and catalytic steam reforming reactions shown below:

1. steam reforming:



2. thermal decomposition (or cracking):



Few of the primary pyrolysis products of biomass are thermally stable at the typical temperature of a reformer, and it is suspected that the catalytic reforming reactions (eq. 1) will be in competition with thermal decomposition reactions (eq. 2). Information on the thermal decomposition of model oxygenated compounds in the gas phase can be found in the literature (Evans and Milne, 1986; Evans and Milne, 1987; Furimsky, 1983; Rajadurai, 1994; Schraa et al, 1994; Suryan et al, 1989; Vuori, 1986).

EXPERIMENTAL WORK

We have performed experimental studies on steam reforming reactions of oxygen-containing model compounds present as major components in the pyrolysis oil. The reaction pathways and relative reactivity of these model compounds are being examined to determine whether a single catalyst formulation can reform both the complex and simple oxygenates present in pyrolysis oil while limiting undesirable side reactions that lower hydrogen yields. Three types of model compounds were examined. Ketones and aldehydes were represented by acetic acid, acetone, and hydroxyacetaldehyde. The phenolic series included phenol, anisole, *o*-cresol, resorcinol, 2,6-dimethylphenol, guaiacol, and syringol. The furan family of model compounds consisted of furan, 2-methylfuran, 2,5-dimethylfuran, 2-furfuraldehyde, furfuryl alcohol, 5-methylfurfural, and 5-hydroxymethylfurfural. In general, the lignin portion of the biomass yields more hydrogen on a weight or mole basis than the carbohydrate fraction (cellulose and hemicellulose). Therefore, we expect the oxygenated aromatics such as furans and phenolics to produce higher yields of hydrogen than anhydrosugars and other carbohydrate-derived products.

Because there are two undesirable products, CO and CH₄, the hydrogen yield obtained will be less than the stoichiometric maximum according to reactions 1 and 2. The steam reforming of methane is kinetically favored at higher temperatures. However, this condition also increases the production of CO, which will be converted to CO₂ and H₂ in a second water-gas shift reactor operating at low temperatures. The formation of coke may account for a decrease in hydrogen production as well. Some of the oxygenated products derived from the carbohydrate component of biomass, especially anhydrosugars, are known to dehydrate rapidly to form carbon.

Experiments have been carried out in a vertical, dual bed quartz reactor housed in a tubular furnace with four independently controlled temperature zones. A molecular beam mass spectrometer (MBMS) was used for real

time analysis of products. A series of model compounds, pyrolysis vapors and oils, and the major components of biomass (lignin, cellulose, and hemicellulose) were steam reformed with the UCI G-90C catalyst. Table 1 summarizes some of these results, and shows that complete conversion of all samples was achieved but that in a few cases, hydrogen yields were far from stoichiometric maximums. In another set of experiments, different commercially available catalysts were screened for their ability to reform model compounds. All catalysts performed well, with high conversions (>99%) and H₂ yields averaging 89.5% (±5.3%). There was no clear indication that one catalyst was better than the others within experiment error limits.

Table 1. Catalytic Steam Reforming of Model Compounds, Biomass, and Related Materials^a

Sample	M _{C1} HSV	Conversion ^b	H ₂ yield	CO ₂ yield
methanol	0.015	> 99.95%	95%	93%
acetic acid	0.0081	> 99.95%	86%	90%
HAA (20 wt% in H ₂ O)	0.0081	> 99.95%	96%	103%
phenol (20 wt% in MeOH)	0.013	> 99.95%	99%	98%
syringol (20 wt% in MeOH)	0.013	> 99.95%	100%	100%
ADP (41 wt% in MeOH) ^c	0.075	99.7%	69%	47%
xylan ^d	-0.03	> 99.95%	100%	93%
levoglucosan ^d	-0.03	> 99.95%	100%	87%
cellulose ^d	-0.03	> 99.95%	102%	98%
cellobiose (18 wt% in H ₂ O)	0.0014	> 99.95%	83%	85%
aspen ^d	-0.06	> 99.95%	62%	60%
lignin ^d	-0.06	> 99.95%	41%	35%

a Averaged results from triplicates. Reaction conditions were 600°C, τ=0.25s, S/C=10-13. Catalyst used: UCI G-90C.

b Limited by the detection capability of the MBMS instrument. Also see discussion in text.

c Steam-to-carbon ratio = 4.5.

d Samples pyrolyzed in batches of 5-10 mg at 600°C. Residence time before reaching the catalyst bed was about 0.5s.

