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Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oil

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Abstract

Hydrogen is the prototype of the environmentally cleanest fuel of interest for power generation using fuel cells and for transportation. The thermochemical conversion of biomass to hydrogen can be carried out through two distinct strategies: (a) gasification followed by water-gas shift conversion, and (b) catalytic steam reforming of specific fractions derived from fast pyrolysis and aqueous/steam processes of biomass. This paper presents the latter route that begins with fast pyrolysis of biomass to produce bio-oil. This oil (as a whole or its selected fractions) can be converted to hydrogen via catalytic steam reforming followed by a water-gas shift conversion step. Such a process has been demonstrated at the bench scale using model compounds, poplar oil aqueous fraction, and the whole pyrolysis oil with commercial Ni-based steam reforming catalysts. Hydrogen yields as high as 85% have been obtained. Catalyst initial activity can be recovered through regeneration cycles by steam or CO_2 gasification of carbonaceous deposits.

Introduction

Renewable lignocellulosic biomass has been considered as a potential feedstock for gasification to produce syngas (a mixture of hydrogen and carbon monoxide) for the last few decades. However, the economics of current syngas production processes favor the use of hydrocarbons (natural gas, C_2-C_5, and naphtha) and inexpensive coal. An alternative approach to the production of hydrogen from biomass is fast pyrolysis of biomass to generate a liquid product (also known as bio-oil) and catalytic steam reforming of the whole oil or its fractions. This latter approach has potential to be cost competitive with the current commercial processes for hydrogen production. The objective pursued in this work is to prove the feasibility of a process strategy based on the use of biomass, of either agricultural or forest origin, as a feedstock to small and medium size (< 250 tonnes/d biomass input, dry basis) regional pyrolysis plants to produce bio-oil, that would be subsequently converted to hydrogen via catalytic steam reforming. The second step of the process could be carried out at a different location (bio-oil is easily transportable), with the existing infrastructure for hydrogen use or distribution. The above process strategy is conceptually possible thanks to the significant advances in fast pyrolysis technology made in the 80's and 90's,[1-4] the improved understanding of the composition of the bio-oils and their fractionation,[5] and the knowledge-base accumulated in the past few years of how to steam reform oxygenates derived from carbohydrates and lignin.[6-8]

Fast pyrolysis technologies have reached near commercial status. Circulating fluid bed processes have been installed in the USA (50 tonnes/d) and in Italy (15 tonnes/d), while a bubbling fluid bed pilot process is under development in Spain (3 tonnes/d).[9-10] The basis of these technologies is the understanding of pyrolytic mechanisms. When biomass is rapidly heated its constitutive macromolecules depolymerize and dehydrate.[11-12] Volatile intermediates are formed and exit the reaction zone when appropriate fluid-dynamics are applied.[1,3] Since these intermediates undergo subsequent cracking in the vapor phase when exposed to high temperatures, the yield and nature of the bio-oil is a function of the secondary cracking severity.[12-13]

It is well documented that yields of bio-oil can reach 75 wt%.[5] The bio-oil produced from fast pyrolysis of biomass contains 75-85 wt% organics and 15-25 wt% water. The latter is the result of the moisture content in the biomass feed and dehydration reactions which proceed in parallel with the thermal depolymerization reactions. The organics are predominantly a mixture of aldehydes, alcohols and acids derived from the carbohydrate fraction of biomass and phenolics from lignin.[5,8] Thermal depolymerization reactions can be conducted in such a way that the hemicellulose and cellulose yield volatile compounds which are predominantly monomeric with small amounts of oligomers. However, lignin depolymerization invariably produces more oligomers than monomers. The oligomers, both from the carbohydrate and the lignin are found in the vapor phase due to their carry over as aerosols. By an appropriate choice of the condensation sequence we can separate the bio-oil into an oligomer-rich fraction and a monomer-rich fraction, the latter being water-soluble. Alternatively, the whole bio-oil can be split into two fractions via a simple addition of water (a water/bio-oil weight ratio of 2 is normally used). Fast pyrolysis thus produces two bio-oil fractions: a monomer-rich aqueous fraction (containing typically 20 wt% organics that can be concentrated by evaporation or nanofiltration) and a hydrophobic fraction composed mainly of oligomers derived from lignin.[5,8]

Steam reforming can be conceivably conducted with the entire bio-oil or with each of its fractions. Figure 1 shows the schematic diagram of the proposed process. The solid line specifies the route leading to co-products hydrogen and "depolymerized lignin". Lignin-derived oligomer-rich fraction can be used as a feedstock for the production of resins with formaldehyde.[14] Such resins can become a valuable co-product (a substitute for phenol-formaldehyde) which will lower the production costs of hydrogen from the aqueous fraction as demonstrated in related technoeconomic studies.[8,15] Another viable application of the lignin-derived fraction is the production of cyclohexyletheres, a new class of high octane fuel additives, which is under development.[16]

The economics of the whole bio-oil reforming are less favorable than for the co-product strategy. However, the hydrogen yields obtained from the whole oil are higher than when only the aqueous, carbohydrate-derived fraction is processed. In addition, since hydrogen is the only product, this option is independent of co-product markets.

