THE COPROCESSING OF FOSSIL FUELS AND BIOMASS FOR CO$_2$ EMISSION REDUCTION IN THE TRANSPORTATION SECTOR

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ABSTRACT

Conversion of biomass to alcohol for displacement of petroleum fuels can effectively mitigate CO$_2$ emissions. Coprocessing biomass with natural gas to produce methanol can maximize the amount of petroleum displaced and minimize mitigation cost. This paper discusses process simulations and reaction rate studies of a biomass gasification process aimed at these goals.

KEYWORDS

Hydrocarb; biomass; methanol; transportation; alternative fuel.

INTRODUCTION

Research is underway to evaluate the Hydrocarb process for conversion of carbonaceous raw material to clean carbon and methanol products. These products are valuable in the market either as fuel or as chemical commodities. As fuel, methanol and carbon can be used economically, either independently or in slurry form, in efficient heat engines (turbines and internal combustion engines) for both mobile and stationary single and combined cycle power plants. When considering CO$_2$ emission control in the utilization of fossil fuels, the coprocessing of those fossil fuels with biomass (which may include wood, municipal solid waste, and sewage sludge) is a viable mitigation approach. By coprocessing both types of feedstock to produce methanol and carbon--and sequestering all or part of the carbon--a significant net CO$_2$ reduction is achieved if the methanol is substituted for petroleum fuels. Biomass removes CO$_2$ from the atmosphere by photosynthesis and is thus a prime feedstock for mitigation of CO$_2$ emission from mobile sources. Since the availability of biomass will, in most cases, determine the amount of petroleum that can be displaced, it is essential to obtain maximum yield of fuel from the biomass conversion process.

Basic Hydrocarb Process

The Hydrocarb process would use carbonaceous feedstock or combination of feedstocks to produce, in addition to pure carbon, the coproducts, hydrogen, methane, or methanol (Fig. 1). A simplified block flow diagram is shown in Fig. 2 for converting biomass and natural gas to carbon and methanol. It combines three basic steps: (1) a hydropyrolyzer (HPR) in which the carbonaceous material is hydrogasified with a recycled hydrogen-rich gas to form a methane-rich gas, (2) a methane pyrolyzer (MPR) in which methane is decomposed to carbon and hydrogen, and (3) a methanol synthesis reactor (MSR) in which the CO is catalytically combined with hydrogen to form methanol (MeOH or CH$_3$OH) and the remaining hydrogen-rich gas is recycled to the first step (HPR). The principal distinguishing features of the process are that the hydropyrolysis is an exothermic reaction which does not require

internal heating, the methane pyrolysis is an endothermic process which does require heating, and the recycled hydrogen-rich gas conserves the energy balance in the process.
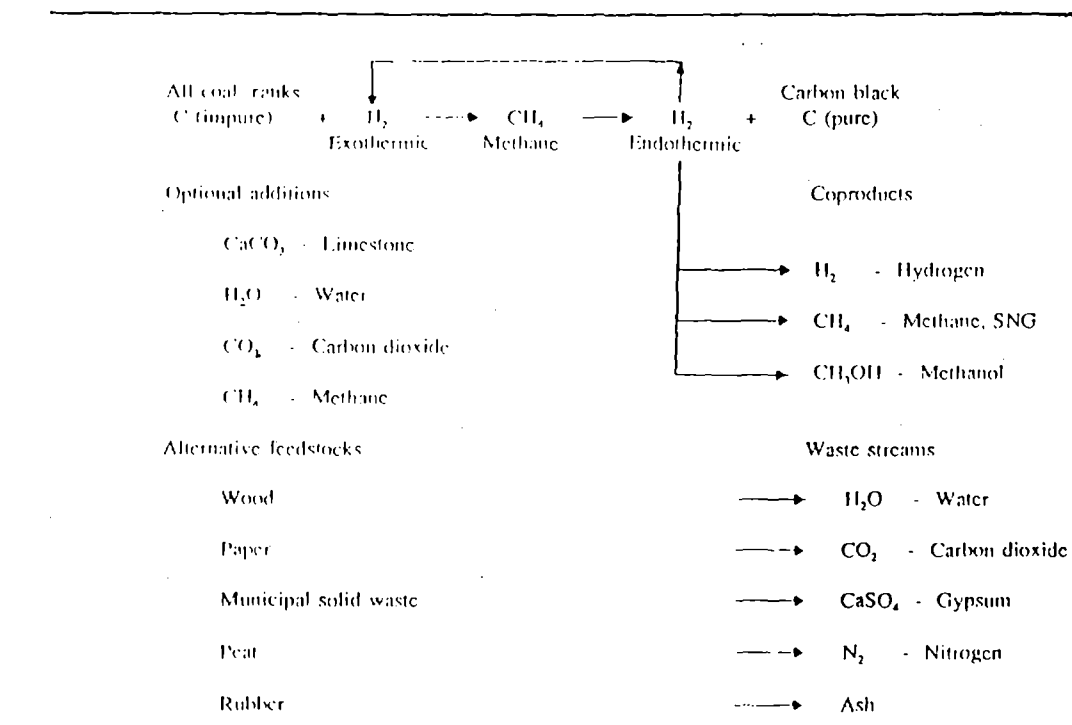