The effects of different operating conditions on conversion, H₂ yield, and catalyst performance were studied using model compounds. Temperature has the most profound effect on steam reforming reactions. High conversions (>99.95%) were obtained for the three small molecules, methanol, acetic acid, and HAA at 421°C and above. However, the lignin-derived compound, ADP, was more difficult to reform, and temperatures above 600°C were required for complete conversion. At temperatures of 421°C, 500°C, and 600°C, conversions were 21%, 81%, and 99.7%, respectively. These results were compounded by catalyst deactivation as indicated by decreased hydrogen yields obtained when experiments were repeated using the same catalyst.

Within experimental error limits, varying the residence time from 0.1 to 0.4 s and increasing the steam-to-carbon ratio from 4.5 to 7.5 did not show significant effects on hydrogen yield at 600°C and M_{C1}HSV = 0.075 mol_{carbon}·mL_{catalyst}⁻¹·h⁻¹ (UCI G-90C catalyst). However, methane formation showed significant dependence on residence time and steam-to-carbon ratio. As the residence time increased from 0.1 to 0.4 s, a decrease in methane formation was observed with acetic acid and HAA, but both methanol and ADP/MeOH produced more methane. As expected, less steam also favored the formation of methane. At 700°C, there was no significant change in hydrogen yield when the steam-to-carbon ratio was increased from 4.5 to 7.5.

The thermal decomposition reactions of oxygen-containing model compounds were studied. Results suggest that both thermal decomposition and catalytic reforming reactions take place during steam reforming. Thermal decomposition of the oxygenates competes with the catalytic steam reforming reactions of both the starting material and its secondary cracking products in the bed. The thermal cracking reaction may be promoted by the reactor walls as well as the catalyst support and we found that only a few compounds are stable enough to reach the catalyst bed without thermal cracking. However, a highly active catalyst, such as the UCI G-90C, can effectively steam reform all compounds and secondary products into H₂ and CO₂. The remaining difficulties are how to effectively feed the pyrolysis oil into the reactor, and which catalyst will maintain high activity for extended periods of time; planned future experiments will address these issues.

In addition to experiments conducted in the microscale reactor, tests were also performed in an enhanced and scaled-up fixed bed steam reforming reactor. These experiments tested the extent of char formation and hydrogen yield as a function of operating conditions. Two compounds, acetic acid and a 40 syringol:60 methanol (w:w) mixture, were tested using catalyst UCI G-90C. Some of the results are shown in Table 2. Carbon was formed on the catalyst bed in all experiments, but the extent of deposition was strongly dependent on the temperature profile. Around 500°C, only 70% of the carbon in the feed was recovered in the gaseous products. Part of the char was entrained in the gas stream and collected with water in the condenser. The accumulation of char in the bed caused the pressure at the reactor entrance to increase continuously during the experiment. In spite of char formation, however, the catalyst did not lose any activity and the composition of the gas remained unchanged during the run. The char was reactive enough to be largely gasified by steam when the feed was interrupted. Increasing the temperature to 600°C at the bed exit improved gas phase carbon recovery to 80% of the feed, and although char formed at this temperature, it was not entrained in the gas. Char formation was minimal when the exit temperature was raised to 710°C, and a 98% carbon recovery and constant pressure drop along the catalyst bed were achieved throughout the 90 minute experiment.