We have also shown (Figure 1) the approach of stabilizing (via controlled depolymerization of the oligomers, selective dehydration and, probably, esterification/ etherification) the aqueous fraction of the bio-oil to yield a biomass-derived oxygenates that could be stored, transported and converted very much like any other hydrocarbon or alcohol. We are not reporting on this effort in the context of this paper but we want to emphasize the significance of this bio-oxygenate as a "potential new biofuel".

Because biomass fast pyrolysis has almost reached the commercial status, this work has focused on the catalytic steam reforming of bio-oil, its fractions, and representative components. At this stage of the work we have concentrated our efforts in the reforming of the aqueous fraction and the whole bio-oil.

Experimental Section

Tests were carried out in two systems: a bench-scale fixed-bed unit and a 2 inch diameter fluidized bed reactor.

The schematic of the bench-scale system is shown in Figure 2. The reactor is a stainless steel tube (1.65 cm id x 42.6 cm length) housed in a tubular furnace equipped with three independently controlled heating zones. The reactor was packed with about 100 g of a commercial, nickel-based catalyst (particle size: 2.4-4.0 mm). Most studies were carried out using the UCI G-90C catalyst and a dual-catalyst bed of 46-1 and 46-4 from ICI Katalco. Steam was generated in a boiler and superheated. The organic feed from a diaphragm metering pump was sprayed using N_2 and mixed with superheated steam in a triple nozzle injector. Products exiting the reactor were passed through a condenser. The condensate (just water in most cases) weight, as well as the volume and compositions of the permanent gas output were recorded periodically. An on-line IR gas analyzer was used to monitor CO/CO_2 concentrations and a MTI-QUAD GC was used to measure concentrations of H_2, N_2, O_2, CO, CO_2, CH_4, and other light hydrocarbons. The reformer system was interfaced with a computer to monitor temperatures and other important parameters.

The schematic of the fluidized bed system is shown in Figure 3. The two-inch-diameter inconel reactor is heated by a three-zone furnace. 150-200g of commercial nickel-based catalysts from UCI ground to the particle size of 150-250µ are fluidized using superheated steam which is also a reactant in the reforming process. Liquids are fed using a diaphragm pump and a specially designed oil injection nozzle supplied with a cooling jacket. The oil temperature in the injector is maintained below boiling point to prevent deposition of nonvolatile components. The product collection line includes a cyclone that captures fine catalyst particles and, possibly, char generated in the process, and two heat exchangers to condense excess steam. The outlet gas flow rate is measured by a flowmeter and a dry test meter. The gas composition is analyzed by a MTI gas chromatograph. The unit is connected to the G2/OPTO control and data acquisition system.

The bio-oil and its aqueous fraction were prepared at NREL. A poplar oil[17] generated by fast pyrolysis in the NREL vortex reactor system was separated into aqueous (carbohydrate-derived) and organic (lignin-derived) fractions by simply adding water to the oil with a weight ratio of water:oil = 2:1. The aqueous fraction (55% of the whole oil) contained ca. 20% organics ($CH_{1.5-1.9}O_{0.6-0.8}$) and 80% water.

Results and Discussion

The overall steam reforming reaction of bio-oil (or any oxygenate with a chemical formula of $C_nH_mO_k$), is given by:

$$C_nH_mO_k + (2n-k)\,H_2O = n\,CO_2 + (2n + m/2-k)\,H_2 \tag{1}$$

The stoichiometric yield of hydrogen is 2+m/2n-k/n moles per mole of carbon in the feed, and k/n for the aromatic phenolics from lignin is less than for most carbohydrate-derived products such as sugars.

Our initial work focused on demonstrating high efficiency of catalytic steam reforming as a method for conversion of bio-oil to hydrogen. The findings obtained from rapid screening experiments carried out using a microreactor interfaced with a molecular beam mass spectrometer, have been discussed in details elsewhere.[7-8] It was concluded that steam reforming of oxygenated organic compounds faces a serious competition from gas-phase thermal decomposition prior to entering the catalyst bed and the acid-catalyzed reactions at the acidic sites of the catalyst support. These competing thermal cracking reactions may result in the formation of carbonaceous materials (coke), which could block the reactor and even deactivate the catalyst. 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. Therefore, a special emphasis during bench-scale experiments was placed on how to feed bio-oil or its fractions into the reactor.

Tests were carried out using the bench-scale fixed-bed system to obtain the global and elemental mass balances, yield of hydrogen, and the carbon-to-gas conversion. We quantified the distribution of gas products under conditions of complete conversion of the pyrolysis oil feedstock, and studied the catalyst lifetime and the efficiency of its regeneration. Initially, we used model compounds (methanol, acetic acid, syringol and *m*-cresol, both separately and in mixtures) then real bio-oil (and its aqueous fraction). Representative results are listed in Tables 1 and 2. Profiles of the output gas composition are shown for the 3-component mixture in Figure 4 and for the poplar oil aqueous fraction in Figure 5.