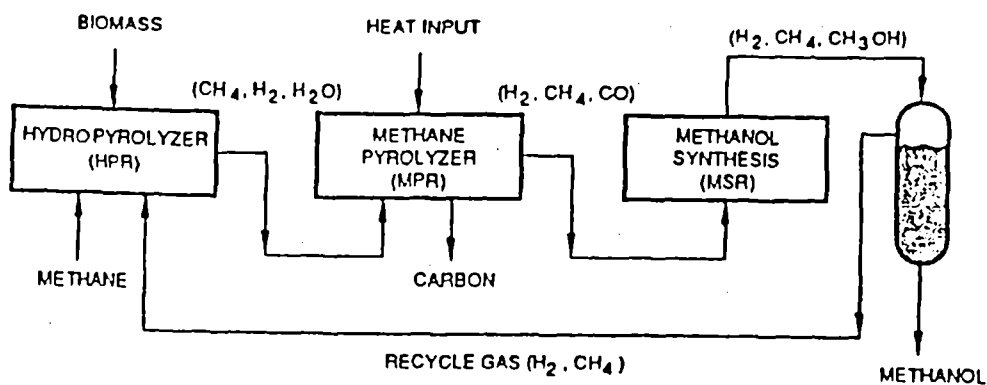Fig. 1. Production of a clean carbon fuel and coproducts.

Fig. 2. Hydrocarb process block diagram.

PROCESS CHEMISTRY

The first two steps of the Hydrocarb process have been successfully tested, albeit at different conditions than those to be discussed here, at pilot plants operated by Rheinbraun in Germany (hydropyrolysis of coal) and UOP in the U.S. (continuous methane pyrolysis); the third step, methanol synthesis, is practiced on a commercial scale with natural gas as feedstock. Process design calculations using thermochemical equilibrium data indicate that the Hydrocarb reactors should operate in the range of 50 atm (5 MPa) pressure with temperatures in the range, 800°-900°C for the HPR, 1000°-1100°C in the MPR, and the MSR at 260°C. In addition to literature data, kinetic data were needed for designing the hydropyrolyzer with biomass feedstock and for the thermal decomposition of methane at the design conditions. The following experimental study was therefore undertaken.

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Hydropyrolysis of Biomass

The pyrolysis and hydropyrolysis of biomass in the form of poplar wood sawdust having particle size less than 150 μm in diameter were investigated in a 25 mm ID and 2.5 m long tubular reactor facility at Brookhaven National Laboratory (Steinberg et al., 1993). The tests were conducted at temperatures up to 800°C and pressures between 30 and 50 atm. The experiments were performed in two different modes, depending on the heat-up rate. In the low heat-up rate mode, the biomass was first loaded in the reactor at room temperature. Hydrogen was then introduced into the system to a desired initial pressure level. The reactor was slowly heated up at a rate of less than 10°C/min. The change in the pressure in the reactor and the composition of the effluent gas were monitored with time. In the higher heat-up rate mode, the reactor was heated and pressurized with hydrogen up to the desired reaction conditions before introducing the biomass. The variations of pressure and gas composition versus time were then recorded and analyzed. From these data, rates of reaction and degree of conversion were determined.