Increasing the steam-to-carbon ratio to a value of 10 (runs 42 and 43) resulted in a higher carbon conversion and lower char formation. A further increase to 14.4 (run 44) did not improve the results and resulted in decreased catalytic activity. Because these three experiments were carried out using the same catalyst bed, this result suggests that syringol causes significant deactivation of the catalyst. This is consistent with the experience of steam reforming naphtha in which the aromatic content of the feed has to be low enough to ensure long term catalyst survival. Raising the catalyst temperature while maintaining a similar steam-to-carbon ratio to that of run 38 resulted in a better carbon conversion, however, an increase in pressure drop along the catalyst bed because of char accumulation was observed (run 46-a).

The accumulated char can be converted to CO by introducing CO₂ into the bed if the temperature is maintained above 800°C. After 90 minutes of operation (run 46-a), the feed of steam and syringol/methanol solution was interrupted and 750 sccm of CO₂ were fed to the reactor and the temperature maintained at 830°C in the bed. After 60 minutes, the char retained on the catalyst surface was completely gasified because no CO was detected in the outlet gas. When the syringol/methanol mixture was reformed after this gasification experiment, no loss of catalytic activity from the initial level was observed.

PROCESS CONVERSION EFFICIENCIES

Using an ASPEN Plus™ model of a biomass gasification and reforming process (Mann, 1995, 2), the amount of hydrogen that can be produced from biomass by fast pyrolysis and steam reforming was estimated. Two methods were used to estimate the efficiency of this process. The first method looks at the ratio of the amount of hydrogen produced to the stoichiometric maximum amount of hydrogen possible according to the water gas shift and steam reforming reactions. The second method calculates the ratio of the energy value of the hydrogen produced and export steam to the energy value of the biomass feed plus purchased electricity. The amount of

Table 2. Steam Reforming of Model Compounds Using a Commercial Reforming Catalyst (UCI G-90C):
Experimental Conditions, Carbon Balance and Hydrogen Yield

Compound	S/C molar		Space velocity ⁽¹⁾		Temp. (°C)			Carbon ⁽²⁾	H ₂ yield	mol of gas/100 mol of carbon feed				
	run#	ratio	M _{Cl} HSV	GHSV	T-4	T-5	T-6	balance (%)	(%)	H ₂	CO ₂	CO	CH ₄	C ₂ H ₄
Acetic acid	29	5.9	0.069	2710	476	487	511	73.6	60.8	121.6	60.5	9.2	3.9	0.06
	34	5.8	0.069	2721	497	498	520	68.2	57.3	114.7	56.3	9.5	2.3	0.06
	25	5.6	0.067	2614	507	535	599	80.1	64.7	129.5	59.9	17.2	2.9	-
	26	5.8	0.067	2614	505	533	594	80.8	65.5	131.0	61.0	17.0	2.8	-
	24	5.8	0.067	2606	504	547	661	83.9	68.5	137.0	59.0	23.6	1.3	-
	27	5.8	0.067	2627	508	547	658	87.3	70.5	140.9	60.9	24.9	1.5	-
	23	6.0	0.064	2509	510	560	708	88.3	70.9	141.7	59.3	32.4	0.5	-
	28	6.0	0.067	2632	510	558	706	88.6	70.9	141.8	58.1	29.9	0.6	-
	30	5.7	0.068	2646	548	610	709	91.9	72.0	144.0	58.6	32.8	0.6	-
	31	6.1	0.068	2646	555	615	708	94.8	74.8	149.6	59.8	34.4	0.7	-
	32	6.0	0.066	2602	608	667	710	97.9	75.6	151.2	58.3	38.9	0.7	-
	33	6.0	0.066	2602	617	661	709	97.9	74.0	148.1	56.7	42.5	0.9	-
	Syringol and methanol mixture 40:60 (w/w)	38	6.1	0.069	2688	609	670	708	94.7	74.6	194.4	52.3	40.3	2.1
42		10.0	0.058	2288	521	617	705	97.5	77.6	202.3	59.0	36.4	2.1	-
43		10.0	0.059	2313	519	626	703	99.7	79.5	207.4	62.4	35.3	2.0	-
44		14.4	0.059	2313	513	616	702	96.2	78.2	203.1	61.3	32.6	2.2	0.13
46-a		7.4	0.056	2205	667	755	829	98.5	75.9	197.1	49.3	49.1	0.1	-
46-b	6.9	0.056	2205	667	757	829	98.3	76.5	198.9	49.7	48.5	0.1	-	

⁽¹⁾ M_{Cl}HSV in (mol_{carbon}·mL_{catalyst}⁻¹·h⁻¹); GHSV: methane equivalent gas hourly space velocity in (h⁻¹).