During the processing of the three-component mixture of 67% acetic acid, 16% *m*-cresol, and 16% syringol 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 99% and the carbon conversion to gas was 96% (Table 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 is used in commercial naphtha reforming plants to reduce coke formation and extend catalyst lifetime. It showed an excellent and steady performance *without any coke deposition* on the catalyst. The gas composition (Figure 5) remained constant throughout the whole run. The overall mass balance (including carbon, hydrogen, and oxygen) was 104%, and for carbon 105%, indicating that there may be a systematic error in our measurement. An excellent hydrogen yield of 86% of the stoichiometric amount was obtained, and the total hydrogen potential may be as high as 98% 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.

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.

The aqueous fraction of NREL-made poplar oil 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 = 20-30) 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°C) at the reactor entrance. A portion of water and other volatiles in the sprayed droplets evaporate during mixing with the superheated steam and the remaining nonvolatiles will contact the catalyst surface directly. 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).

The carbon conversion of the aqueous fraction to gas products was almost quantitative in both runs that used the same catalyst bed (Table 2). We observed similar levels of mass balance closures as in the experiments using model compounds: global 99%, carbon 105%, and hydrogen 97%. The methane concentration (with N_2 excluded) increased from 0.56% in the first run (2 h, t=0.03 s) to 2.2% in the second run (4 h, t=0.02 s), and both values were much higher than that (0.01%) obtained from the 3-component model compound mixture (17 h, 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.

Lowering steam-to-carbon ratio did not change much the overall H_2 yield, but only caused an increase in CO yield due to the WGS reaction. We also observed some thermal decomposition of the bio-oil fraction, which resulted in the accumulation of carbonaceous deposits in the region between the injection nozzle and the catalyst bed. There was a progressive formation of carbonaceous deposits in the catalyst bed. As a result, the hydrogen yield gradually decreased, as shown in Figures 6 and 7. Therefore, it seems necessary to regenerate the catalyst in order to achieve high performance over a long period of time. This can be effectively achieved by gasification with either CO_2 (a co-product of the process) or steam. Experiments using both model compounds (e.g., acetic acid) and the poplar oil aqueous fraction proved validity of this regeneration. The H_2 yield profiles before and after regeneration by steam are also shown in Figures 6 and 7, indicating the recovery of H_2 yield after a 12 h treatment at 800°C and ambient pressure.

The steam reforming of the whole bio-oil in the fixed-bed reactor was much less successful than in the case of model compounds or the carbohydrate-derived oil fraction. Thermal decomposition of the oil resulted in fast accumulation of carbonaceous deposits on the catalyst and in the freeboard (above the bed). Therefore, only a very small fraction of the catalyst (top layer) was effectively used in the process while the most of it was not accessible to contact the oil. In addition, this caused a pressure buildup in the reactor and forced termination of the tests after 30-40 minutes. Figure 8 shows how the concentration of hydrogen and carbon dioxide in the product gas decreased with time, especially after 20 minutes on stream. The total mass balance closure was in this case 92%, however, only 62% of bio-oil were converted to gases and the hydrogen yield was only 41% of the stoichiometric, that corresponds to 4 kg of hydrogen from 100 kg biomass. Additional amounts of hydrogen could be produced from methane and carbon monoxide present in the gas that would increase the final yield to 65%, which is still significantly less than obtained from the carbohydrate-derived oil fraction.

The carbon/coke deposits could be efficiently removed from the reactor freeboard and from the catalyst surface by steam gasification carried out at 800°C. However, the time required for this process was almost four hours, much longer than that available for reforming. Because of these reasons we concluded that the fixed-bed configuration was not appropriate for steam reforming of the whole bio-oil. We believe that the application of the fluidized bed reactor will eliminate, or at least lessen most of the problems encountered in the fixed-bed unit. Even if we are not able to prevent partial carbonization of the oil, the bulk of the fluidizing catalyst will remain in contact with the oil droplets in the reactor, which will greatly increase the reforming efficiency and extend the catalyst time-on-stream.

Preliminary tests of the whole oil reforming that were performed in the fluidized bed unit are encouraging: the oil can be injected into the bed using an appropriately designed nozzle and the cracking/reforming reactions proceed well while the catalyst can conceivably be continuously regenerated in a second reactor. Complete results will be presented within the next few months.

Summary and Conclusion

1. Biomass can be converted to bio-oil using a fast pyrolysis technology. The yield of bio-oil for a fluidized bed process is on the order of 75% biomass weight.
2. Bio-oil or its aqueous fraction can be reformed to generate hydrogen by a thermocatalytic process using commercial, nickel-based catalysts. The hydrogen yield obtained in a fixed-bed reactor from the aqueous fraction was up to 85% of the stoichiometric value which corresponds to almost 6 kg of hydrogen from 100 kg of wood.
3. Catalysts are easy to regenerate by steam or CO_2 gasification of carbonaceous deposits.
4. Fixed-bed is not the right reactor choice for reforming whole bio-oil. We believe, based on initial results, that fluidized bed will significantly improve the process efficiency.
5. The proposed strategy can be applied to any lignocellulosic biomass, either from agriculture or from forest operations. Residues as well as plantations and agricultural crops are equally suited as feedstocks to the process. The concept of using biomass via a regionalized system of production of bio-oils is entirely compatible with our strategy.

