

BIOMASS-TO-HYDROGEN VIA FAST PYROLYSIS AND CATALYTIC STEAM REFORMING

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Abstract

Pyrolysis of lignocellulosic biomass and reforming the pyrolytic oils is being studied as a strategy for producing hydrogen. Novel technologies for the rapid pyrolysis of biomass have been developed in the past decade. They provide compact and efficient systems to transform biomass into vapors that are condensed to oils, with yields as high as 75-80 wt.% of the anhydrous biomass. This "bio-oil" is a mixture of aldehydes, alcohols, acids, oligomers from the constitutive carbohydrates and lignin, and some water derived from the dehydration reactions. Hydrogen can be produced by reforming the bio-oil or its fractions with steam. A process of this nature has the potential to be cost competitive with conventional means of producing hydrogen.

The concept of hydrogen from biomass offers significant opportunities for novel research and development. Using a renewable resource feedstock is an alternative to conventionally producing hydrogen from petroleum and natural gas. As a consequence, the environmental benefit of zero net carbon dioxide emissions approaches a pollution-free energy system. An additional benefit is that a regionalized system of hydrogen production can be envisioned using this technology. Small and medium-sized pyrolysis units (<500 Mg/day) could provide the bio-oil to a centralized reforming unit to be catalytically converted to H_2 and CO_2 . Therefore, storage and transportation problems associated with hydrogen production become less important in the economics of the process. The reforming facility can be designed to handle alternate feedstocks, such as natural gas and naphtha, if necessary.

Thermodynamic modeling of the major constituents of the bio-oil has shown that reforming is possible within a wide range of temperatures and steam-to-carbon ratios. Existing catalytic data on the reforming of oxygenates have been studied to guide catalyst selection. Tests performed on a microreactor interfaced with a molecular beam mass spectrometer showed that, by proper selection of the process variables: temperature, steam-to-carbon ratio, gas hourly space velocity, and contact time, almost total conversion of carbon in the feed to CO and CO_2 could be obtained. These tests also provided possible reaction mechanisms where thermal cracking competes with catalytic processes. Bench-scale, fixed bed reactor tests demonstrated high hydrogen yields from model compounds and carbohydrate-derived pyrolysis oil fractions. Reforming bio-oil or its fractions required proper dispersion of the liquid to avoid vapor-phase carbonization of the feed in the inlet to the reactor. A special spraying nozzle injector was designed and successfully tested with an aqueous fraction of bio-oil.

A process diagram for the pyrolysis and reforming operations is presented and discussed, along with initial production cost estimates. A window of opportunity clearly exists if the bio-oil is first refined to yield valuable oxygenates so that only a residual fraction is used for hydrogen production.

1 Introduction

Steam reforming of hydrocarbons, partial oxidation of heavy oil residues, and gasification of solid fuels to yield syngas (a mixture of H_2 and CO), followed by shift conversion to produce H_2 and CO_2 , are well established processes. Renewable lignocellulosic biomass has been considered as a potential feedstock for gasification to produce syngas. However, economics of current processes favor the use of hydrocarbons (natural gas, C_2-C_5 , and naphtha) and inexpensive coal. An alternative approach to the production of H_2 from biomass is the catalytic steam reforming of liquid streams generated from various biomass conversion processes such as pyrolysis, hydrolysis, and solvolysis that also yield valuable oxygenate products. This latter approach has potential to be cost competitive with the current commercial processes for hydrogen production.

The proposed technology for producing hydrogen would be comprised of two stages: fast pyrolysis of biomass to generate bio-oil and catalytic steam reforming of the oil or its fractions. Recent developments in pyrolysis processes allow for conversion of 75% of biomass into a liquid product (bio-oil). This bio-oil is made of oxygenated organic compounds [1,2]: acids, alcohols, aldehydes, ketones, furans, substituted phenolics and complex oxygenates derived from biomass carbohydrates and lignin. Very little ash and char are present in the bio-oil when appropriate filtration technology is used in the pyrolysis process [3].

An efficient steam reforming of the oil using no external heat can result in a hydrogen yield of 12.6 wt.% of dry biomass. This yield is similar to that from the biomass gasification/water-gas shift process (11.5 wt.%). The yield of hydrogen for the stoichiometric reaction between wood (poplar) and steam using externally supplied heat is 17.2 wt.%. These values were calculated using current yields for fast pyrolysis [4-6] and gasification [7] processes. An advantage of the pyrolysis process is that it is less severe and does not require an oxygen supply.

Our current objectives for the project are:

- To establish the proof of concept: can biomass-derived pyrolysis compounds be steam reformed?
- To determine H_2 yields from (a) model compounds and (b) pyrolysis oils or their fractions at reasonable severities and catalyst productivity.
- To identify technological hurdles and address them systematically to provide workable solutions.
- To develop a process flow diagram based on the data obtained during the research project.
- To assess the economics: under which conditions is our approach economically viable?

2 Fast pyrolysis: bio-oil yields and composition

Several fast pyrolysis technologies, at the pilot and demonstration levels, have been reported to give high yields of bio-oil, including fluid beds [4-6], transport reactors [8,9], and cyclonic reactors [10,11]. The common feature of all these technologies is rapid heating of the biomass particles at temperatures comprised between 450 and 550°C, and short residence time of the volatile products in the reaction chamber (a fraction of a second to a few seconds). For example, a 76 wt.% yield of bio-oil can be obtained from fluid bed fast pyrolysis of dry poplar ($\text{CH}_{1.47}\text{O}_{0.67}$) [4]. The organic fraction of the bio-oil represents 85 wt.% and its elemental composition is $\text{CH}_{1.33}\text{O}_{0.53}$. About 15 wt.% of the bio-oil is water from the dehydration reactions. Additional water will result from the moisture in the feedstock. The water is well dispersed within the organic fraction of the bio-oil due to the hydrophilicity of the carbohydrate-derived compounds that constitute the major fraction of the bio-oil.

Reliable values of oil, water, char and gas yields are limited in the literature; most published work contains unclosed and/or unreported material balances. The composition of bio-oil has been quantitatively reported from fluidized bed studies conducted at the University of Waterloo [4-6]. It is shown for several feedstocks in Table 1, together with the composition of the bio-oil derived from the cyclonic (vortex type) reactor located at NREL [11].

Variations in the composition of pyrolysis oil as shown in Table 1, should be expected as a function of raw material, pyrolysis treatment severity (temperature, residence time, and heating rate profiles) and using or not using catalysts during the pyrolytic step. However, the information presented in Table 1 indicates that the bio-oil is essentially a mixture of two acids (acetic and formic), numerous aldehydes and alcohols plus a significant fraction of lignin (denoted as pyrolytic lignin, a low to medium molecular weight material). The unidentified compounds range from a large number of carbohydrate-derived components [12] to monomeric lignin-derived products having alcohol characteristics [1].

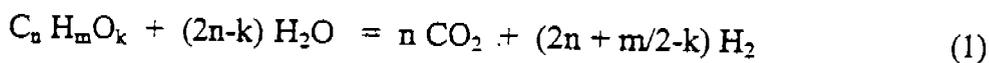
3 Thermodynamics

Thermodynamic simulations of reforming model oil components as well as bio-oil have been performed in order to determine equilibrium yields of hydrogen. These simulations were performed on ASPEN Plus using model compounds representative of the bio-oil. The results are listed in Table 2, together with stoichiometric yields (moles and wt %). In general, the lignin-derived phenolics have a higher potential for producing hydrogen than the products from carbohydrates. This is because, for an oxygenated compound with a chemical formula of $\text{C}_n\text{H}_m\text{O}_k$, the stoichiometric yield of hydrogen is $2+m/2n-k/n$ moles per mole of carbon in the feed (eq. 1), and k/n is usually in the fractions for the aromatic phenolics from lignin, while k/n is close to 1 for most carbohydrate-derived products such as sugars.