At the low heat-up rate, the reaction proceeds in two steps. The first step, biomass pyrolysis, takes place at temperatures of 300 to 400°C and then hydropyrolysis takes place at 700°C and above. This was confirmed by experiments using pressurized thermogravimetric analysis (PTGA). Under conditions of rapid heat-up at higher temperature and higher hydrogen pressure, gasification and hydrogasification of biomass are especially effective in producing CO_2 and methane. An overall conversion of 88 to 90 wt% of biomass was obtained. This agrees with previous work on flash pyrolysis and hydropyrolysis of biomass under rapid heat-up and short residence time conditions (Steinberg and Fallon, 1981). Initial rates of biomass conversion increase significantly with increases in hydrogen pressure. At 800°C and 51.3 atm the initial rate of biomass conversion to gaseous components was 92% per min.

Thermal Decomposition of Methane

The reaction rate of methane decomposition was investigated in the temperature range 700 to 900°C at pressures ranging from 28 to 56 atm using the same reactor facility at Brookhaven (Steinberg et al., 1993). In these experiments, methane was fed into the reactor continuously. Gas from upstream and downstream of the reactor was analyzed on-line to calculate the reaction rate. The variations in methane concentration vs. residence time under different operating conditions are shown in Figure 3.
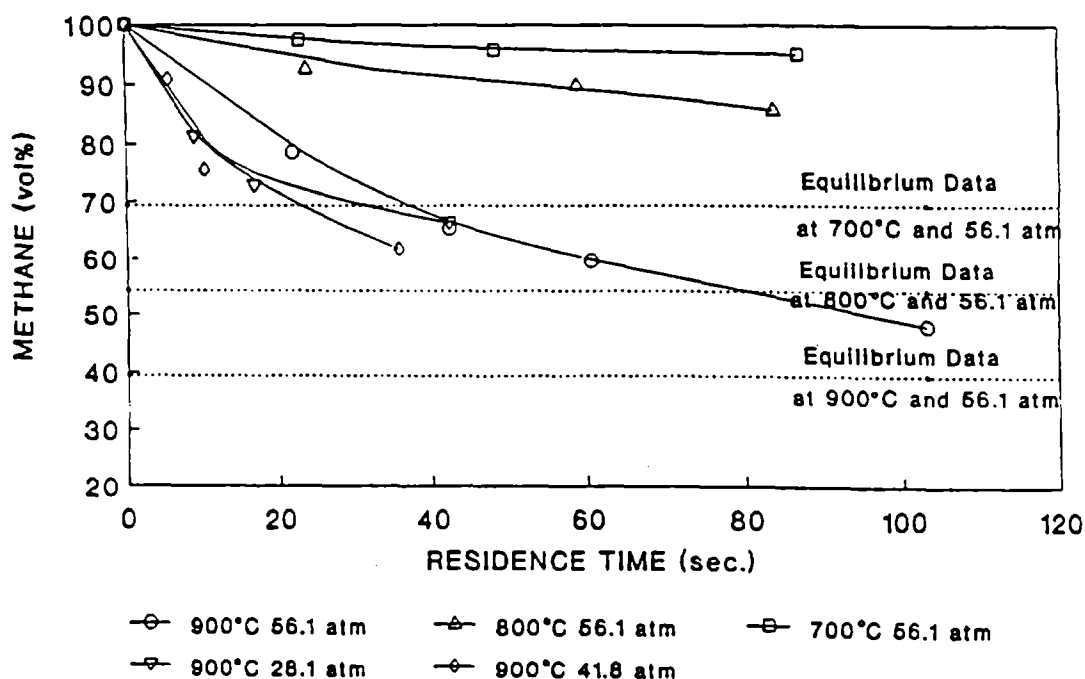

Fig. 3. Methane concentration vs. residence time.