⁽²⁾ Carbon recovered in the gas-phase products.

hydrogen produced when all of the pyrolysis oil is reformed is 30,415; 304,152; and 1,013,842 standard m³/day for 27 T/day, 272 T/day, and 907 T/day plants, respectively. Eighty percent less hydrogen is produced in the phenolic resin coproduct option. The stoichiometric efficiency and energy conversion efficiency of the process to reform all of the pyrolysis oil obtained from biomass are 55.3% and 86.5%, respectively. For the coproduct option, these efficiencies are 39.4% and 62.8%. It should be noted that the energy conversion efficiency does not take into account any of the energy savings that would result in producing phenolic resins from this process instead of the conventional technology.

ECONOMIC ANALYSIS

The technical and economic feasibility of producing hydrogen from biomass by fast pyrolysis and steam reforming has been studied in parallel with laboratory efforts. Because all necessary experimental data on the process have not been obtained, the economic assessment performed was preliminary. Based on feedstock availability estimates, three plant sizes were studied: 27 T/day, 272 T/day, and 907 T/day. The potential profitability of the process being studied can be assessed by comparing economic results to hydrogen market selling prices, currently between \$5/GJ and \$15/GJ. Results indicate that hydrogen can be produced to compete with current hydrogen production methods on the large and medium scale. The necessary hydrogen selling price is highly dependent upon the biomass feedstock cost, and unless very low-cost biomass can be obtained, some of the scenarios will not produce hydrogen at competitive prices.

Possible sources of error in this analysis are in equipment cost estimation, feedstock and product market predictions, and invalid economic assumptions. In particular, economic estimates for producing hydrogen from pyrolysis oil contain a significant amount of error because adequate experimental data are not available. Furthermore, fast pyrolysis is not fully understood, and the chemistry and yields that can be obtained on a consistent basis are unknown. The total error can be reduced by looking at ranges of profitability, such as the range of hydrogen selling price versus a range of biomass feedstock costs. As more information on the development of biomass-based technologies becomes available, these analyses can be modified to give a more representative process cost. The material and energy balance results from the ASPEN Plus™ simulation were used to determine the size and corresponding cost of major pieces of equipment for the gasification-based process. The estimated capital cost was then scaled to the appropriate size for the pyrolysis-based process.

Operating costs for the processes studied include feedstock costs, electricity to run the compressors (\$0.05/kWh), water for steam generation and cooling (\$330/m³), and labor. The feedstock cost was assumed to be the cost of the pyrolysis oil (Gregoire 1992). Economic analyses were conducted for two cases: first, the pyrolysis oil was assumed to be purchased, and thus includes a rate of return for the producer; second, the pyrolysis oil was assumed to be produced in-house and thus the cost reflects only that of production. In this make-versus-buy assessment, the production scenario yields the most profitable results. However, the alternative concept is more likely for two reasons. Once developed, a regionalized system in which the pyrolysis oil is produced in several small units will probably involve multiple oil producers. Second, as more feasible coproduct options are developed, only a portion of the oil will be purchased and used for hydrogen production.

The revenue from steam produced for export is taken as an operating cost credit. The assumption that the steam will be able to be sold is probably valid for the medium and large plants as they will most likely be located in more industrialized centers to take advantage of other infrastructure. However, it may be difficult to sell the steam produced by the small plant, because this size represents small refueling stations located near the demand

for hydrogen. In the analysis of the coproduct option, the revenue from selling the P/N fraction is also taken as a credit. To obtain a conservative result, the selling price of the adhesives coproduct was assumed to be 75% of the value of phenol.

