



Project Summary

Hynol Process Evaluation

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Fuel-cell vehicles (FCVs) have the potential to offer a major improvement in efficiency relative to current motor vehicles. The potential of FCVs to nearly eliminate pollutant emissions and reduce the economic pressures of petroleum imports will be a major factor contributing to the sustainability of the current system of highway transport. Greenhouse gas emissions, of which the transportation sector is a major contributor, are another part of the sustainability issue. FCVs and the fuels used in them also offer the potential for an economical and effective technological option for mitigation of anthropogenic carbon dioxide (CO₂) emissions. The hydrogen that is required for fuel cells can be produced from natural gas (which contributes to greenhouse gas emissions) and from biomass (which does not). This report examines process alternatives for the optimal use of these resources for production of FCV fuel, emphasizing maximum displacement of petroleum and maximum reduction of overall fuel-cycle CO₂ emissions at least cost. Three routes are evaluated: (i) production of methanol from biomass and from natural gas by independent processes, (ii) production of methanol or hydrogen by hydrogasification of biomass using natural gas as co-feedstock supplemented with, and without, the use of carbonaceous municipal wastes as co-feedstocks, and (iii) production of methanol or hydrogen by addition of natural gas to a biomass-to-methanol process originally designed for biomass only. The results show that the combined use of natural gas and biomass in a single process can reduce net fuel-cycle CO₂ emissions by 20% relative to separate systems and reduce the cost of fuel production to a range competitive with the current cost of gasoline. A plant optimized for effi-

ciency and size, with 25% of the feedstock energy consisting of biomass, should be able to produce methanol at a cost of \$0.42/gal (\$6.09/GJ), or hydrogen at \$5.98/GJ. This technology represents a "no regrets" approach to CO₂ mitigation and a cost-effective use of biomass as a source of fuel energy.

This Project Summary was developed by the National Risk Management Research Laboratory's Air Pollution Prevention and Control Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The economic, environmental, and health impacts of an ever increasing population of vehicles, and the dependence on foreign sources for the petroleum needed for the U.S. system of road transport, add up to an unsustainable situation. National goals have been established by the National Energy Strategy of 1991, the Energy Policy Act of 1992, and the Clean Air Act Amendments of 1990 for the development of alternative fuels that could reduce the environmental and economic impacts of petroleum fuels. New technologies that can effectively deal with many of the problems of road transport are nearing commercialization. Among the new technologies, fuel-cell vehicles (FCVs) offer an attractive solution to these problems for the foreseeable future. An alternative to petroleum fuel should be compatible with the existing refueling infrastructure, provide a driving range comparable to gasoline used in current vehicles, and be compatible with FCVs when they enter the commercial market. FCVs require hydrogen—either as compressed gas or as a liquid hydrogen-carrier that can be reformed on board to produce hydrogen. Hydrogen or methanol (the preferred liq-

uid hydrogen-carrier that is most easily reformed or used directly in special fuel cells) can be produced from biomass. A fuel produced entirely from renewable biomass, such as short-rotation woody crops or perennial grasses, would have the important advantage that it would not contribute to greenhouse gas emissions. From that standpoint, as well as the renewable standpoint, it could reduce the sustainability problem of transportation fuels. There are two major barriers to this approach: (i) the amount of biomass that could be produced as energy crops on land that is suitable for that purpose (<5.8 quads)^a could not displace a major fraction of the U.S. transportation fuel needs even if there were no competing uses, and (ii) cost: an alternative to gasoline must be competitive in selling price if it is to gain acceptance in the marketplace. The production cost of fuels produced from biomass alone is much higher than the production cost of gasoline. By use of natural gas as a co-feedstock, the yield of methanol or hydrogen can be greatly increased and the cost reduced to a competitive market price. The object of this report is to evaluate thermochemical processes by which biomass and natural gas could be utilized most effectively to displace petroleum and reduce greenhouse gas emissions at least cost.

Procedure

Two basic approaches are considered in detail for the production of transportation fuel from biomass and natural gas: (i) biomass alone is converted to liquid transportation fuel (methanol) by the best currently available technology and natural gas is used in a separate conventional process to produce methanol, and (ii) it is assumed that the same two feedstocks are utilized in a single thermochemical process to produce methanol. The primary objective is to compare the methanol yield, production cost, and net overall CO₂ emission for the two approaches and, by that comparison, assess the relative merits of the latter technology, called Hynol. These evaluations were conducted by computer simulations using the *Aspen Plus* process simulation software which enables calculation of material and energy balances, thermal efficiency, and CO₂ emissions for any variety of input assumptions, including alternative configurations of the components, and design details of those components. A critical factor in comparisons of this type is the uniformity of

the assumptions on which they are based. Equal values of input variables, including biomass composition, plant size, reactor performance, mechanical efficiencies, heat-recovery efficiencies, and cost bases, were used everywhere possible.