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A gas residence time of about 2 min. is required for the reaction to reach near equilibrium composition at 50 atm and 900°C. From a first order Arrhenius rate model, the activation energy for methane decomposition is determined to be 31.3 kcal/mol CH_4 (131 kJ/mol). This low value suggests that the high-surface-area submicron carbon particles formed in the reactor catalyze the methane decomposition reaction. At 900°C, the rate constant was approximately independent of pressure in the range investigated, 28 to 56 atm. The rate of methane decomposition increases with methane partial pressure to the first order. It is concluded that the rate of methane decomposition is favored by higher temperatures and pressures, while the thermochemical equilibrium of methane decomposition is favored by lower pressures. By extrapolating to higher temperatures using the derived rate equation, the residence time to reach near equilibrium at 50 atm would be 41 sec. at 1000°C and 12 sec. at 1100°C.

PROCESS SIMULATION COMPUTER MODEL

A process simulation computer model was developed based on well-known thermodynamic data taking into account equilibrium among the gaseous species CH_4, CO, CO_2, H_2, and H_2O and carbon in the solid phase. This detailed model allows the complete determination of the mass and energy balances around each reactor and around the entire process for various feedstock types and for various pressure and temperature conditions in each reactor. From numerous simulations, we cite here only two which are most relevant to CO_2 emissions reduction (Dong, et al., 1992). In one configuration we obtain a net zero CO_2 emission, and in the other configuration we maximize the production and utilization of methanol as transportation fuel and substantially reduce CO_2 emission, although not to zero.

Figure 4 shows a process flow diagram for zero CO_2 configuration: poplar wood and natural gas are feedstocks and the product carbon is sequestered while the methanol is utilized. All stream compositions are indicated in the diagram.
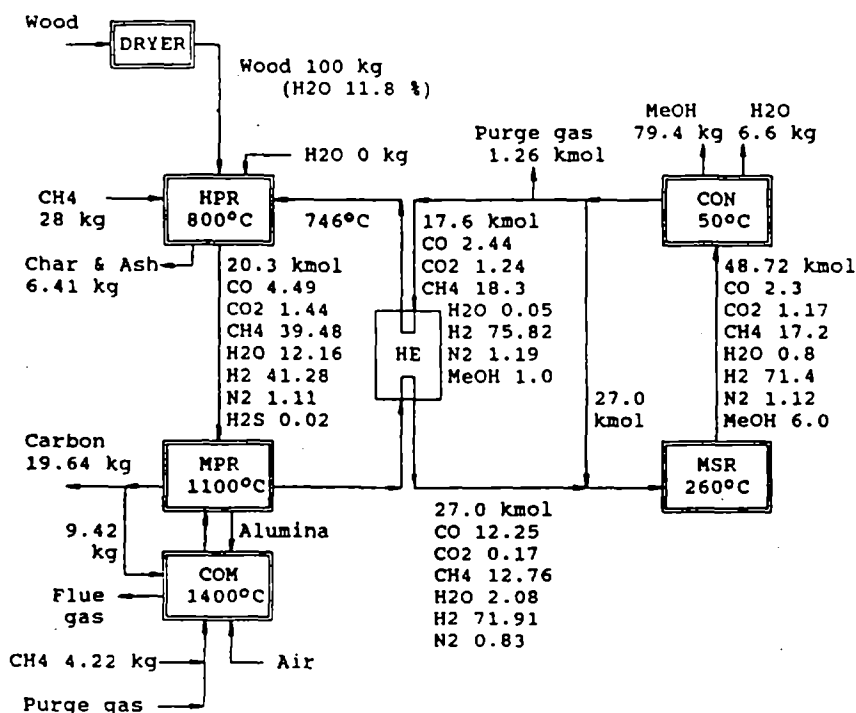

Fig. 4. Hydrocarb process simulation for zero CO_2 emission.
Carbon efficiency = 42.57%, Thermal efficiency = 50.33%.
Sequester 19.64 kg carbon per 100 kg dry biomass feed.