Table 1. Pyrolytic oil compositions from different feedstocks/reactors

Process	Fluidized bed (UW) ^c			Vortex (NREL) ^d
	poplar	maple	spruce	oak
Feedstock				
Temperature, °C	504	508	500	650
Product	Yield (wt % of m.f. wood)			
acetic acid	5.4	5.8	3.9	5.0
formic acid	3.1	6.4	7.2	3.3
hydroxyacetaldehyde	10.0	7.6	7.7	4.3
glyoxal	2.2	1.8	2.5	3.0
methylglyoxal		0.65		
formaldehyde		1.2		2.2
acetol	1.4	1.2	1.2	1.8
ethylene glycol	1.1	0.6	0.9	
levoglucosan	3.0	2.8	4.0	3.8
1,6-anhydroglucofuranose	2.4			
fructose	1.3	1.5	2.3	
xylose				0.9
glucose	0.4	0.6	1.0	
cellobiosan	1.3	1.6	2.5	
oligosaccharides	0.7			
pyrolytic lignin ^b	16.2	20.9	20.6	24.9
unidentified	11.9	17.1	12.9	5.8
total oil ^a	65.8	67.9	66.5	55.3
water ^a	12.2	9.8	11.6	10.4
char	7.7	13.7	12.2	12.4
gas	10.8	9.8	7.8	12.2
mass closure	96.5	101.2	97.7	90.3

^a Oil + water = bio-oil. ^b Material precipitated by addition of water. ^c From [6]. ^d Private communication.



Thermodynamic calculations indicate that the equilibrium yield of hydrogen (as percentage of the stoichiometric yield) under typical steam reforming conditions (750°C and S/C=5) does not vary much for these oxygenates, averaging around 85%. The small variation in this yield reflects the true ratio (5+k/n) of steam-to-carbon in the catalytic reformer: external steam supplied (S/C=5) plus that derived from the feed (S/C=k/n). A further water-gas shift (WGS) operation to convert all the CO formed in the reformer would improve the overall yield to about 97%. If coking could

Table 2. Hydrogen yields from steam reforming

Sample	Formula	Stoichiometric H ₂ Yield		Equilibrium H ₂ Yield	
		moles ^a	% (by wt.) ^b	% (of st.) ^c	(+ WGS) ^{c,d}
methane	CH ₄	4.00	50.3%	85.6%	95.0%
methanol	CH ₄ O	3.00	18.9%	87.1%	96.8%
acetone	C ₃ H ₆ O	2.67	27.8%	85.2%	96.2%
ADP ^e	C ₁₁ H ₁₄ O ₃	2.36	27.0%	84.7%	96.4%
guaiacol	C ₇ H ₈ O ₂	2.29	26.0%	84.6%	96.5%
syringol	C ₈ H ₁₀ O ₃	2.25	23.5%	84.8%	96.6%
lignin	C ₇ H ₉ O ₃	2.21	22.1%	84.9%	96.7%
furfuryl alcohol	C ₅ H ₆ O ₂	2.20	22.6%	84.9%	96.7%
poplar oil ^e	CH _{1.33} O _{0.53}	2.14	19.7%	85.2%	96.9%
poplar	CH _{1.47} O _{0.47}	2.07	17.2%	85.5%	97.1%
furfural	C ₅ H ₄ O ₂	2.00	21.0%	84.6%	96.9%
5-HMF ^e	C ₆ H ₆ O ₃	2.00	19.2%	84.9%	97.0%
xylan	C ₅ H ₈ O ₄	2.00	15.3%	85.8%	97.3%
cellulose/levoglucosan	(C ₆ H ₁₀ O ₅) _n	2.00	14.9%	85.8%	97.3%
HAc, HAA ^e	C ₂ H ₄ O ₂	2.00	13.4%	86.3%	97.5%
formic acid	CH ₂ O ₂	1.00	4.4%	87.7%	98.9%

^a Moles of H₂ produced per mole of carbon in the reactant being reformed.

^b Amount of H₂ formed divided by the sample molecular weight.

^c Equilibrium moles of H₂ predicted at 750°C and S/C=5 divided by the stoichiometric yield.

^d With additional moles of CO present under 750°C and S/C=5 to be shifted in a downstream water-gas shift (WGS) reactor.

^e ADP: 4-Allyl-2,6-dimethoxyphenol; 5-HMF: 5-Hydroxymethylfurfural; HAc: acetic acid; HAA: hydroxyacetaldehyde. Poplar oil is on water-free basis.

Table 3. H₂ yields from steam reforming of poplar oil (CH_{1.33}O_{0.53})

Temperature (°C)	Steam-to-carbon ratio (S/C)	% of stoi. H ₂ yield at equilibrium (reforming only)
500	5	57.0%
500	10	76.3%
600	5	76.9%
600	10	90.4%
700	5	84.6%
700	10	92.8%
800	5	84.7%
800	10	91.7%
900	5	82.8%
900	10	89.9%

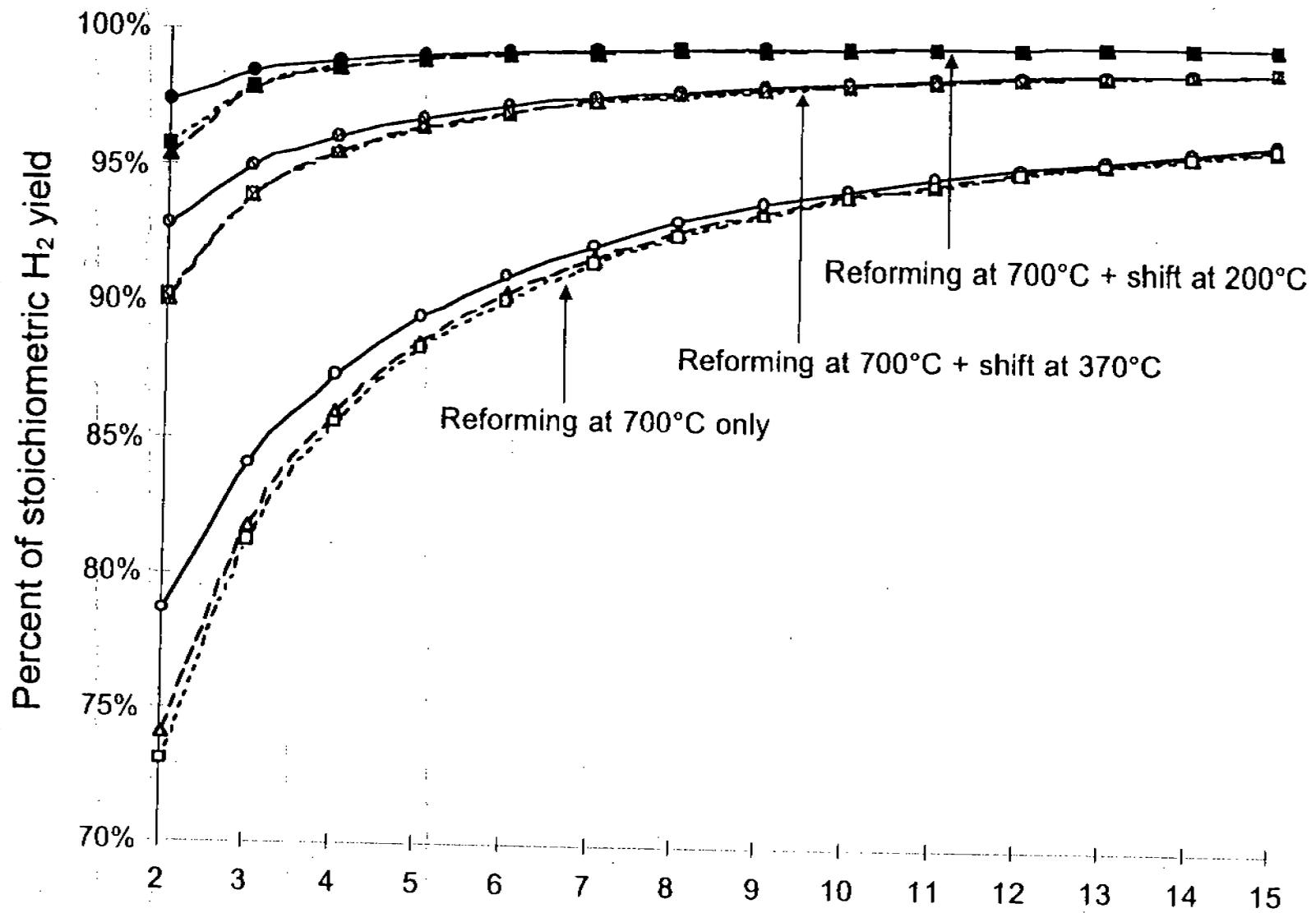


Figure 1. Thermodynamic equilibrium analysis showing the effect of steam-to-carbon ratio on the yield of hydrogen at selected reformation and shift conversion conditions. Feed: syringole (○), HAA (Δ), and furfural (□).