Using this procedure, a process consisting of a biomass gasifier developed by Battelle Columbus Laboratory (BCL) and modified by Princeton University to produce methanol was examined in detail to establish a basis for methanol yield when biomass is used as the sole feedstock. This gasifier utilizes an external combustor to provide the energy for biomass gasification and operates at atmospheric pressure. The gases produced are reformed at 14 atm^b pressure and 847°C, after which a shift reactor and Selexol unit prepare a synthesis gas which is fed to a methanol converter. All components are conventional commercial design or, in the case of the gasifier, have been demonstrated on a large scale. Similar calculations were performed for the Hynol process which consists of a biomass hydrogasifier, a steam reformer, and a methanol converter operating at higher pressure (30 atm) than the other system. The reformer also operates at higher temperature (950-1000°C). The Hynol system (Figure 1) consists of two process loops: a gasification loop contains the gasifier, desulfurizer, reformer, heat recovery steam generators (HRSGs), distillation unit, and compressor. The second Hynol loop contains a methanol converter, a recycle compressor, and a condenser. A recycle stream, predominantly hydrogen, is returned from the methanol converter to the gasifier, thus connecting the two process loops. This hydrogen recycle, which is passed through a heat exchanger to recover high temperature heat from the reformer, is a unique feature that distinguishes Hynol from other systems: the recycle stream entering the gasifier provides sufficient enthalpy for gasification so that no external combustor, or internal partial oxidation of the biomass, is necessary. Thus, a higher overall conversion efficiency is expected for Hynol as well as a leveraging of methanol yield due to the natural gas added. Another important distinction of this gasifier is that no tars are expected to be produced, allowing heat recovery before desulfurization.

A base-case Hynol system was set up and analyzed, consisting of a biomass preparation block, a gasification block, a steam reforming block, a distillation block, and a methanol synthesis block. Material

and energy balances on each block and the overall electric power were determined for operation of the integrated system. Adjustments were then made in operating conditions to bring the overall power requirements in balance with the power that can be recovered within the system. The basis for comparison of process configurations and operating performance with regard to CO₂ emissions, methanol yield, and cost was that no electric power import be required. A sensitivity analysis of the base case established the effects of the operating variables for which assumed values were required, including biomass carbon conversion, steam/carbon ratio, reformer and methanol converter approach-to-equilibrium, reformer temperature, and natural-gas-to-biomass feed ratio. Guided by the relative effects of these variables, process optimization was carried out using reactor pressures and heat exchanger pressure drops as inputs.

Results and Discussion

Table 1 gives the composition and conditions of the principal streams identified in Figure 1, assuming 100 kg of dry biomass feed containing 10 wt% moisture. These compositions correspond to a natural gas feed rate of 3.79 kg-mols as process feed and 2.60 kg-mols as reformer fuel. This ratio of total natural-gas-to-biomass is optimum for overall fuel-cycle CO₂ emission reduction as indicated by Figure 2. Fuel-cycle CO₂ emissions include those from biomass cultivation, harvest, and delivery to the plant; natural gas extraction, purification, and transport to the plant; production of methanol from the feedstocks; transport of the methanol to vehicle refueling stations; and use of that fuel in FCVs. The net overall CO₂ emission reduction is determined by comparison with gasoline where the fuel cycle emissions include those from oil extraction, transport, and refining; and the distribution and use of gasoline in conventional vehicles.