The capital and operating costs for each of the scenarios studied are shown in Table 3. These costs were calculated using a feedstock cost of \$16.50/T, a representative cost of waste biomass, for the small and medium size plants and \$46.30/T, the expected cost of biomass from a DFSS, for the large plant. For the medium size plant, operating costs would increase significantly if biomass could only be obtained from a DFSS.

Table 3: Capital (MM\$) and Operating Costs (MM\$/year) for the Pyrolysis-Based Process

Plant size	Reforming Entire Oil			Coproduct Option		
	sm	med	lg	sm	med	lg
Operating costs if oil is:						
produced in-house	0.46	3.31	18.16	0.48	3.49	18.76
purchased	1.02	8.87	36.56	1.04	9.05	37.18
Fixed	0.16	0.27	0.33	0.16	0.27	0.33
Variable	0.10	1.01	3.37	0.10	1.00	3.32
Byproduct credit (steam) *	-0.10	-0.97	-3.24	-0.08	-0.78	-2.59
Feed if oil is:						
produced in-house	0.30	3.00	17.7	0.30	3.00	17.70
purchased	0.86	8.56	36.1	0.86	8.56	36.12
Capital Costs**	3.07	20.2	58.7	2.89	18.2	52.6

* Revenue from adhesives byproduct is not taken as a credit here so that level comparisons can be made.

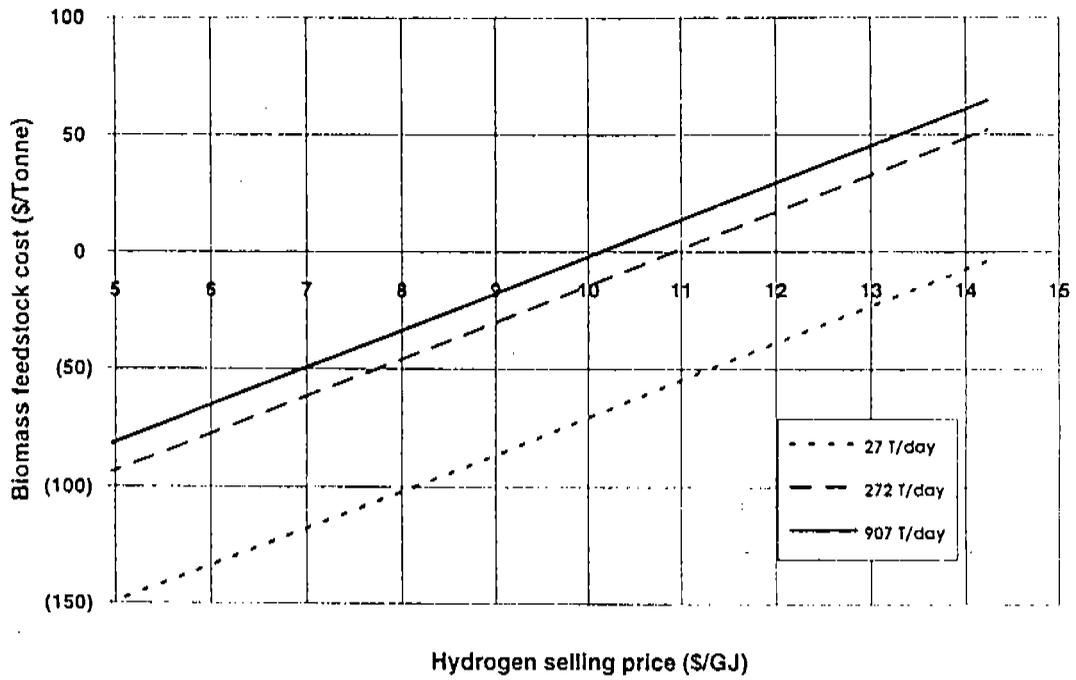
** Reforming operation only; pyrolysis capital costs are included in the cost of the feed.