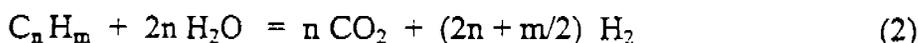
be avoided, the conversion of oxygenates to hydrogen would be almost quantitative through the combination of reforming and water-gas shift.

Figure 1 shows the approach to maximum stoichiometric yields of hydrogen as a function of S/C at a temperature of 700°C, which is in the lower end of temperatures used in current hydrocarbon reformers. The beneficial yield effect of the shift reaction is clearly established. The equilibrium yields of hydrogen from a typical bio-oil (of poplar) [4] as a function of temperature and steam-to-carbon ratios (S/C) were also calculated (Table 3). Results suggest that a wide range of combinations of the two key operating variables can be chosen to approach stoichiometric yields. Temperatures higher than 700°C and S/C greater than 5 are recommended for high efficiency conversion.

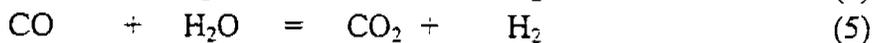
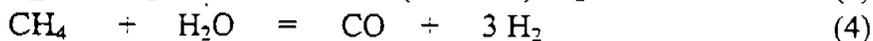
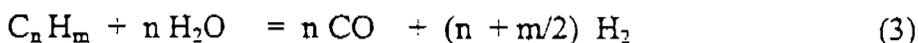
4 Catalytic reforming of oxygenates

4.1 Literature review

Processes of steam reforming C1-C5 hydrocarbons, naphtha, gas oils, and simple aromatics are well known and commercially practiced. When the objective is to maximize the production of H₂, the stoichiometry describing the overall process is:



In a hydrocarbon reformer, the following reactions take place concurrently:



At normal operating conditions, reforming of higher hydrocarbons (eq. 3) is irreversible [13], whereas the methane reforming reaction (eq. 4) and the shift conversion reaction (eq. 5) approach equilibrium. A large molar ratio of steam to hydrocarbon will ensure that the equilibrium for reactions (4) and (5) is shifted towards H₂ production.

The main problem in the steam reforming of hydrocarbons is carbon formation. Three types of carbon may be formed: whiskers, encapsulating deposits ("polymers"), and pyrolytic carbon [14]. The carbon formation is related to the kinetics, and hence the selectivity, of the catalyst. Significant improvements have been made in controlling coke formation by promoting the classical Ni-alumina or Ni-silica/alumina formulations with Ca and/or K and by the use of magnesia as magnesium-aluminum spinel [15].

The reforming operation requires relatively high steam-to-carbon molar ratios ($S/C = 3.5 - 5.0$ for methane), adequate temperature profiles in the tubular reactor (low inlet temperature increased along the tube length to a maximum of $750-775^{\circ}\text{C}$ due to the structural constraints of the Ni-Cr alloys used), and a Ni-based catalyst (20-30 wt.% as NiO) on a refractory support having appropriate steam adsorption characteristics. The reforming operation is not very sensitive to pressure which is essentially dictated by the applications of the product H_2 [16]. Space velocities ($G_{C_1}\text{HSV}$, as volume of C_1 equivalent/h/volume of catalyst) used in tubular reformers are typically in the order of $1500-2000 \text{ h}^{-1}$.

Aznar et al [17] have demonstrated that steam reforming syngas obtained from the gasification of lignocellulosics is possible using commercially available Ni-based catalysts (Topsoe R-67 and RKS-1). Rapid deactivation of the catalyst takes place after a few hours only. Tars produced during gasification contain a high percentage of polycyclic aromatics, while pyrolysis oil is essentially a mixture of carbohydrate-derived fragments and lignin-derived phenolics [1].

Literature on the steam reforming of oxygenates falls within two categories: (a) reforming simple alcohols, such as methanol and ethanol; and (b) reforming oxygenated aromatics, i.e. cresols. A detailed review on this subject has been given elsewhere [18]. The steam reforming of methanol is a special case and a large body of information has been accumulated [19]. A variety of catalysts are capable of carrying out the conversion at low temperatures and the product slate is markedly affected by the type of catalyst and the experimental conditions used. A different mechanism intermediated by methyl formate was initially proposed by Takahashi et al [20] and based on the formation of methylformate ester on the catalyst surface between two adsorbed species, H_3CO and HCO . The ester is hydrolyzed to methanol and formic acid. The latter decomposes directly to CO_2 and H_2 with 100% selectivity, i.e. no CO is formed. Ethanol reforming has also been studied to produce acetic acid [21] and to hydrogen by Garcia and Laborde [22]. Steam reforming of oxygenated aromatics has been directed towards the dealkylation of cresol.

When considering the bio-oil composition shown in Table 1, it is clear that challenges in catalytic steam reforming will be linked to the ability to handle both the "pyrolytic lignin" fraction and the carbohydrate-derived fraction: acetic acid, aldehydes, sugars and anhydrosugars, and oligomers. It is likely that the oligomeric fragments, either lignin- or carbohydrate-derived, once condensed as bio-oil, cannot be revolatilized without significant char formation. Thus, our strategy will be either (a) to separate the "pyrolytic lignin" (which has a potential market of its own as a phenolics substitute for the production of adhesives) from the condensed bio-oil and steam reform the aqueous fraction which, while still containing some substituted, but monomeric phenolics, will predominantly be constituted of the carbohydrate-derived components; (b) to carry out a fractional condensation of the pyrolytic vapors to separate the oligomers and thus directly recover a "light" fraction comprised essentially of mixed monomers; or (c) try to reform the entire uncondensed vapors by coupling the reformer to the pyrolysis unit.

Given the chemical diversity of the bio-oil aqueous fraction, and according to the literature reviewed, Ni-based catalysts operating in the 700-800°C range ought to be able to carry out the steam reforming conversion. An appropriate temperature profile through the reactor will have to be developed experimentally to carefully control coke formation.

4.2 Rapid screening and mechanistic studies

A series of model oxygen-containing compounds, biomass and its main components (cellulose, xylan, and lignin), and bio-oil and its various fractions were screened under identical conditions using a commercial catalyst, G-90C, from United Catalyst Inc. (UCI). We also tested a number of research and commercial steam reforming catalysts and a WGS catalyst and determined H₂ yields using four model compounds (methanol, acetic acid (HAc), an aqueous solution of hydroxyacetaldehyde (HAA), and a methanol solution of 4-allyl-2,6-dimethoxyphenol (ADP)) under the same operating conditions. Methanol steam reforming was used as a standard test for checking the performance of the system as well as catalyst deactivation.

These experiments were performed in a vertical dual-bed microreactor coupled to a molecular-beam mass spectrometer (MBMS) [23,24]. This system has the advantage of simultaneously detecting, unconverted reactants, intermediates and products at the exit of the microreactor by rapidly sampling through a supersonic, free-jet expansion nozzle. This expansion cools the reaction products and forms a molecular beam that is ionized and analyzed by a quadrupole mass spectrometer. The microreactor was housed in a tubular furnace with four independently controlled temperature zones. The dual bed configuration of this reactor enabled us to study either the differences between thermolysis and catalysis or to compare the performances of two catalyst under the same temperature conditions. Mass spectra in the m/z range of 1-350 were obtained for pyrolysis and catalysis products with the MBMS operated under 25 eV EI ionization conditions. The detection limit of the MBMS corresponded to conversions of approximately 99.95% for most of the samples, i.e., from the sample signal without catalyst at more than 1.0×10^6 counts/s (cps) to less than the instrument lower limit of 500 cps (noise = ± 250 cps) with catalyst. Among the most important parameters for steam reforming are catalyst bed temperature(s), molar steam-to-carbon ratio (S/C), gas hourly space velocity (G_{C_1} HSV, as defined above), and residence time (t , calculated from the void volume of the catalyst bed divided by the total flow rate of gases at the inlet of the reactor; void fraction = 0.4).

Under conditions of 600°C, S/C=10-13, G_{C_1} HSV = 180-1680 h⁻¹, and $t=0.1$ s (vapor residence time was similar because the feed flow rate was small compared with that of the helium carrier gas and steam), essentially complete conversion of all oxygenates was achieved, and in most cases, the yield of hydrogen was high, and close to stoichiometric values. However, there were several cases where the hydrogen yield was far below that predicted by stoichiometry and thermodynamic calculations, because of the formation of carbonaceous materials during vaporization or pyrolysis of the feed prior to entering the catalyst bed.