Methanol can be produced also from biomass or natural gas separately, and it is, therefore, pertinent to compare the efficiency of the Hynol process with the performance of the best options for using the same biomass and natural gas feedstocks for production of methanol by separate routes. For this purpose, the Princeton system that utilizes the Battelle gasifier was taken as the most efficient method for biomass, and the conventional steam reforming route used for commercial methanol production was taken for natural gas conversion. This comparison shows that the Hynol route would achieve 20 % greater combined net CO₂ emission reduction than the other options for use of

^a1 quad = 10¹⁵Btu = 1.055x10¹⁸J

^b1 atm = 101 kPa

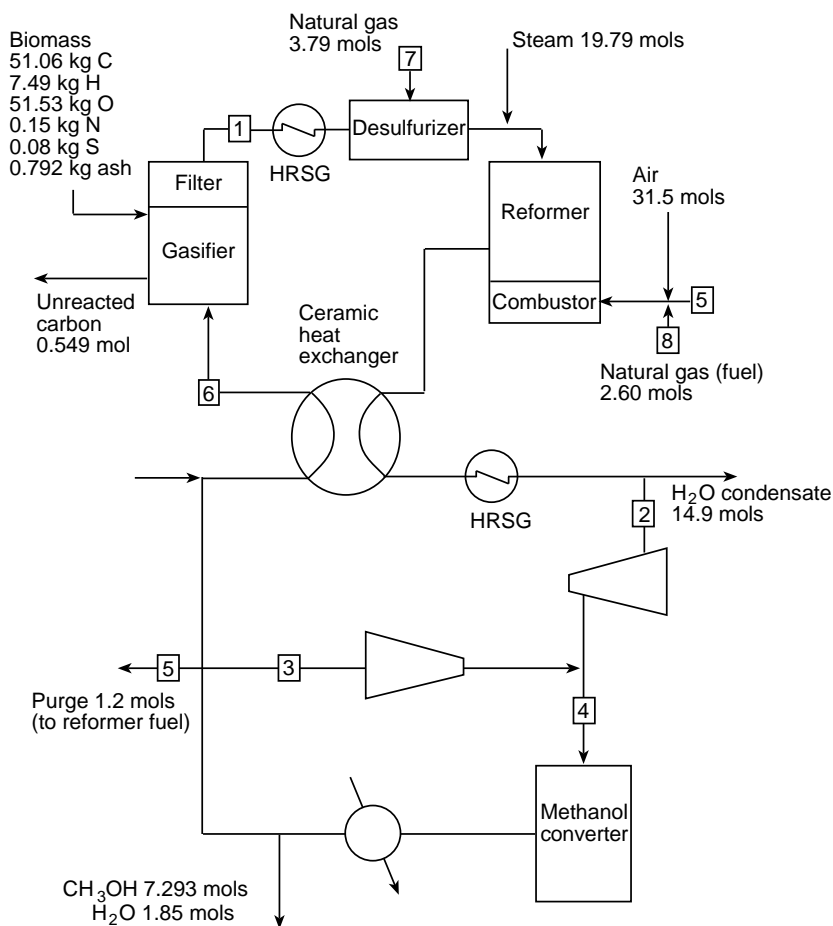


Figure 1. The Hynol process.

Table 1. Composition of Hynol Process Principal Streams Identified in Figure 1

	Stream composition, kg-mols							
	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8
H ₂ O	2.997	0.168	0.163	0.265	0.0008	1.407	0	0
H ₂	6.10	26.23	193.93	220.16	0.9361	8.714	0	0
CO	1.698	6.540	17.63	24.17	0.0851	0.7923	0	0
CO ₂	0.9006	2.335	10.77	13.10	0.0520	0.4838	0.00758	0.0052
CH ₄	2.713	0.247	4.92	5.165	0.0237	0.2210	3.589	2.462
C ₂ H ₆	0	0	0	0	0	0	0.1061	0.0728
N ₂	0.847	0.935	18.74	19.68	0.0905	0.8421	0.08717	0.0589
CH ₃ OH	0	0	2.44	2.44	0.0118	0.1096	0	0
Sum	15.26	36.45	248.6	285	1.20	12.57	3.79	2.60
Deg C	800	51	40	51	40	950	90	90
Atm	29	22.3	30.0	36.0	30	29.5	28.0	1.5

those resources. Given the fact that biomass supply will be the limiting factor that determines the extent to which petroleum can be displaced by that resource, it is important that the use of natural gas as co-feedstock greatly leverages the yield of transportation fuel (by a factor of 4.8). As a result of this leveraging and increased gasoline displacement, the CO₂ emission reduction from the overall vehicle population is twice as great as that which could be expected if biomass alone were used as a source of alternative fuel for FCVs.