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Table 1. Fixed-Bed Bench-Scale Results with Model Compounds

Feed	S/C[a]	$G_{C_1}HSV$[b]	% C-to-gas conversion	% st. yield of H_2 (+WGS)[e]	Time on stream (h)
acetic acid	4.7	1973[c]	101	73 (98)	6
	12.8	777[c]	104	86 (100)	8
syringol/	6.3	2454[c]	100	75 (96)	4
MeOH	7.4	1985[c]	101	76 (97)	4
3-comp.	6.5	1053[c]	96	78 (91)	11
mixture	4.9	1053[d]	105	86 (98)	17

[a] Molar ratio of steam to carbon. [b] Gas hourly space velocity on C_1 basis (h^{-1}). [c] UCI G-90C catalyst. [d] ICI 46-1/4 catalysts. [e] Assuming all CO being converted to H_2 in a down stream WGS unit.

Table 2. Fixed-Bed Bench-Scale Results with Poplar Oil Aqueous Fraction

S/C[a]	$G_{C_1}HSV$[b]	% C-to-gas conversion	% st. yield of H_2 (+WGS)[f]	Time on stream (h)
19	1110[c]	97	103 (108)	2
30	1000[d]	102	103 (108)	4
35	860[c]	99	86 (88)	1
24	850[d]	100	89 (92)	1
12	860[d]	97	82 (88)	1
7	860[d]	98	79 (90)	1
5	1010[c]	92	75 (85)	6
10	1230[d]	102	78 (86)	6
23	870[e]	92	73 (76)	1
15	850[e]	89	71 (75)	1
10	760[e]	86	71 (76)	4

[a] Molar ratio of steam to carbon. [b] Gas hourly space velocity on C_1 basis (h^{-1}) with ICI 46-1/4 catalysts. [c] Fresh catalyst used. [d] Used the same catalyst as the previous run above it. [e] UCI G-91 catalyst. [f] Assuming all CO being converted to H_2 in a down stream WGS unit.