The economic feasibility of producing hydrogen by steam reforming oil from fast pyrolysis was studied using the DCFROR method. This method calculates the internal rate of return (IRR) that will be earned on the initial capital investment over the life of the project. Given this rate and a feedstock cost, the necessary selling price of the product can be calculated. Often, the IRR is specified as the minimum acceptable rate for an investor to finance a project; therefore, the perceived risk of the project can be incorporated into the IRR. Because the process of producing hydrogen from biomass currently carries higher risks than conventional hydrogen-generating processes, the IRR specified in this study was 15%, while the going rate for conventional processes is between 9% and 12%. All costs and prices are expressed as January 1995 dollars and a 20-year plant life is assumed.

The results of the DCFROR analysis are shown in Figures 1 through 4. These figures give the biomass feedstock price that is necessary to compete in the current hydrogen market. A 37% tax rate and a 15% IRR were used to calculate selling prices. With the market value of hydrogen between \$5/GJ and \$15/GJ, these figures show that hydrogen can be produced to compete with current hydrogen production methods on the large and medium scale. The necessary hydrogen selling price is highly dependent upon the biomass feedstock cost, and unless very low-cost biomass can be obtained, some of the scenarios will not produce hydrogen at competitive prices. This is particularly true on the small scale. Many of the processes studied, however, yield competitive hydrogen prices at reasonable and even high biomass costs.

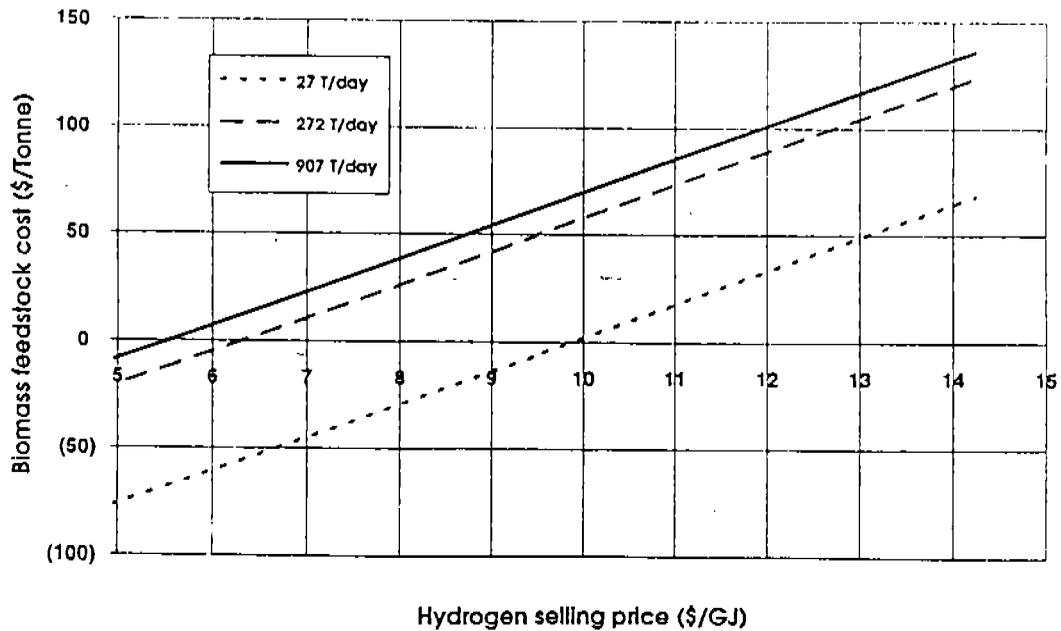
Figure 1 represents the case of reforming the entire pyrolysis oil (no coproducts) where the feedstock cost was assumed to be oil purchased from outside suppliers; Figure 2 assumes that the oil was produced in-house. Figures 3 and 4 show the necessary hydrogen selling price for the adhesives coproduct option for pyrolysis oil