A thermochemical process such as Hynol that utilizes natural gas as co-feedstock with biomass has the additional advantage that it can be configured to produce either methanol or hydrogen. Hydrogen, although not compatible with the existing vehicle refueling infrastructure, is the ideal fuel for FCVs and the most favorable in terms of environmental benefits and petroleum displacement potential. Simulations of the Hynol process for production of hydrogen were, therefore, also examined. Figure 3 and Table 2 show this re-configuration which replaces the methanol converter and condenser with shift reactors and pressure swing adsorbers (PSAs). The results show that 21.74 kg-mols of hydrogen can be produced (and compressed to 5000 psi) from the same feedstocks used for methanol production with a thermal efficiency of 68.1 % and a total fuel-cycle CO₂ emission reduction of 1091 kg when utilized in FCVs and compared to gasoline used currently. This compares to 68.4 % thermal efficiency and 724 kg CO₂ emission reduction for the methanol production case.

Cost estimates were carried out for both methanol and hydrogen production. A plant size of 7870 tonnes (biomass) per day was assumed in accordance with Princeton's evaluation of the optimal balance between economy of scale for the plant and the cost of biomass delivered from remote sources. The delivered cost of woody biomass for that plant, produced in North Central region of the U.S., was \$61/tonne and a price of \$2.37/GJ was assumed for natural gas. Other cost assumptions included a capital recovery factor of 15.45%; 13% after-tax rate of return, including 2.7% inflation rate; and 26% corporate income tax rate. The cost estimate for the production of methanol on this basis is \$0.416/gal (\$6.09/GJ) and \$5.98/GJ for hydrogen. Compared to the production cost of gasoline and the fuel economy of gasoline in current vehicles, methanol used in dedicated conventional vehicles would cost about 2.4 cents per

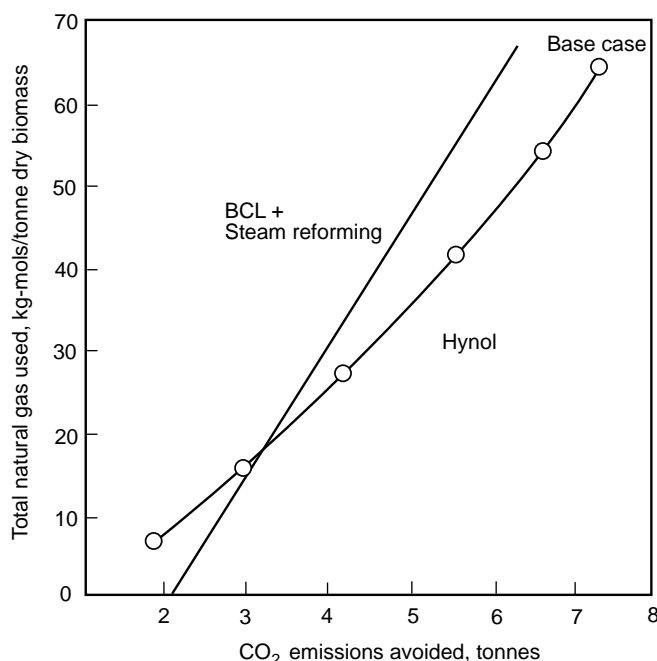


Figure 2. Total fuel-cycle CO₂ emission reduction performance of Hynol process as a function of the ratio: natural gas feed/biomass fed. Assumes methanol is used in FCVs, displacing conventional vehicles using gasoline.

vehicle mile vs 2.2 cents for gasoline at current crude oil prices. Compared to projected oil prices for the year 2010, the cost of methanol used in either flexible-fuel vehicles or dedicated ICEVs would be competitive with gasoline. As indicated in Figure 4, methanol or hydrogen used in FCVs should cost significantly less per vehicle mile than gasoline for any scenario.

Comparisons were made with other CO₂ mitigation technology; namely, the recovery and sequester of CO₂ from coal-fired power plants for which a cost of \$119/tonne of CO₂ reduction has been published as the lowest current estimate for a U.S. power plant. By contrast, the use of Hynol methanol in dedicated conventional vehicles would cost \$52/tonne, and in FCVs would have a negative cost of -\$33/tonne. The economic as well as the environmental benefits of FCVs using Hynol methanol would be substantial even without considering the additional benefits due to reduction of external and social costs of the petroleum displaced and will increase further when hydrogen's distribution infrastructure problems are solved.

The feasibility of utilizing carbonaceous municipal wastes, such as landfill gas and sewage sludge, as co-feedstocks for the Hynol process were examined, both as partial substitutes for natural gas and

woody biomass and for total displacement of those feedstocks. The results indicate that these materials could be used in amounts that are determined only by the quantities available at a given site. Co-feeding with natural gas and woody biomass will yield greatest petroleum displacement potential and most effective in terms of CO₂ emission reduction.