The thermal efficiency of the process was determined to be 50.3% which includes the energy necessary to heat the MPR supplied by burning methane in the MPR heater. The net CO_2 emission for this system is zero as calculated as by:

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Net carbon   Carbon emitted from the combustion of methanol as fuel <u>minus</u> carbon removed
emission = from the atmosphere by photosynthesis of biomass <u>minus</u> carbon sequestered
(as CO_2)   <u>plus</u> carbon emitted as CO_2 from the MPR combustor (fueled by natural gas,
                 purge gas, and carbon)

Figure 5 shows a configuration in which the methane feedstock is increased and more methanol is produced while all the carbon produced in the MPR is used, in addition to methane and purge gas, to supply heat to the MPR. The thermal efficiency for this system is 72.5% and the net CO_2 emission is 94 lb/CO_2/10^6Btu (40.6 kg CO_2/GJ) which is 55% less than the displaced gasoline emission. The configuration shown in Figure 5 maximizes the methanol production and minimizes the methanol production cost.
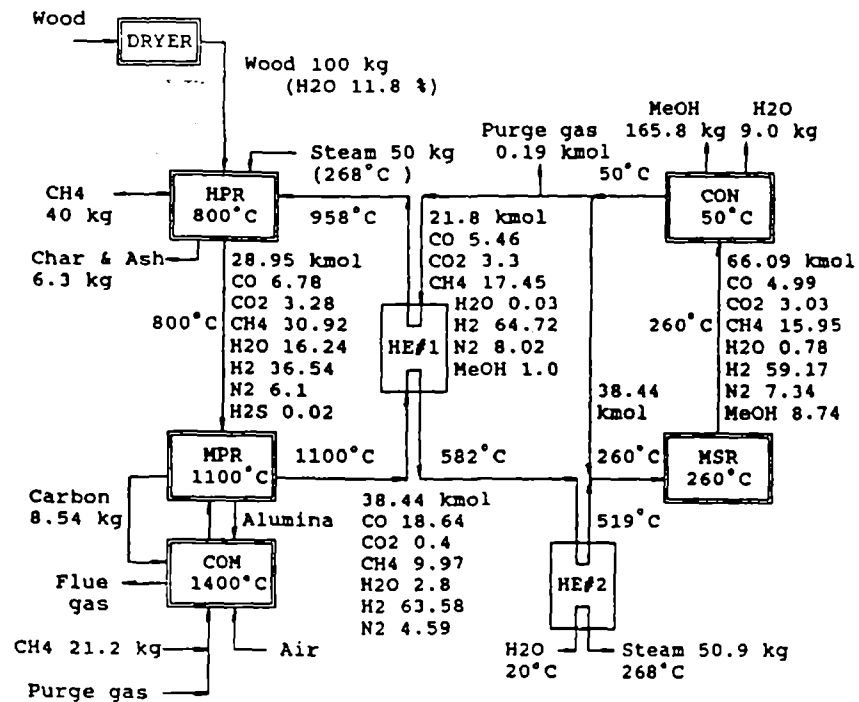
Fig. 5. Hydrocarb process simulation for maximum methanol yield and minimum production cost. Carbon efficiency = 67.8%, Thermal efficiency = 72.5%, CO_2 emission = 94 lb/10^6Btu. No carbon sequestered.

To show the efficiency of the Hydrocarb technology for methanol production and CO_2 reduction, a comparison is made with separate conventional biomass gasification and natural gas reforming plants. Table 1 summarizes this comparison based on fixed unit amounts of biomass and natural gas fed to each plant and compares the methanol yield with a Hydrocarb plant configured according to Figure 5. The biomass gasification plant is based on a range of values from four gasification processes evaluated by Larson and Katofsky (1992). It is seen that a Hydrocarb plant can produce from 11 to 25% more methanol than two individual plants utilizing the same feedstocks. Furthermore the CO_2 emission per unit methanol energy (lb CO_2 emitted/10^6Btu) is 20 to 35% less than the two combined plants.