**Figure 1: Selling Price of Hydrogen From Steam Reforming
Entire Biomass Pyrolysis Oil, After Tax, 15% IRR**



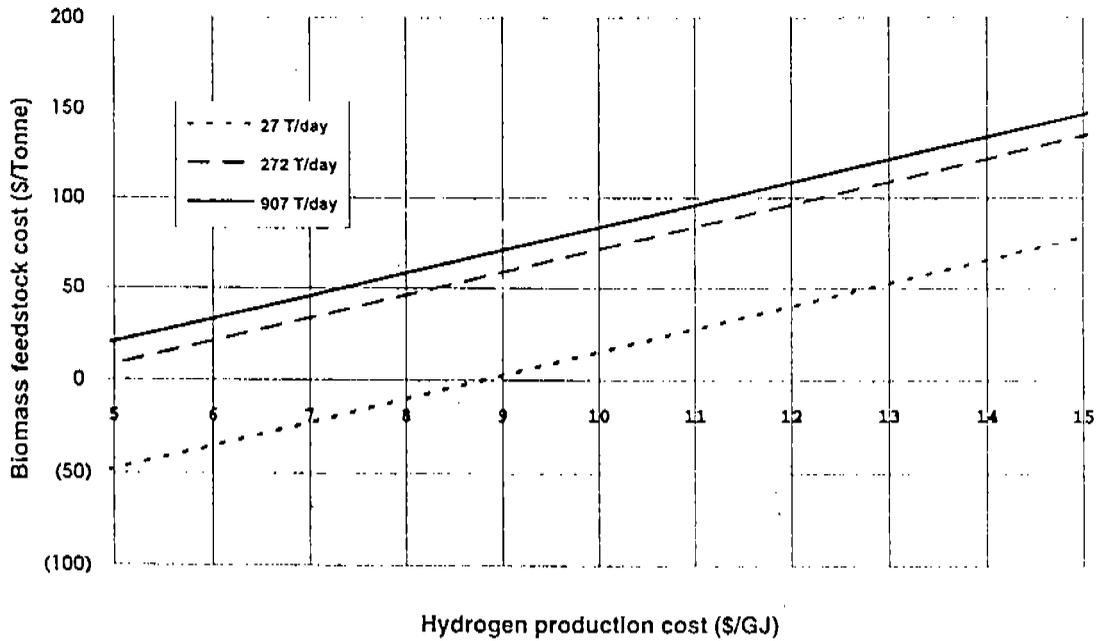
Feedstock is considered to be purchased

**Figure 2: Selling Price of Hydrogen From Steam Reforming
Entire Biomass Pyrolysis Oil, After Tax, 15% IRR**



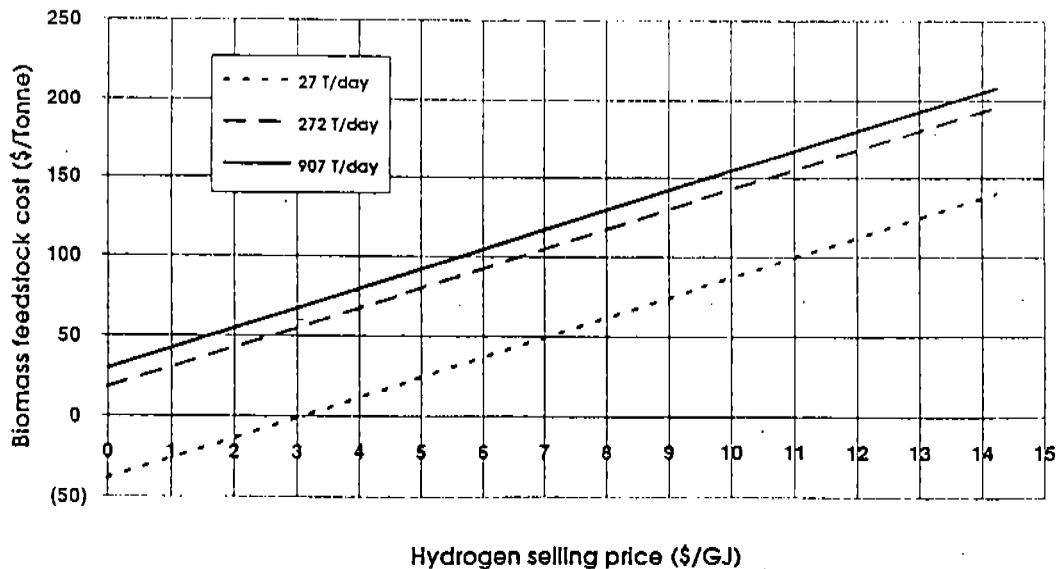
Feedstock is considered to be produced in-house