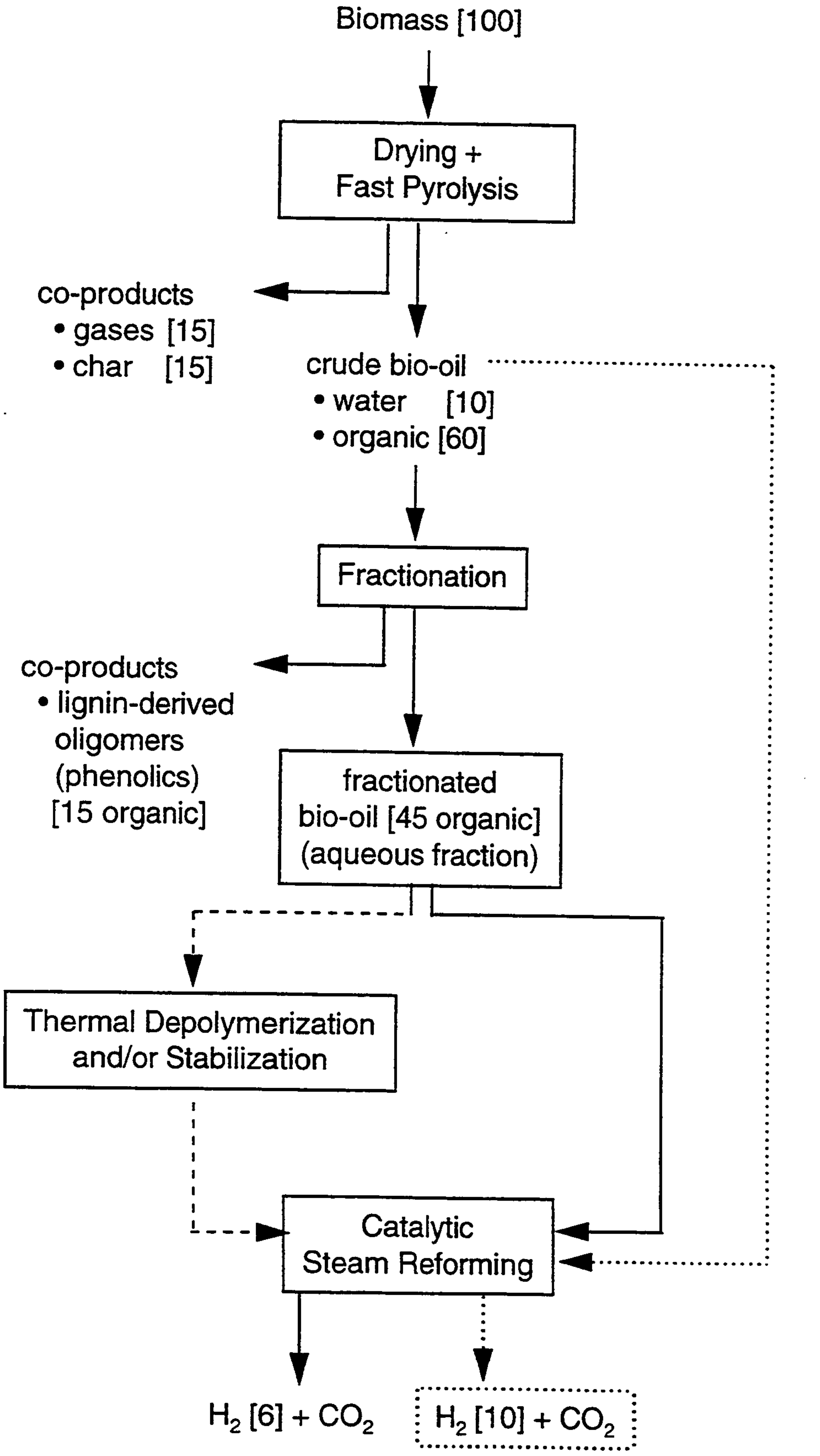
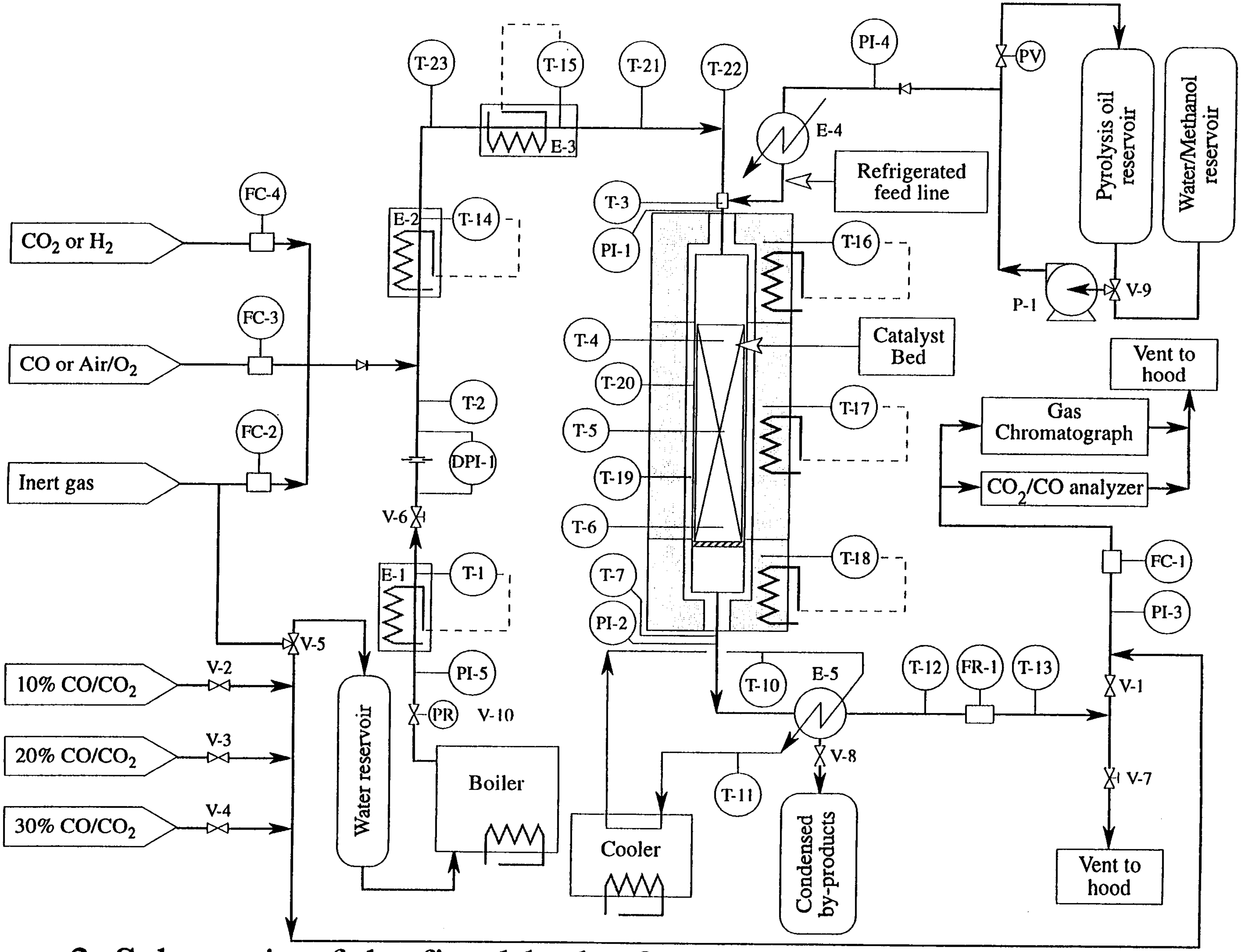