Comparison was also made between Hynol and a modification of the Princeton system that would allow its use of natural gas as co-feedstock with woody biomass for production of methanol (Figure 5, Table 3). Those modifications include the enlargement of the reformer to allow addition of natural gas and steam and enlargement of the compressor, heat recovery system, and methanol synthesis reactor to compensate for the increased throughput. Assuming the same feed rates of natural gas and biomass, and the same steam/carbon ratio for reforming, the results show a thermal efficiency of 64.7% and a total fuel-cycle CO₂ emission reduction of 660 kg when the methanol is used in FCVs. The shift reactor and Selexol unit, normally required when biomass is the only feedstock, are no longer needed when natural gas supplements biomass as feed. This configuration has not been optimized and is expected to improve with further analysis.

Conclusions and Recommendations

In addition to specific conclusions regarding the Hynol process as a potential technology for production of transportation fuel, a number of general conclusions regarding the use of biomass and natural gas as national resources for production of alternative fuels are discussed from the perspective of achieving maximum environmental and economic benefit.

Among the latter are:

- A sustainable system of road transport for the future will require a large reduction of the environmental and economic impacts of the current vehicle and fuel technologies
- Greenhouse gas emissions are a central issue of current road transport and must be a criterion in evaluating future vehicle/fuel systems.
- Clean alternative fuels can be produced from renewable biomass produced on dedicated energy plantations, and such fuels could eliminate most of the net overall fuel-cycle CO₂ emissions from the vehicles using them. Liquid alternative fuels produced from biomass can provide the driving range and compatibility with the existing refueling infrastructure that are needed to compete with existing fuels, but cannot be produced from biomass alone at a cost that would allow wide acceptance in a free market. Even if marketable, the amount of bio-fuel that could be produced on a sustainable basis from energy crops would not be sufficient to displace enough petroleum to appreciably affect greenhouse gas emissions from U.S. road transport. Biomass and natural gas used together could overcome the limitations of each when used in a process to convert them to liquid fuel as methanol.
- Any alternative fuel considered for a sustainable future transportation technology should be compatible with fuel cell vehicles. More than any other factor, vehicles powered by fuel cells offer great potential for increased fuel economy and reduction of vehicle emissions, including greenhouse gases. Fuel cell vehicles will require hydrogen fuel, either as compressed gas or as a liquid hydrogen-carrier. Methanol is the liquid hydrogen-carrier most easily and efficiently converted to hydrogen on-board a vehicle and can be produced from biomass, natural gas, or a combination of both.