Other commercial and research catalysts tested were capable of reforming the model compounds and high conversions (>99%) were observed [24]. The H₂ yields for all catalysts and model compounds were high, averaging 90% (±5%) of the stoichiometric. Within our experimental error limit, there is no clear indication of one catalyst being better than the others. The yields were reproduced very well (typically within ±2-3%; the worst within ±5-6%). Among the different model compounds, we observed that methanol and HAA yield slightly more H₂ than HAc and ADP.

Among the various operating parameters studied, temperature has the most profound effect on steam reforming reactions. Methanol can be steam reformed at 300°C; HAc and HAA are reformed in high conversions (>99.95%) at above 350°C. The lignin model compound, ADP, was more difficult to reform with steam, requiring temperatures above 600°C for complete conversion. Within experimental error limits, varying residence time from 0.04 to 0.15 s and increasing S/C from 4.5 to 7.5 showed no significant effects on the yield of hydrogen under the conditions of 600°C and G_{C₁}HSV = 1680 h⁻¹; however, it did on the yield of CH₄.

The microreactor-MBMS system also allows the study of reforming mechanisms through the continuous monitoring in real time of the intermediate products present in the gas phase at low conversions. Acids, ketones, alcohols and aldehydes were represented by HAc, acetone, ethylenediol, glycerol, and HAA. The phenolic series included phenol, anisole, cresols, resorcinol, 2,6-dimethylphenol, guaiacol, syringol, and ADP. The furan family of model compounds consisted of furan, 2-methylfuran, 2,5-dimethylfuran, 2-furfuraldehyde, furfuryl alcohol, 5-methylfurfural, and 5-hydroxymethylfurfural. A complete report on HAc and HAA has been published [25], and details of these studies are to be published in separate papers being prepared. HAc produced significant amounts of carbon on the catalyst during steam reforming. No intermediate was detected during steam reforming of HAA and phenol above 400°C. Phenol was the only intermediate detected at both 400 and 600°C from *o*-cresol steam reforming, while significant amounts of cresols, phenol, benzene, and toluene were observed from thermolysis of *o*-cresol at both 400 and 600°C. The results obtained for guaiacol and syringol are consistent with the weakening effect of MeO substituents.

The results obtained for these model compounds suggest that there are significant differences in steam reforming mechanisms of hydrocarbons and oxygenates. Most of the oxygenates found in bio-oils are thermally unstable. At the operating conditions of a typical steam reformer, these oxygenates undergo homogeneous (gas-phase) thermal decomposition, as well as cracking reactions on the acidic sites on the catalyst support. These reactions compete with the catalytic steam reforming reaction to hydrogen. However, a complete conversion of both the oxygenate feed and its decomposition products to hydrogen can be achieved with commercial Ni-based catalysts under reasonable operating conditions, if char formation prior to reaching the catalyst bed and coking on the catalyst can be eliminated, or at least controlled.

4.3 Bench-scale reformer studies

A bench-scale, fixed-bed reactor, shown in Figure 2, was used to establish the global and elemental mass balances and the carbon-to-gas conversion, to quantify the distribution of gas products under conditions of complete conversion of the pyrolysis oil feedstock, and to study the lifetime and regeneration of catalysts. It has been described in detail in our previous publication [24]. The reactor main body is a stainless steel tube (1.65 cm i.d. x 42.6 cm length) housed in a tubular furnace equipped with three independently controlled heating zones. Steam was generated in a boiler and superheated up to 850°C. The organic feed from a diaphragm metering pump was sprayed with ambient N₂ gas followed by mixing with superheated steam in a triple nozzle inlet. Products exiting the reactor were passed through a condenser. Every 4-5 min, the condensate (water in most cases) weight, volume and compositions of the permanent gas output were recorded. An on-line IR gas analyzer was used to monitor CO/CO₂ concentrations and a MTI-QUAD GC was used to measure concentrations of H₂, N₂, O₂, CO, CO₂, CH₄, and other light hydrocarbons. The reformer system was interfaced with a computer to monitor temperatures and other important parameters (once every 30 s).

We initially used model compounds (methanol, acetic acid, syringol and *m*-cresol, both separately and in mixtures), then real bio-oil and its aqueous fraction. Most studies were carried out using the UCI G-90C catalyst; in several latest testings we used a dual-catalyst bed of 46-1 and 46-4 from ICI Katalco. The dual-catalyst bed configuration is detailed in Figure 3. Representative results are listed in Table 4 for the steam reforming of acetic acid, syringol/methanol mixture, a three-component feed made of acetic acid, *m*-cresol, and syringol, and an aqueous fraction obtained from a poplar pyrolysis oil. Profiles of the output gas composition are shown for the 3-component mixture in Figure 4 and for the bio-oil aqueous fraction in Figure 5.

Acetic acid: Results show that the temperature of the reforming section of the bed determines the extent of the carbon conversion to gas products. At temperatures below 500°C, only 73% of the carbon contained in the feed was converted to gas products. It was observed that a significant amount of carbon was formed during these experiments. Part of this carbon was entrained from the bed by the gas stream and was collected in the condenser. The accumulation of carbon in the bed caused the pressure at the reactor entrance to increase continuously during the experiment. An increase in temperature to 535°C in the reforming zone of the catalyst bed improved the recovery of carbon in the gas products up to 80% of that in the feed, and although carbon was still formed, it was not entrained by the gas but retained in the upper section of the catalyst bed. We observed that the carbon deposited in the catalyst bed during the steam reforming of acetic acid was gasified, at least partially, by steam and that after the steam treatment the pressure at the reactor entrance recovered the initial value. Further increase in the reforming temperature resulted in a lower extent of carbon deposition on the catalyst. Formation of carbon deposits was minimal when the temperature was raised to 665°C. At this temperature, the average carbon recovery was 98% and the pressure drop along the catalyst bed was stable throughout the experiment (90 min).

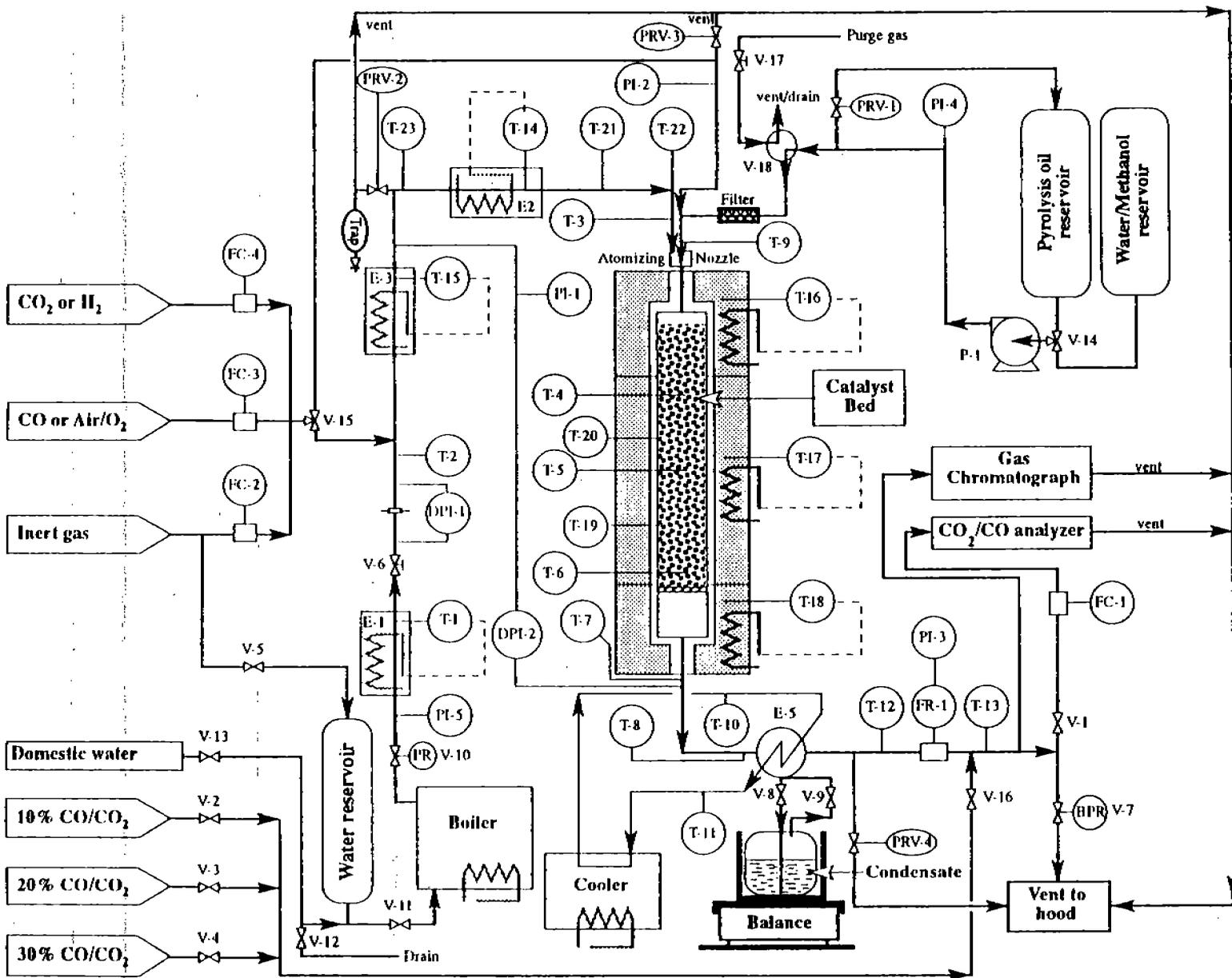


Figure 2. P&I diagram of the Fixed-Bed Catalytic Steam Reforming unit.