Figure 1. Process diagram for the production of hydrogen from biomass via fast pyrolysis and catalytic steam reforming



gure 2. Schematic of the fixed-bed reformer system

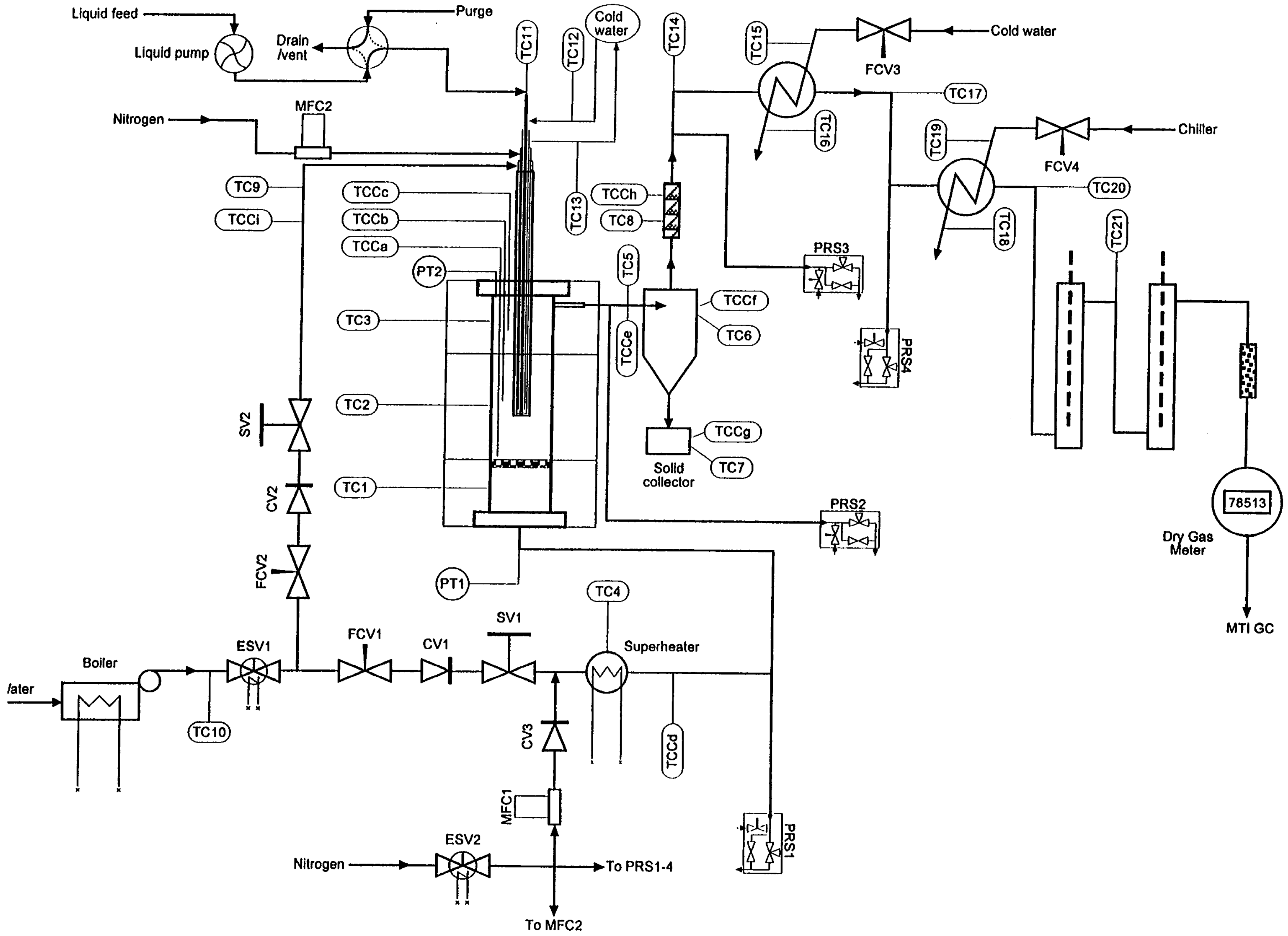