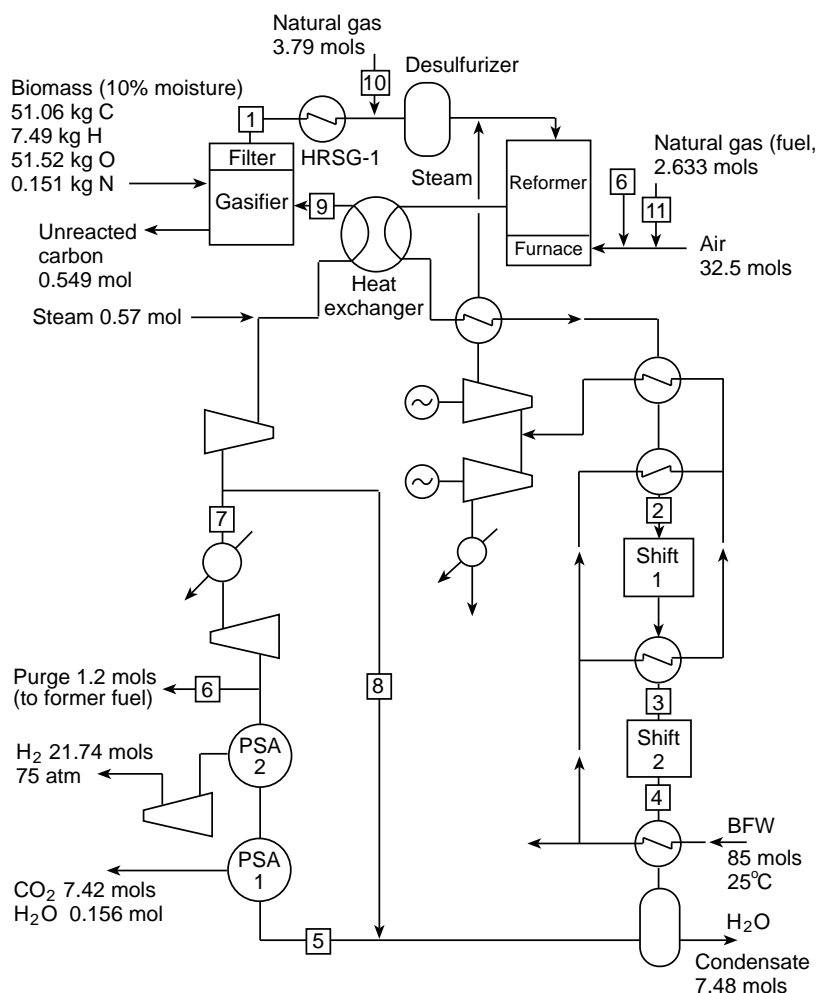


Figure 3. Hynol process configured for hydrogen production (BFW = boiler feed water).

- Methanol can be produced from biomass and natural gas at a cost that will be competitive with current gasoline costs and provide major reduction of net CO₂ emissions as well as elimination of particulates and criteria pollutant (carbon monoxide, volatile organic compound, and nitrogen oxide) emissions when used in fuel cell vehicles. Using natural gas as the primary energy source, and biomass providing 25% of the energy input for methanol production, the amount of petroleum displaced would be leveraged by a factor of 4.8 relative to the use of biomass alone, and the production cost would be reduced by 40%. Overall CO₂ emission reduction would be twice as great as the potential for CO₂ reduction using bio-fuels alone.
- Thermochemical processes can produce either methanol or hydrogen for FCVs, leveraging the yield of either fuel and reducing its cost by using natural gas as co-feedstock. Municipal carbonaceous wastes such as sewage sludge, landfill gas, digester gas, and solid wastes normally flared or sent to landfills should be acceptable co-feedstocks with energy crops for production of methanol or hydrogen. Landfill gas or digester gas can displace part of the natural gas used by the process, limited only by the amount of such waste gas available at a given location.
- The BCL process, using only biomass and no natural gas, will yield 14.77 kg-mols of methanol per tonne of biomass at a cost of \$12.4/GJ. Used in FCVs, that methanol will displace 134 gallons^c of gasoline with a net overall fuel-cycle CO₂ emission reduction of 2.04 tonnes. The thermal efficiency

Table 2. Composition of Streams Identified in Figure 3 for Hydrogen Production

	Stream composition, mols										
	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10	Stream 11
H ₂ O	2.240	13.057	10.062	7.632	0.1562	0	0	0	0.570	0	0
H ₂	6.214	26.593	29.588	32.018	32.45	1.0122	9.697	0.453	9.262	0	0
CO	1.042	5.761	2.766	0.3361	0.350	0.0331	0.3173	0.0142	0.0303	0	0
CO ₂	0.4055	1.995	4.990	7.420	7.420	0	0	0	0	0.00758	0.00526
CH ₄	3.127	0.6284	0.6283	0.6284	0.655	0.0619	0.5930	0.0266	0.5665	3.589	2.493
C ₂ H ₆	0	0	0	0	0	0	0	0	0	0.1061	0.0737
N ₂	0.8535	0.9407	0.9407	0.9407	0.9806	0.0927	0.8878	0.0398	0.848	0.08717	0.0606
Sum	13.88	48.98	48.98	48.98	42.02	1.20	11.50	0.515	11.55	3.79	2.633
Deg C	800	407	167	227	40	40	40	40	900	150	150
Atm	30.5	22.9	21.9	22.3	20.8	1.5	20.8	20.8	31.0	30.3	1.5