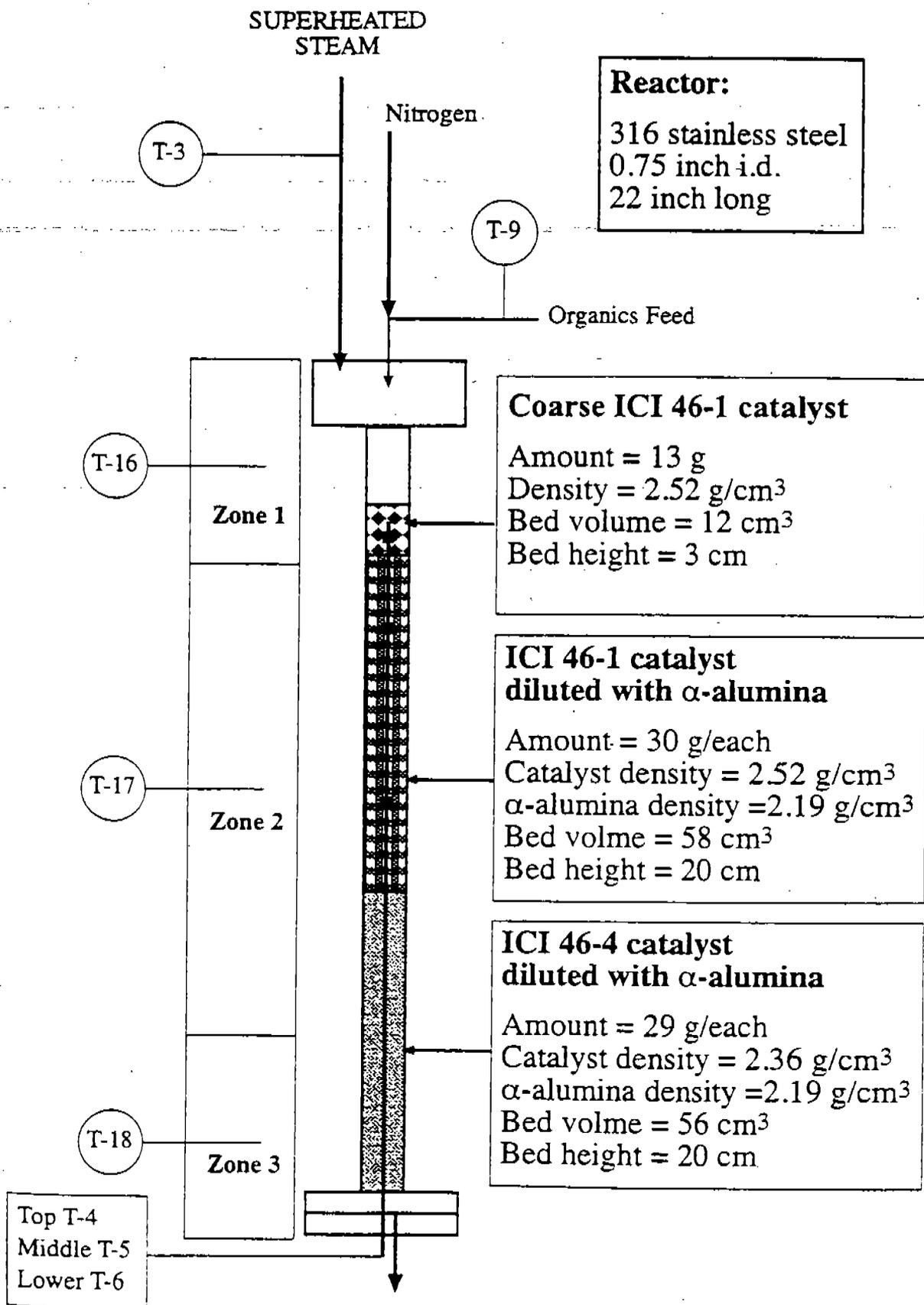


Figure 3. A schematic diagram detailing the dual-catalyst bed configuration.

Below 600°C, hydrogen yield grows with the rising in the reforming temperature due to the increase in the amount of carbon converted to gas products. Above 600°C, where carbon conversions approaching 100% are obtained, hydrogen yield tends to decrease as the temperature increases. This behavior is due to the thermodynamics of the reforming process, since WGS reaction (3) is displaced towards the formation of CO and water at high temperature. This results in a lower hydrogen concentration at the reformer exit. Thus, a unit for the steam reforming of acetic acid using commercial nickel-based catalysts does not differ conceptually from the process for the steam reforming of naphtha or methane, and must include high- and low-temperature shift reactors to obtain an optimal yield of hydrogen. In this context, higher temperatures in the reformer are favorable because they reduce not only the extent of carbon deposition on the catalyst bed but also the yield of methane, thus resulting in a higher yield of hydrogen after the conversion of carbon monoxide in the shift reactors.

Syringol: The steam reforming of syringol was studied at conditions similar to those employed for the reforming of acetic acid. Syringol was dissolved in methanol at a weight concentration ratio of 40:60, which corresponds to a mixture in which 53% of the carbon is provided by syringol. Methanol was selected since it was verified that this solvent was readily reformed in the range of experimental conditions to be tested without leaving any appreciable amount of carbon on the catalyst surface. As a general trend, syringol does not react as well as acetic acid during steam reforming using the UCI G-90C catalyst. At 670°C, the conversion of the carbon in syringol to gas products was estimated to be only 90%. Raising the catalyst temperature to 700°C and above resulted in almost complete carbon conversions (Table 4). Similar to the reforming of acetic acid, the increase in temperature during the steam reforming of syringol also results in the displacement of the gas composition: a decrease in the contents of methane, hydrogen and carbon dioxide, together with an increase in the amount of carbon monoxide.

Three-component mixture: Two long-duration runs using a 3-component mixture were performed in order to compare performances of catalysts from two manufacturers. This mixture contained approximately 67% acetic acid, 16% *m*-cresol and 17% syringol, to represent the components of the carbohydrate fraction and the lignin fraction in bio-oil. We observed some coke deposits on the top portion of the UCI G-90C catalyst bed. The overall mass balance (carbon, hydrogen, and oxygen) was 98.8% and the carbon conversion to gas was 96.1%. The other catalyst tested for steam reforming of the 3-component mixture was the 46-series from ICI Katalco (46-1/46-4). This dual catalyst bed (Figure 3) showed an excellent and steady performance without any coke deposition on the catalyst. Figure 4 shows the reactor temperature profiles, the output gas flow rate (very steady), and the gas composition, which remained constant throughout the whole run. The overall mass balance (including carbon, hydrogen, and oxygen) was 104.3%, and for carbon 105.1%, indicating that there may be a systematic error in our measurement. An excellent hydrogen yield of 85.6% was obtained, and the total hydrogen potential may be as high as 97.6% with a second water-gas shift reactor. These results confirm that both the UCI G-90C and especially the ICI 46-series catalysts can efficiently convert oxygenates to hydrogen.

Aqueous fraction of bio-oil: Steam reforming of bio-oil or its fractions was found to be more difficult than that of model compounds. The main problem that needed to be solved was feeding the oil to the reactor. Bio-oil cannot be totally vaporized; significant amounts of residual solids are often formed that block the feeding line and the reactor. Thus, the simple injection system used for model compounds had to be modified to allow spraying bio-oil and its fractions in to the catalytic reactor without prior char formation. Because the process economics favors the separation of lignin-derived phenolics as co-products (discussed below), we only used the aqueous, mostly carbohydrate-derived fraction to generate hydrogen.