Figure 3. Schematic of the fluidized bed reformer

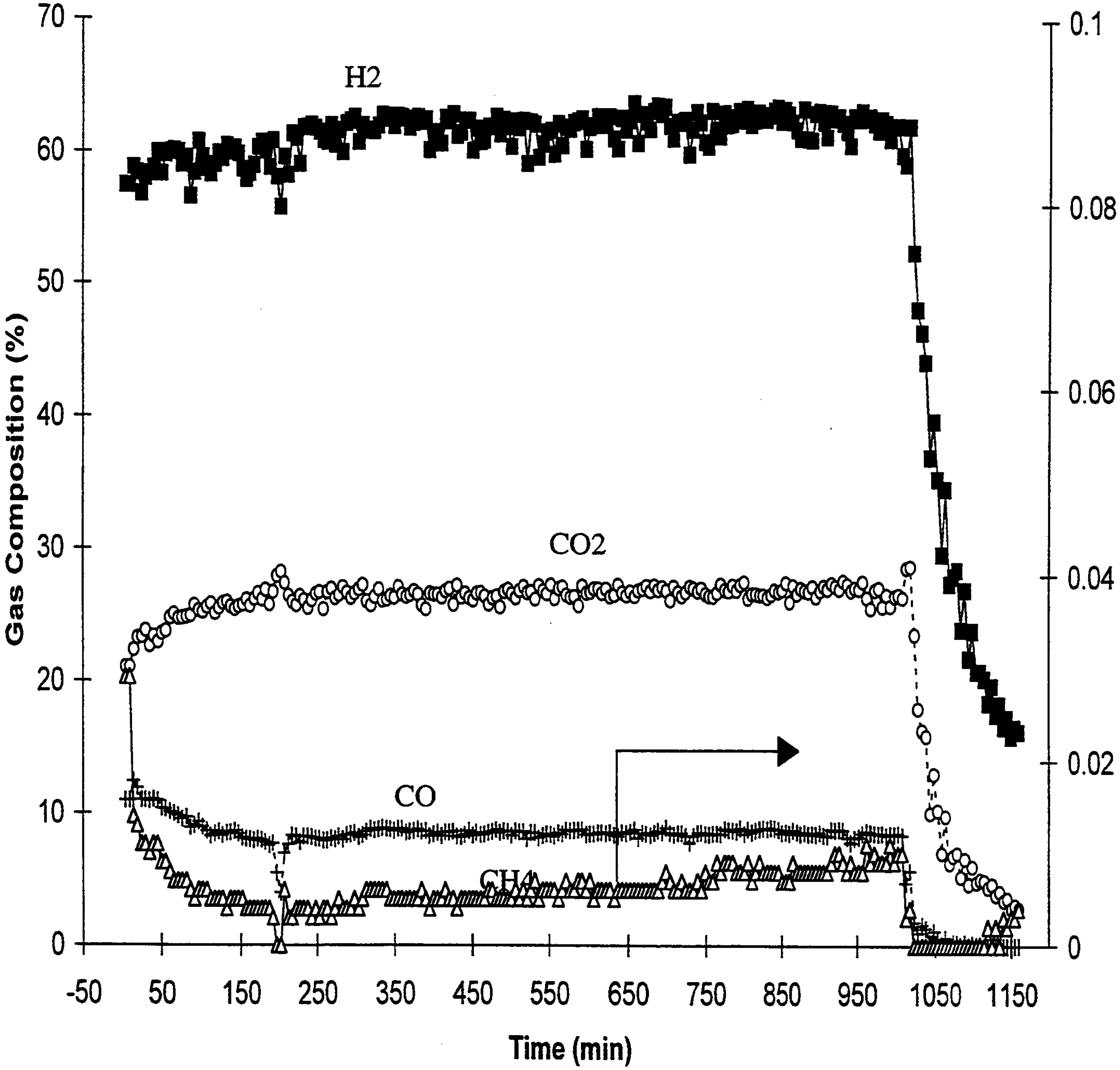


Figure 4. Product gas composition from reforming of a three-component mixture of acetic acid, m-cresol, and syringol