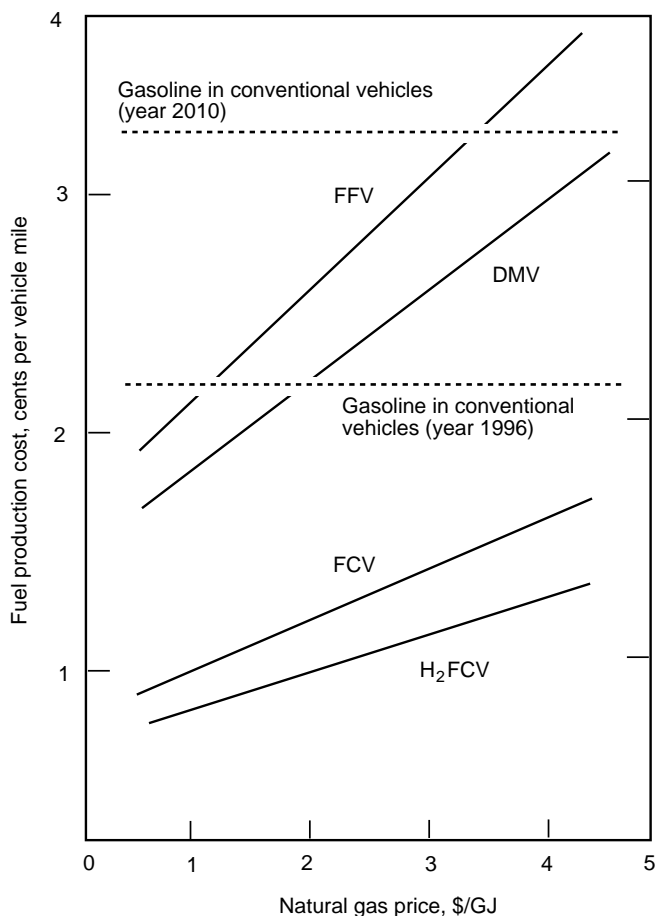


Figure 4. Comparison of fuel production costs with gasoline. Basis: gasoline fuel economy = 27 miles per gallon used in internal combustion engines (ICEs). FFV = M85 in flexible fuel ICEVs, DMV = M100 in dedicated ICE vehicles, FCV = methanol in fuel-cell vehicles, H₂FCV = hydrogen in fuel-cell vehicles. (1 mi = 1.6 km)

of the BCL process is 51.1% with no electric power import.

- Natural gas can be used as co-feedstock to enhance the methanol yield of a process designed exclusively for biomass by adding it, with steam, to the gasified biomass entering the reforming step. The result eliminates the need for a shift reactor and Selexol unit, which are normally required without natural gas addition. Import of electric power, or use of biomass to produce electric power for the process, will also be no longer required. Overall efficiency will be marginally less than the Hynol process, but should not require development or demonstration of new technology.

Conclusions specific to the Hynol process are:

- Optimum performance with respect to overall net fuel-cycle CO₂ emission reduction from FCVs using ethanol will be obtained with natural gas comprising 75% of the Hynol feedstock energy. One tonne of biomass and 6.276 kg-mols of natural gas will yield 72 kg-mols of methanol at a cost of \$6.09/GJ and displace 944 gallons of gasoline with a net overall fuel-cycle CO₂ emission reduction of 7.24 tonnes. The thermal efficiency is estimated at 68.4% with no electric power import.
- Desulfurization must take place prior to reforming to protect the reformer tubes and catalyst. Zinc oxide at 268°C will reduce the equilibrium H₂S concentration entering the reformer to the required level of 0.02 ppm. Maximum thermal efficiency will require recovery of heat as high-pressure steam between the gasifier at 800°C and the desulfurizer at 268°C.

This can be accomplished only if tars are not formed during biomass gasification. Biomass carbon conversion as low as 82% can be accepted if ungasified carbon is utilized as part of the fuel for the reformer furnace. This can be accomplished by using it in a separate furnace to preheat combustion air.

- Acceptable performance will be obtained with a reformer operating within a -30K temperature-equivalent approach to equilibrium. Acceptable performance will require that the methanol converter operate at a temperature-equivalent approach to equilibrium not exceeding +18K. This is a critical variable and the design value should be +12K or less. The Lurgi type methanol reactor is superior to the ICI design for this system because the medium-pressure steam recovered provides a significant amount of the electric power required by the process.

The following suggestions are made:

1. The sustainability of road transport, in terms of minimization of its impacts by means of technological improvements, will be effectively realized by the introduction of fuel-cell vehicles. The greatest environmental benefits will accrue if those vehicles use non-petroleum fuels, especially those derived from both biomass and natural gas. Those resources should be used together and not separately for fuel production.
2. Mitigation of greenhouse gas emission should be undertaken in the area of road transport before it is considered for stationary sources, because the cost will be considerably less and additional benefits will be obtained that would not occur if CO₂ were recovered after combustion in power plants.
3. These simulation results do not substitute for pilot tests. Technical assumptions made for this assessment of the Hynol process need to be verified by actual tests in hardware. They include: the ability to operate the gasifier without tar formation, the ability to operate a reformer at 950°C and 32 atm pressure, the ability to attain 87% carbon conversion of the biomass, and the ability to operate a ceramic heat exchanger (or any other type) at 950°C hot-side inlet and 110-900°C on the cold side with a pressure differential of 10 atm between sides.

