**THE COPROCESSING OF FOSSIL FUELS AND
BIOMASS FOR CO₂ EMISSION REDUCTION IN THE
TRANSPORTATION SECTOR**

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October 1993

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**Prepared for
U.S. Department of Energy
Office of Fossil Energy
Washington, DC 20585**

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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 CO₂ 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 while sequestering all or part of the carbon a significant net CO₂ reduction is achieved if the methanol is substituted for petroleum fuels in the transportation sector. Biomass removes CO₂ from the atmosphere by photosynthesis and is thus a prime feedstock for mitigation of CO₂ 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 in the conversion process.

Basic Hydrocarb Process

The basic Hydrocarb Process would use carbonaceous feedstock or combination of feedstocks to produce, in addition to pure carbon, the coproducts, hydrogen, methane or methanol. Figure 1 is a schematic of the process which combines 3 basic steps; (1) a hydrolypyrolyzer (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 CH₃OH) and the remaining hydrogen-rich gas is recycled to the first step (HPR). A simplified block flow diagram is shown in Fig. 2 for converting biomass and natural gas to carbon and methanol. The principal distinguishing features of the process are that the hydrolypyrolysis is an

Figure 1

PRODUCTION OF A CLEAN CARBON FUEL AND CO-PRODUCTS

Figure 2

Hydrocarb process block diagram

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.

Process Chemistry

The first two steps of the Hydrocarb process have been demonstrated, although at different conditions than Hydrocarb in the laboratory and pilot plant; 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 reactors should operate in the range of 50 atm pressure with temperatures in the range, 800°-900° for the HPR, 1000°-1100°C in the MPR and the MSR at 260°C. In addition to literature data, kinetic chemistry data were needed for designing the hydrogasifier with biomass feedstock and for the thermal decomposition of methane at the design conditions. The following experimental study was therefore undertaken:

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.⁽¹⁾ The tests were conducted at temperatures up to 800°C and pressures between 30 and 50 atm.¹ 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 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 CO₂ 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.⁽²⁾ Initial rates of biomass conversion increase significantly with increase 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 using the same BNL reactor facility was investigated in the temperature range 700 to 900°C at pressures ranging from 28 to 56 atm.⁽³⁾ 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. 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 CH₄. This low

¹1 atm = 101.3 kPa

Figure 3 Methane concentrations vs. residence time.

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 of the reactors. From numerous computer runs we cite here only two configurations which are most relevant to CO_2 emissions reduction.⁽⁴⁾ 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. 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:

$$\begin{array}{lcl} \text{Net } \text{CO}_2 \text{ Emission per} & = & \text{CO}_2 \text{ emitted from the combustion of methanol as fuel } \underline{\text{minus}} \\ \text{unit energy of} & & \text{the } \text{CO}_2 \text{ photosynthesized in wood } \underline{\text{minus}} \\ \text{methanol used as fuel} & & \text{sequestered } \underline{\text{plus}} \text{ CH}_4 \text{ burned in MPR combustor} \end{array}$$

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 Lbs/ CO_2 /MMBTU (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.

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 shows these data and is based on feeding fixed unit amounts of biomass and natural gas to each plant and compares with the cofeedstock Hydrocarb plant for maximum methanol production. The biomass gasification plant is based on a range of values from 4 gasification processes evaluated by Larson and Katofsky.⁽⁶⁾ 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/MMBTU) 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.

Figure 4

HYDROCARB PROCESS SIMULATION
ZERO CO₂ EMISSION

Run No. 1 (Pressure: 50 atm)

Carbon efficiency = 42.57 %
Thermal efficiency = 50.33 %
CO₂ emission = 0 (sequester carbon)

Figure 5

HYDROCARB PROCESS SIMULATION

MAXIMUM METHANOL YIELD OPTION - MINIMUM PRODUCTION COST

Run No. 2 (Pressure: 50 atm)

Carbon Efficiency = 67.8 %
Thermal Efficiency = 72.5 %
CO₂ emission = 94 lb/MOSTO
(No carbon sequestered)

**Table 1. COMPARISON OF METHANOL PRODUCTION AND CO₂ 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*	99.4 - 93.0*
Net CO ₂ emission, kg	144	0	168
LbsCO ₂ /MMBTU MeOH (LHV)	94	0	180 - 193
kgCO ₂ /GJ MeOH (LHV)	40.6	0	77.8 - 83.8
Gasoline displaced, gal	35.8	10.9 - 8.6	21.5 - 20
Net CO ₂ reduction from displaced gasoline, kg	178	98 - 77	0

* The range of values represent the 4 gasification processes evaluated by Larson and Katofsky⁽⁶⁾ (1992).