Poplar pyrolysis oil generated in the NREL vortex reactor system was extracted using ethyl acetate and water (weight ratios of 1:1:1 for oil:ethyl acetate:water). The resulting aqueous fraction (55% of the whole oil) contained 25% organics and 75% water. It was successfully fed to the reactor using a triple-nozzle spraying system with minimal accumulation of char in the reactor inlet. A large excess of steam (S/C = 20 and 30 in the two runs) was used, together with a high flow rate of nitrogen, to allow for proper oil dispersion and heat transfer required to maintain a sufficiently high temperature (>500°) at the reactor entrance. The ICI 46-series catalysts performed satisfactorily with no coke formation. We observed a stable gas production rate and composition throughout the whole 4-hour-long experiment (Figure 5).

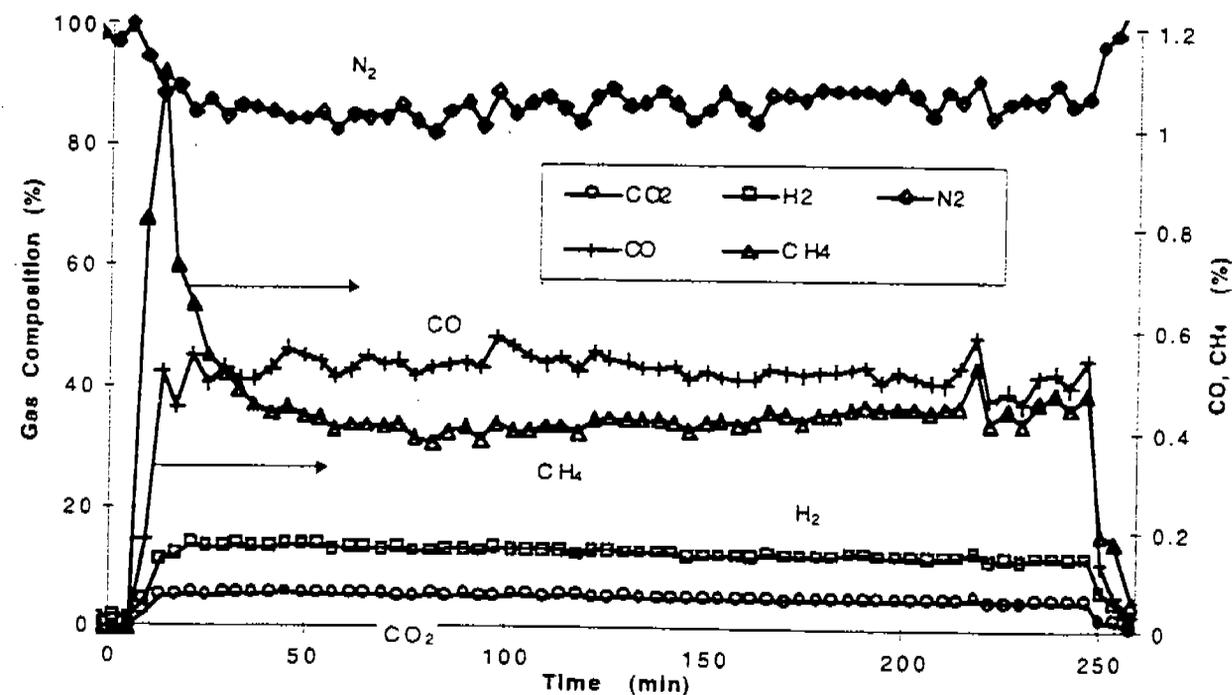


Figure 5. Composition of gaseous products during the steam reforming of bio-oil aqueous fraction using the ICI 46-series catalyst.

The carbon conversion of the aqueous fraction to gas products was almost quantitative in both runs that used the same catalyst bed (Table 4). We observed similar levels of mass balances as in the experiments using model compounds: global 99%, carbon 105%, and hydrogen 97% (assuming a formula of CH₂O for the organics in the aqueous fraction). The methane

concentration (with N_2 excluded) increased from 0.56% in the first run (2 hrs, $t=0.03$ s) to 2.2% in the second run (4 hrs, $t=0.02$ s), and both values were much higher than that (0.01%) obtained from the 3-component model compound mixture (17 hrs, $t=0.09$ s). This was likely caused by the shorter residence time forced by the large flow rate of steam and nitrogen used in the experiment, and also possible incomplete reduction or reoxidation of the catalyst.

Summary: It can be concluded that oxygenates present in bio-oil can be effectively steam-reformed using commercial catalysts under conditions similar to those used for the steam reforming of naphtha: $S/C=5$, >700 °C, and $G_{C_1}HSV$ around 2000 h^{-1} . Excellent mass balances and high yields of hydrogen have been obtained in most cases. A catalyst formulation, such as the UCI G-90C and the ICI 46-series, used for the reforming of naphthas, can be effectively employed in converting bio-oil to hydrogen.

5 Process design and economics

Two scenarios for the production of hydrogen from pyrolysis oil can be envisioned:

(1) A regionalized system of hydrogen production with small and medium-sized pyrolysis units providing condensed bio-oil to a centralized reforming unit. At the reforming plant, the separation of the lignin-derived oligomers will generate a "clean" aqueous stream with simple carbohydrate-derived soluble organics which will be fed to the reformer.

(2) Transport the biomass to a larger pyrolysis unit and feed the uncondensed vapors directly to an integrated adjacent reforming unit located in the same plant premises. In this case, we can also condense the heavier fraction of the pyrolysis vapors via fractional condensation and feed the remaining uncondensed vapors to the reformer.

The first case has the advantage of the availability of cheaper feedstocks, which include biomass residues. In the integrated system, however, the costs of entirely condensing the vapors to produce the bio-oil and transporting it to the hydrogen facility are avoided.

A conceptual process design to make hydrogen from pyrolysis oil is shown in Figure 6. Because of the low sulfur content of biomass, a sulfur removal system is not likely to be required. Also, according to thermodynamic simulations and the screening results, a temperature reformer ramping up to $700-750$ °C will be needed.

In the process being evaluated, pyrolysis oil, its fractions or the uncondensed vapors are fed with steam into a catalytic reactor. Laboratory experiments will choose the most suitable catalyst and reactor configuration; the base-case will use a fixed-bed catalytic reactor. The reaction will occur at 700 °C, and the ratio of steam to oil will be determined by experimental results and economic optimization, although it is clear that it will be in the 5 to 7 range. 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.

The purpose of performing techno-economic, or systems analyses is several-fold. First, in a research environment, the economic feasibility of a given project can be assessed. Additionally, results of any of these levels of analysis are useful in guiding experimental planning. Finally, ongoing analysis can be used to track the progress of research.

A determination of the selling price of hydrogen from this process has been made through a detailed techno-economic analysis. The process analyzed (Figure 6) consists of fluid bed pyrolysis of biomass, water and ethyl acetate extraction to recover a phenolic substitute coproduct, and steam reforming to produce hydrogen in a process based on that used for natural gas reforming. The cost of the pyrolysis plant was taken from Beckman and Graham (1993). A pressure swing adsorption system is used to produce a hydrogen product pure enough to be used in fuel cells. Steam is produced through detailed heat integration and is intended to be sold as a by-product.

A combination of ASPEN Plus[®] and spreadsheet models was used to perform material and energy balances, sizing and costing of major pieces of equipment, and the life cycle cost of the process. The design assumes that a number of small pyrolysis operations, using biomass where it is available and thus at lower costs, supply bio-oil to a central extraction and reforming facility. 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 the 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.

The current selling price of H_2 in industry is between \$5/GJ and \$14/GJ, depending on the size of the production facility. This range is for hydrogen as produced by the plant: purified, but not compressed or stored. The rationale for using this basis for deciding the feasibility of our process is that the end-use of the hydrogen, which is not appropriately specified at this time, will dictate the conditions at which it is shipped from the plant. The major assumptions used for the base case analysis are shown in Table 8. The economic feasibility of this process was studied using the discounted cash flow rate of return 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% after tax, while the rate for

conventional processes is between 9% and 12%. For a 37% tax rate, a 15% after-tax IRR corresponds to a pre-tax IRR of 20.4%.