It also can be seen from Table 1 that the biomass leverages natural gas in the Hydrocarb plant so that the yield of methanol per unit of natural gas is as high as 79% greater than the yield from a natural gas reforming plant alone. Conversely, natural gas leverages biomass in the Hydrocarb plant to produce up to 4.2 times the yield of methanol per unit of biomass from a biomass gasification plant alone.

Table 1. Comparison of methanol production and CO_2 reduction obtainable from Hydrocarb and from separate conversion of biomass and natural gas

Factor	Hydrocarb process	Biomass gasification[a]	Natural gas reforming[b]
Feedstock			
Dry biomass (wood), kg	88.2	88.2	0
Natural gas (CH_4), kg	61.2	0	61.2
Thermal efficiency, %	73	64 - 50	64 - 60
Carbon efficiency, %	68	41 - 32	78 - 73
Methanol yield, kg MeOH/kg feedstock	1.88/biomass 2.61/CH_4 1.11/total	0.57 - 0.45	1.56 - 1.46
Total production, kg MeOH	166	50.3 - 39.7[c]	99.4 - 93.0[f]
Net CO_2 emission, kg	144	0	168
lb CO_2/10[6]Btu MeOH (LHV)[d]	94	0	180 - 193
kgCO_2/GJ MeOH (LHV)	40.6	0	77.8 - 83.8
Gasoline displaced, gal.[e]	35.8	10.9 - 8.6	21.5 - 20
Net CO_2 reduction from displaced gasoline, kg	178	98 - 77	0

[a] The range of values represents the four gasification processes evaluated by Larson and Katofsky (1992).

[b] Ranges shown represent performance of different reforming technologies (Wyman et al., 1992).

[c] The sum of the lowest and highest methanol production for the biomass and natural gas individual plants = 132.7 to 119.7 kg MeOH. Thus the Hydrocarb plant with a production of 166 kg yields 11 to 25% more MeOH than the sum of the two individual plants for the same amount of biomass and natural gas feedstock.

[d] Lower heating value

[e] 1 gal. = 3.785 liter

HYDROCARB METHANOL AS AN ALTERNATIVE TRANSPORTATION FUEL

An analysis can also be made with respect to CO_2 emissions when considering methanol's displacing gasoline as a transportation fuel. About 30% of the U.S. anthropogenic CO_2 emission comes from the transportation sector which is about equal to emissions from stationary sources. EPA has estimated that 1.54 gal. of methanol can displace 1 gal. of gasoline in automobiles on a mileage per unit energy basis (Office of Mobile Sources, 1989). Gasoline emits 9 kg CO_2 per gal. For maximum Hydrocarb methanol production configuration (Fig. 5), the CO_2 emitted is 4 kg CO_2 per gal. of gasoline displaced. There is thus a 55% reduction in CO_2 emission by the use of Hydrocarb methanol in displacing gasoline. The next to the last line in Table 1 then indicates the amount of gasoline displaced with the use of Hydrocarb methanol compared to the two individual conventional biomass gasification and natural gas reforming plants. Finally, the last line indicates the net reduction in CO_2 from the displaced gasoline which shows that Hydrocarb methanol can yield from 80% to 130% greater reduction in CO_2 emission than the other conventional biomass gasification plant.

Cost Estimates

The following is a summary of the conclusions of a preliminary economic study of alternate fuel options. The capital cost estimate is based on a comparative analysis with a Texaco Coal gasification process (Fluor Engineers and Constructors, 1981) assuming that equal gas throughput will have the same capital cost when escalated to 1992 dollars. Credit was taken for elimination of the air separation plant and half credit for acid gas removal which are not needed in the Hydrocarb plant. A plant capacity of 5000 dry metric tons of biomass per day (DMT/day) was selected after consideration of the supply area and delivered cost of biomass produced as short-rotation woody crops from energy farms surrounding the plant site. Table 2 gives the economic parameters assumed for methanol production based on the maximum-yield option (Fig. 5) which results in a methanol production cost of $0.405/gal.