Figure 3: Production Cost of Hydrogen From Steam Reforming Biomass Pyrolysis Oil and Selling P/N Fraction, After Tax, 15% IRR



Feedstock is considered to be purchased

Figure 4: Selling Price of Hydrogen from Steam Reforming Biomass Pyrolysis Oil and Selling P/N Fraction, After Tax, 15% IRR



Feedstock is considered to be produced in-house

that is purchased and produced, respectively. As expected, the coproduct option is more economically feasible than reforming all of the pyrolysis oil to produce only hydrogen. Also as expected, the necessary hydrogen selling price is lower when pyrolysis oil is produced rather than purchased. However, this may not be feasible once a system to produce various chemicals and fuels from biomass pyrolysis oil is developed. Hydrogen and an adhesives coproduct can be produced at economically competitive prices for all positive feedstock costs for the medium and small plants whether the oil is purchased (Figure 3) or produced (Figure 4). At positive feedstock costs, the hydrogen produced on the small scale can be sold for at least \$9/GJ if the pyrolysis oil is purchased, and at least \$3/GJ if the pyrolysis oil is produced in-house.

The most economic size for the processes studied depends upon the feedstock cost. If the medium size plant can be supplied with waste biomass at a cheaper price (i.e., \$16.50/T) than the biomass supplied by a DFSS (expected to be \$46.30/T), the necessary hydrogen selling price from the medium size plant is lower than that from the large plant. However, if the medium and large plants must both use biomass from a DFSS, the larger plant is more economically feasible. The medium size plant is more economical than the small plant if biomass at the same feedstock cost is used in each. Figures 1 through 4 also show that there is a larger economy of scale realized in going from the small to the medium size plant than in going from the medium to the large size plant.

CONCLUSIONS

The added flexibility of pyrolysis offers many opportunities for pyrolysis-based processes to be viable options for renewable hydrogen production. It can be designed as a regionalized system of pyrolysis units feeding one centralized reformer or as a combined operation. Additionally, the most economically feasible combination of coproducts can be used to increase the likelihood of commercialization. Such operations are expected to be similar to current petroleum refineries in that they would produce a slate of chemicals and fuels.

Although not complete, the experimental work performed to date has provided new insight into hydrogen production via fast pyrolysis and catalytic steam reforming. Many of the compounds present in pyrolysis oil can be steam reformed using commercially available Ni-based catalysts. Under the reaction conditions that have been tested, complete conversion of many of the model compounds has been achieved. However, hydrogen yields for some of the compounds were not exceptionally high, partly because of problems with sample feeding and the result of competing reactions. The initial experiments on the bench scale fixed bed tubular reactor suggest that controlling coke formation is a key aspect of the catalytic steam reforming of oxygenates. The coke formation is difficult to prevent even by careful choice of the temperature profiles and steam-to-carbon ratio. However, we have proven that CO₂ available from the pressure swing adsorption operation can effectively regenerate the catalyst.

Depending on biomass feedstock costs, the necessary selling price for hydrogen produced by steam reforming biomass pyrolysis oil falls within the current market values (\$5 - \$15/GJ) for many of the cost scenarios studied. As expected, the most feasible process is the hydrogen/adhesives coproduct option. Further coproduct options will be studied to take advantage of the diverse product opportunities of pyrolysis oil. Of the three plant sizes studied, the 272 T/day plant is the most economic if waste biomass at a low price can be obtained. If biomass from a DFSS must be used, the 907 T/day plant is more economic. However, if the small plant is the only size for which cheaper waste biomass can be obtained, local refueling stations, similar to current gasoline stations, would be feasible. It should be noted that this analysis contains a fairly high degree of process and market uncertainty which will be reduced as further data become available.

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