Results indicate that the necessary hydrogen selling price for the base case analysis is \$7.70/GJ. Figure 7 shows the sensitivity of this price to different parameters used in the analysis. The line down the middle of the chart gives the base case scenario. Each parameter was changed relative to the base case and independent of the other parameters. Therefore, the selling price of hydrogen for one of the scenarios represents changing only that parameter (e.g., feedstock cost) relative to the base case. The current selling price of hydrogen is shown at the bottom for easy reference. This figure indicates quite clearly that the process to produce a phenolics substitute and hydrogen from pyrolysis via extraction and steam reforming has significant potential to be economically feasible. A high rate of return can be obtained and the process can sustain a high drop in coproduct selling price before the hydrogen becomes more expensive than current markets will allow. Relative to the market value of hydrogen, this analysis found that the process is able to sustain large changes in capital cost, hydrogen production capacity, and feedstock cost.

6 Conclusions and Future Work

Fast pyrolysis of biomass is an advanced technology to produce a bio-oil in high yields (70-75 wt.% of anhydrous biomass). This bio-oil is a complex mixture of simple aldehydes, alcohols and acids together with more complex carbohydrate and lignin derived oligomeric materials. Fractional condensation of the pyrolytic vapors could separate the simple monomeric materials, which comprise about one third to one half of the bio-oil from the complex oligomeric fraction. Steam reforming of the simple monomeric materials, the entire bio-oil or its fractions is thermodynamically and chemically feasible. Our screening tests have shown that such catalysis is possible using commercially available Ni-based catalysts. Improvements in their formulation may be needed to optimize the activity/selectivity/time-on-stream relationships when reforming the biomass-derived oxygenates. Results obtained at the bench-scale level on the steam reforming of model compounds and their mixtures, as well as bio-oil fractions have substantiated our findings at the microscale level. The challenge seems to be the adequate introduction of the bio-oil or its fractions to contact the catalyst prior to any gas-phase thermal decomposition which would result in unwanted char formation. In addition, progressively increasing the catalyst activity by either temperature ramping or catalyst formulation is an appropriate strategy to minimize coke formation on the catalyst. We have achieved a reasonable comprehension of the spray nozzle design and operating conditions to fulfill these goals.

The preferred implementation strategy consists of small- to medium-size regional fast pyrolysis units which will produce the bio-oil from either dedicated crops or plantations, or will use waste lignocellulosics as feedstocks. The bio-oil produced will be transported to a central separation/reforming unit serving a given region where H₂ and co-products will be produced. The process concept is simple: a desulfurization unit is not needed, and the bio-oil can be atomized in

a flow of steam which is then processed through a reforming unit. By a proper choice of conditions the near equilibrium design can be driven to maximize H₂ production. A pressure swing adsorption unit will purify the gas stream. An economic analysis of the process indicates that the necessary selling price of hydrogen is well within current market values. This analysis studied the co-production of hydrogen and a phenolics substitute for resin manufacture. The process studied was based on pyrolysis oil production at distributed locations followed by extraction and steam reforming at a centralized facility. Relative to the current market price of hydrogen, the economics of this process have been shown to be insensitive to changes in the assumptions made.

An alternate strategy, but less favorable economically, consists of transporting the biomass to a central conversion site where the fast pyrolysis and reforming operations can be conducted jointly. Fractional condensation of the vapors can be carried out in order to recover, for instance, the depolymerized lignin fraction which has value as a mixture of phenolics to be used in resin formulations.

The projected goals for future work are:

- To demonstrate the long-duration catalyst performance as well as its regenerability using bio-oil fractions.
- To determine optimum process conditions at the bench scale.
- To demonstrate the feasibility of alternative reactor configurations such as fluid bed (bubbling or circulating).
- To identify marketable co-products and separation methods.

7 Acknowledgments

We thank the US DOE Hydrogen Program for financial support of this research project under contract DE AC 36-83CH10093.

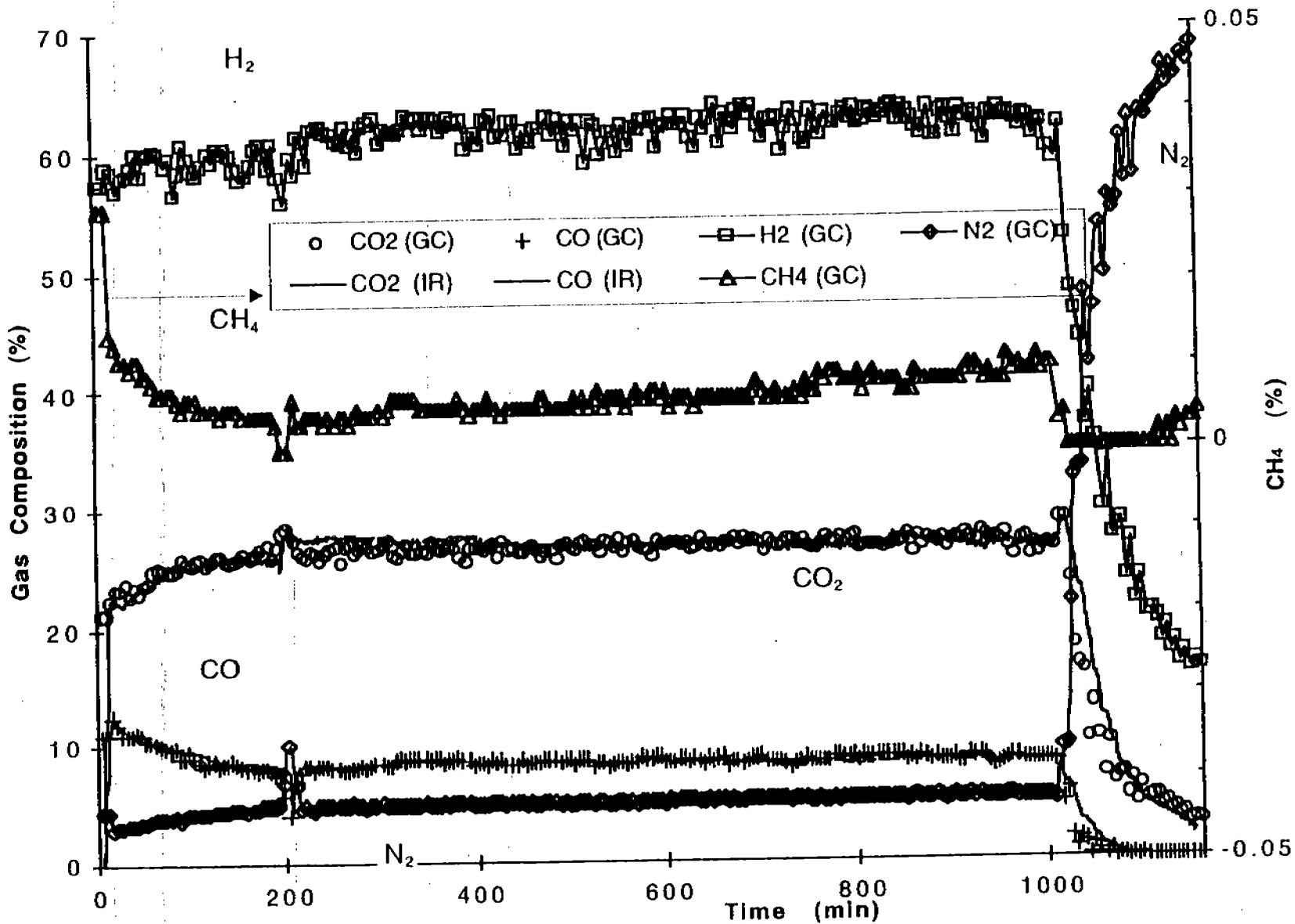
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Table 4. Summary of results for catalytic steam reforming experiments on the bench-scale reformer

Feed	Catalyst	S/C	G _{C1} HSV	Temperatures (°C)			Yield (mol/100 mol of C fed)				C-to-gas conv.	% st. yield H ₂ (+WGS)	Run time, h
				Top	Middle	Bottom	H ₂	CO ₂	CO	CH ₄			
acetic acid	UCI G-90C	4.7	1973	685	716	833	145.8	50.3	49.7	0.055	101	73 (98)	6
	"	12.8	777	710	789	830	171.8	74.9	29.0	0.005	104	86 (100)	8
syringol (MeOH solution)	"	6.3	2454	702	745	830	195.0	45.4	53.9	0.2	100	75 (96)	4
3-comp. mixture	"	7.4	1985	750	803	863	197.3	46.0	54.9	0.1	101	76 (97)	4
	"	6.5	1053	738	na	833	167.6	67.4	28.6	0.00	96	78 (91)	11
	ICI 46-1/4	4.9	1053	782	753	834	187.8	79.8	27.4	0.03	105	86 (98)	17
poplar oil, aq. fraction	"	19.3	1110	480	730	818	206.7	85.2	9.6	1.7	97	103 (108)	2
	"	30.0	1000	530	744	821	205.8	86.6	8.4	6.9	102	103 (107)	4



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Figure 4. Composition of gaseous products during steam reforming of a 3-component mixture using the ICI 46-series catalyst.