Table 2. Hydrocarb methanol production economics based on maximum yield option

Biomass Feedstock	5000 DMT Biomass/Day
Natural Gas Feedstock	4.68×10^6 m³/Day (165×10^6 SCF/Day)
Methanol Production	2.85×10^6 GPD
Capital Investment	838×10^6
Delivered Cost of Biomass	$51.00/DMT
Maximum Distance of Plantation	84 km
Natural Gas Cost	$2.50/$10^6$Btu
Carbon Sequester	$23/ton
O&M	$5.00/DMT Biomass
Return on Equity	25%
Debt/Equity	80%/20%
Total Capital Charge Rate Ind. Inv. on Equity & Taxes	20.9%
Annual Operating Factor	90%
Production Cost of Methanol	$0.405/gal.

An equivalent gasoline price and incremental cost of gasoline displaced is calculated in Table 3. The U.S. national-average gasoline price for the year 1989 was $1.12 per gal. Taking into account methanol displacement, production cost, taxes, markups and distribution cost, the incremental cost of gasoline displaced is equal to $1.01/gal. or 11¢/gal. less than the national average.

Table 3. Incremental cost of gasoline displacement by Hydrocarb methanol

National average gasoline price = $1.12/gal.

Equivalent gasoline price = 1.54($0.405 + $0.12 + $0.07 + $0.06) = $1.01/gal.

where: 1.54 = volumetric ratio, methanol to gasoline
  $0.405 = methanol production cost
  $0.12 = taxes
  $0.07 = markup
  $0.06 = distribution cost

Incremental cost of gasoline displacement = $1.01 - $1.12 = -$0.11/gal.

Impact on Petroleum Displacement

The Energy Policy Act of 1992 (P.L. 102-486) promotes replacement of petroleum motor fuels with alternative fuels to the maximum extent practicable. The intent of the Act is to ensure availability of alternative fuel that will have the greatest impact on (1) reducing oil imports, (2) improving the national economy, and (3) reducing greenhouse gas emissions. The Act sets a 10% replacement goal of petroleum motor fuel with alternative fuels by the year 2000 and 30% by 2010. This means that there would have to be made available a supply of 7.5 quads (1 quad = 1.055×10^{18} J/yr) of alternative fuel by 2010. If biomass supply is limited to 6-12 quads (mainly due to suitable biomass farm areas), then ethanol cannot meet the 30% petroleum displacement goal. On the other hand, Hydrocarb could meet the 30% goal with as little as 2.5 quads of biomass. If we include the addition of MSW (municipal solid waste) as feedstock which is essentially processed biomass, Hydrocarb could further increase the leverage of biomass supply for methanol production.

The number of Hydrocarb plants needed to supply 30% of U.S. highway fuel consumption by 2010 (7.56 quads) amounts to 80 each having a 5000 DMT/day biomass capacity or 40 for 10,000 DMT/day biomass feed capacity. Hydrocarb methanol plants consume 30% less natural gas for the 30% petroleum displacement than when replacing petroleum with compressed natural gas as an alternative fuel. Even if all the petroleum fuel were replaced with Hydrocarb methanol, which would require 8.4 quads of biomass, the natural gas requirement would be 16.5 quads. The U.S. reserve of conventional natural gas is estimated at present to be at least 1000 quads.

CONCLUSION

Our comparisons suggest that the Hydrocarb process has the potential to significantly displace petroleum fuels at a competetive price while reducing CO_2 emissions from the transportation sector. The reaction rate studies and process simulations reported here are the first step in establishing feasibility. The next step, currently underway, is to resolve technical uncertainties of the process with a bench-scale (15-cm I.D. reactors) test facility. This research will be focused on such issues as the control of volatile alkalis during gasification, high-temperature particulate removal, high pressure combustion and indirect heat transfer to the methane pyrolyzer by circulation of inert solids, and high-temperature heat exchanger design.

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