^c1 gal = 3.79 liters

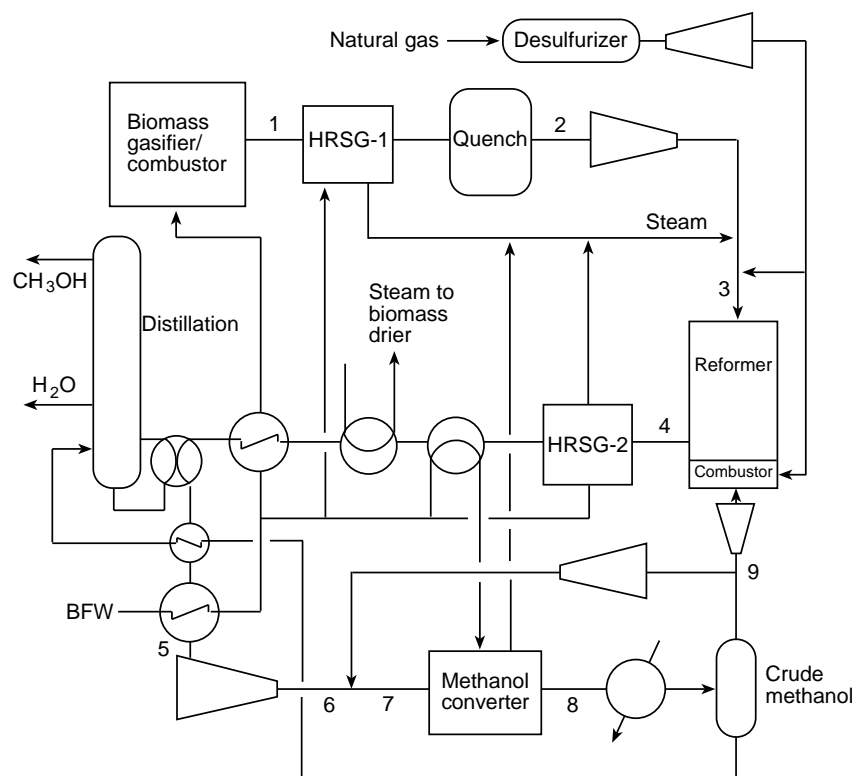


Figure 5. Configuration of biomass-to-methanol process for addition of natural gas.

Table 3. Compositions of Streams Identified in Figure 5

Stream composition, mols									
	Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9
H ₂ O	1.645	2.922	19.85	12.24	0.2193	0.0552	0.0736	2.330	0.0012
H ₂	0.776	0.776	0.776	18.36	18.36	18.356	56.94	41.09	2.493
CO	1.726	1.726	1.726	4.637	4.637	4.637	6.131	1.591	0.0965
CO ₂	0.416	0.416	0.4255	2.774	2.774	2.774	7.337	5.081	0.2949
CH ₄	0.588	0.588	5.086	0.535	0.535	0.535	8.247	8.249	0.4984
C ₂ H ₄	0.194	0.194	0.194	0	0	0	0	0	0
C ₂ H ₆	0.027	0.027	0.160	0	0	0	0	0	0
N ₂	0.016	0.016	0.1253	0.1253	0.1253	0.1253	2.005	2.005	0.1215
CH ₃ OH	0	0	0	0	0	0	0.2192	7.015	0.0141
Sum	5.388	6.665	28.34	38.67	26.65	26.48	80.95	67.36	3.52
Deg K	1200	355	858	1140	313	313	319	533	313
Atm	1.0	1.0	16.89	14.11	9.13	104.5	104.5	104	96
Natural gas used as process co-feedstock, mols						4.75			
Natural gas used as reformer fuel, mols						1.526			
Steam fed to reformer, mols						19.8			
Steam/carbon ratio in reformer						2.50			
Reformer duty, cal/sec						95379			
Methanol product, mols						6.781			

Robert H. Borgwardt is the EPA Project Officer (see below).
The complete report, entitled "Hynol Process Evaluation," (Order No. PB98-127319; Cost: \$41.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:
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