^b Ranges shown represent performance of different reforming technologies.⁽⁶⁾

^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.

Hydrocarb Methanol as an Alternative Transportation Fuel

An analysis can also be made with respect to CO₂ emissions when considering methanol displacing gasoline as a transportation fuel. About 30% of the U.S. anthropogenic CO₂ emission comes from the transportation sector which is about equal to emissions from stationary sources. EPA has estimated that 1.54 gallons of methanol can displace 1 gallon of gasoline in automobiles on a mileage per unit energy basis.⁽⁷⁾ Gasoline emits 9 Kg CO₂ per gallon. For maximum Hydrocarb methanol production configuration (Fig. 5), the CO₂ emitted is 4 Kg CO₂ per gallon of gasoline displaced. There is thus a 55% reduction in CO₂ emission by the use of Hydrocarb methanol in displacing gasoline. The next to the last lines 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 CO₂ from the displaced gasoline which shows that Hydrocarb methanol can yield from 80% to 130% greater reduction in CO₂ 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.⁽⁷⁾ The preliminary capital cost estimate was determined based on a comparative analysis with a Texaco Coal gasification process⁽¹⁰⁾ plant assuming that equal gas throughout 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 reasonable plant capacity handling 5000 dry metric tons of biomass per day (DMT/day) selected mainly by the deliverability and cost of biomass from an area of a fast rotational crop tree plantation (bundled willow).⁽⁹⁾ Table 2 gives the economic parameters assumed for methanol production based on the maximum yield of methanol option (Fig. 5) and results in a production cost of \$0.405/gallon methanol.

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

A further cost comparison was made with other biomass derived alcohol production processes.⁽⁷⁾ A summary is shown in Table 4, comparing ethanol produced by acid and enzymatic hydrolysis, methanol produced by steam-oxygen gasification and ethanol produced by fermentation. Hydrocarb methanol for a 5000 DMT/day biomass plant costs from 50% to 75% on a lower heating value (LHV) basis less than the other ethanol or methanol processes as reported in the literature.

Impact of 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 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 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 CNG (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 per year. The U.S. reserve of conventional natural gas is estimated at present to be at least 1000 quads.

CONCLUSION

The Hydrocarb process has the potential, if the R&D objectives are achieved, to produce alternative transportation fuel from indigenous resources at lower cost than any other biomass conversion process. Our comparisons suggest the resulting fuel can significantly displace gasoline at a competitive price while mitigating CO₂ emissions and reducing ozone and other toxics in urban atmospheres.

Table 2. HYDROCARB METHANOL PRODUCTION PLANT ECONOMICS
BASED ON MAXIMUM YIELD OPTION

Biomass Feedstock	• 3000 DMT Biomass/Day
Natural Gas Feedstock	• 4.68×10^6 M ³ /Day (165×10^6 SCF/Day)
Methanol Production	• 2.85×10^6 GPD
Capital Investment	• \$838 $\times 10^6$
Delivered Cost of Biomass	• \$51.00/DMT
Maximum Distance of Plantation	• 84 Km
Natural Gas Cost	• \$2.50/MMBTU
Carbon Sequester	• \$23/ton
O&M	• \$5.00/ton biomass
Return on Equity	• 25 %
Debt/Equity	• 80 %/20 %
Total Capital Charge Rate	• 20.9 %
Ind. Inv. on Equity & Taxes	
Annual Operating Factor	• 90 %
Production Cost of Methanol	• \$0.40/gallon

TABLE 3. INCREMENTAL COST OF GASOLINE DISPLACEMENT BY
HYDROCARB METHANOL
(As of last quarter 1992)

National Average Gasoline Price = \$1.12/gal.

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

where: 1.54 = volumetric ratio, methanol to gasoline

\$0.405 = methanol production cost

\$0.12 = taxes

\$0.07 = wear-up

\$0.06 = distribution cost

Incremental cost of gasoline

displacement = $\$1.01 - \$1.12 = -\$0.11/\text{gal}$

TABLE 4. PRODUCTION COSTS OF ALCOHOL FUELS
DERIVED FROM BIOMASS

Process	Alcohol production cost, \$/GJ (LHV)
Ethanol by acid hydrolysis	24.4
Ethanol by enzymatic hydrolysis	22.3
Methanol by steam-oxygen gasification	13.4
Ethanol by fermentation of corn	13.3
Methanol by Hydrocarb (3000 DMT/day)	4.8

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