Figure 5. Product gas composition from reforming aqueous oil fraction

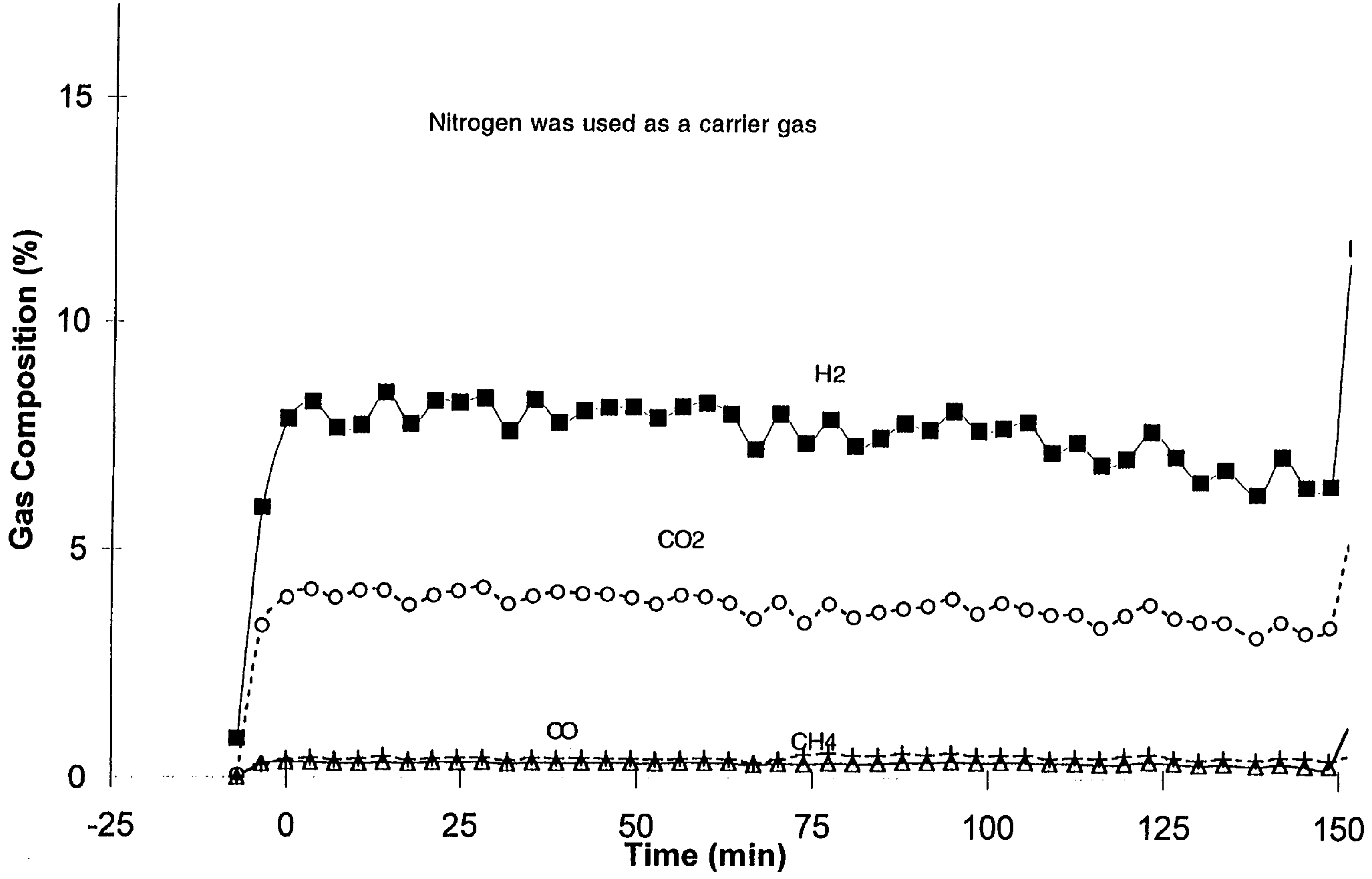


Figure 6. Hydrogen yield from aqueous fraction of poplar oil

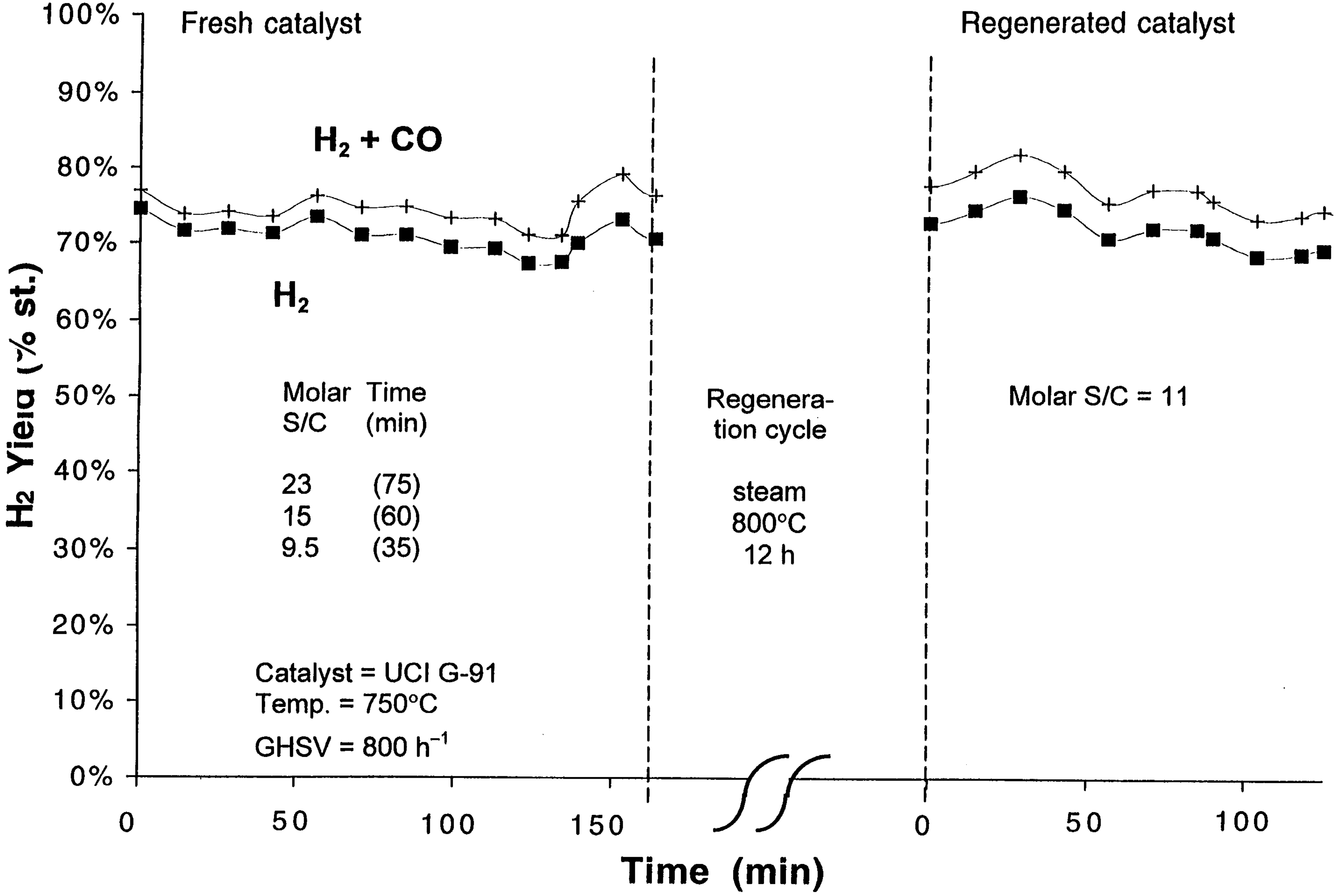


Figure 7. Product gas composition from reforming whole bio-oil