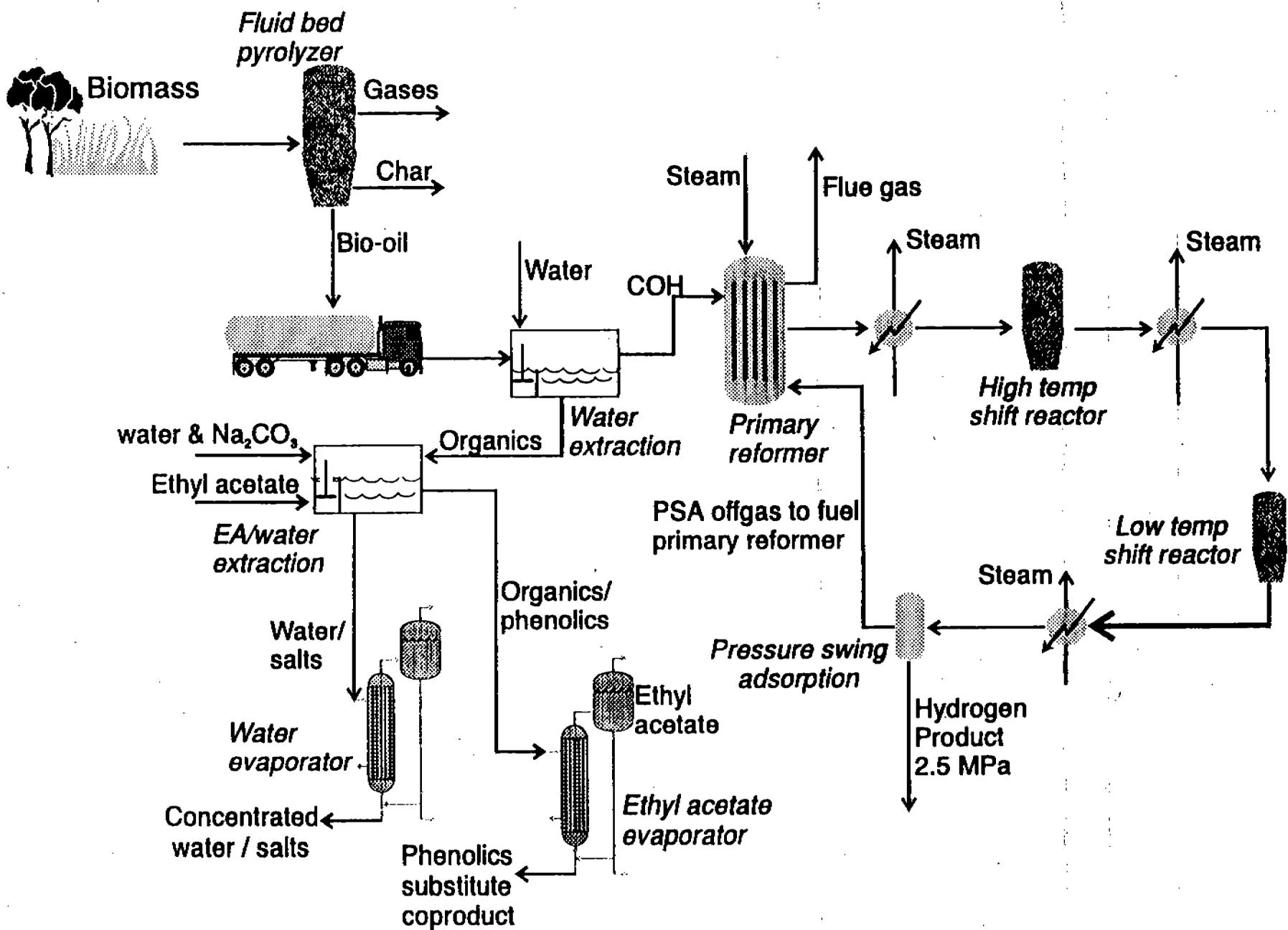


Figure 6. Process flow diagram for the fast pyrolysis and reforming of biomass.

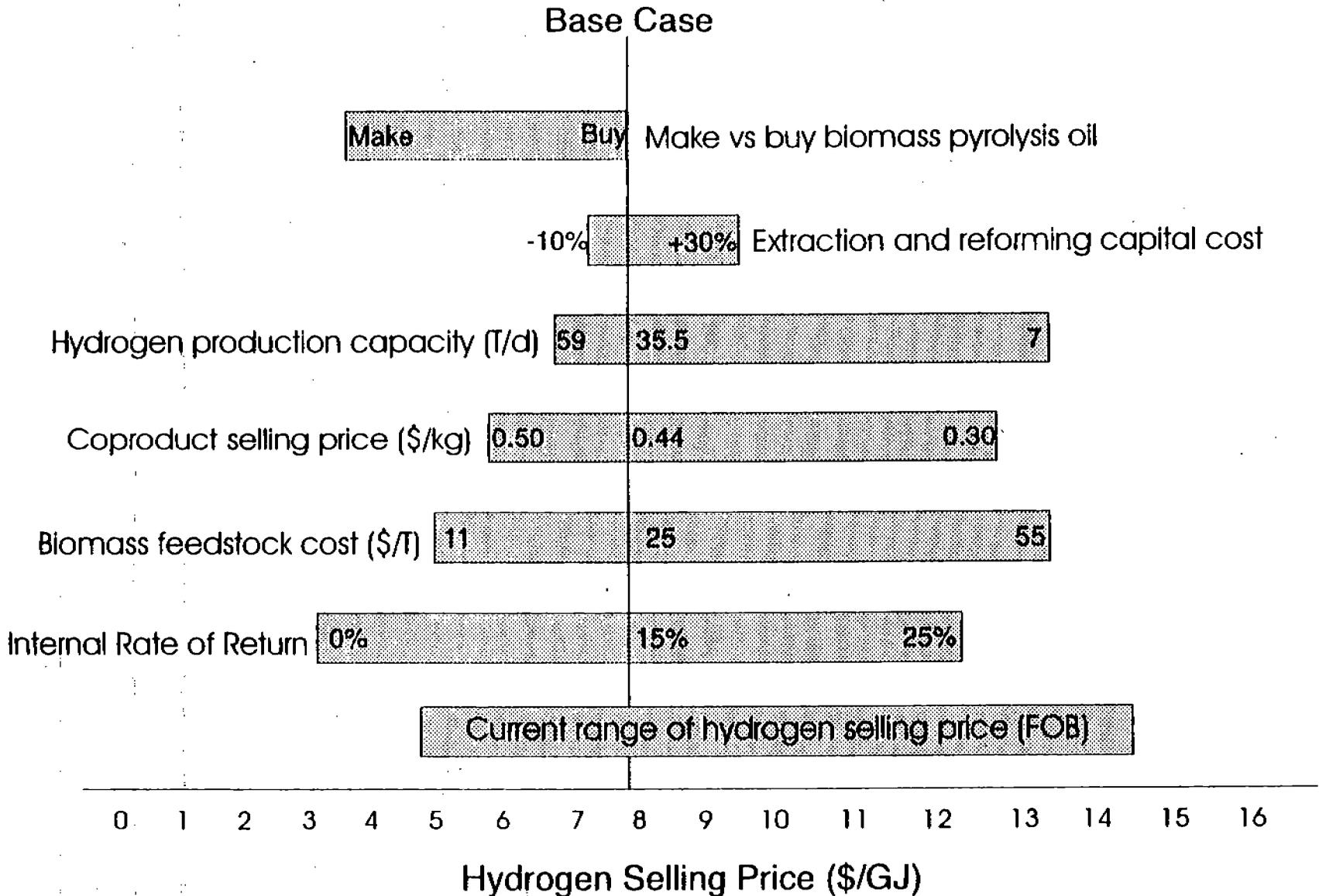


Figure 7. Incidence of the cost of pyrolysis oil (or its fractions) on the hydrogen production cost.