**CONVERSION OF BIOMASS TO METHANOL
AND ITS EFFECT ON CO₂ EMISSIONS**

BNL--44653-Rev.10/90

Meyer Steinberg

DE91 006303

October 1990

Prepared for the
U.S. Environmental Protection Agency
EPA/IAG 89934598-0
AEERL (MD-61)
Research Triangle Park, NC 27711

BIOSYSTEMS AND PROCESS SCIENCES DIVISION
DEPARTMENT OF APPLIED SCIENCE
BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
UPTON, NY 11973

Under contract No. DE-AC02-76CH00016 with the U.S. Department of Energy
Washington, DC

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
ps

CONVERSION OF BIOMASS TO METHANOL AND ITS EFFECT ON CO₂ EMISSIONS

By

Meyer Steinberg
Biosystems and Process Sciences Division
Department of Applied Science
Brookhaven National Laboratory
Upton, New York 11973
October 1990

The purpose for this report is to present a preliminary analysis of various processes for conversion of biomass to methanol fuel with the objective of determining the effect of these processes on net CO₂ emissions. The analysis is made primarily on the basis of first principles of mass and energy balances.

There are at least four systems that can produce methanol from biomass (defined as wood or lignocellulose). These are reviewed and assessed as follows:

1. Destructive Distillation of Wood

This is an ancient process for producing wood alcohol, which is the common term for methanol from wood. The efficiency of energy conversion of methanol from wood by this process is probably less than 10% and there is formation of CO₂ and some char residue. The stoichiometric formula for wood (lignocellulose) is approximately, CH_{1.44}O_{0.66}, which comes from the elemental weight analysis ~50% C, ~44% O and ~6% H₂ and tends to vary within relatively narrow limits with different species of wood. The overall reaction can be represented as follows:

wood → methanol (wood alcohol) + carbon dioxide + char

If all the carbon in wood is released as methanol and CO₂, at 10% energy efficiency then only 6.4% of the carbon in the wood is converted to methanol and the amount of CO₂ that must be photosynthesized from the atmosphere becomes as high as 2150 lbs CO₂/MMBTU of methanol energy. The net emission of CO₂ to the atmosphere is zero because all the carbon released to the atmosphere as CO₂ by the conversion process and the combustion of methanol is removed from the atmosphere by the growth of the biomass (wood).

2. Conventional Steam-Oxygen Gasification of Wood

This process can be represented by the following reactions:

and the overall reaction then becomes:

The endothermic heat of steam gasification only for the first reaction above, requires some combustion of the wood to provide that energy. Using the heat of formation of wood as -30 Kcal/mol and the heat of combustion of -113 Kcal/mol, the combustion process amounts to:

The number of moles of CO_2 released per mole of CH_3OH produced then becomes:

$$\text{moles CO}_2/\text{mol CH}_3\text{OH} = \frac{0.313 + 0.240 + 0.687}{0.687} = 1.80$$

$$\text{and the carbon conversion efficiency of wood to methanol} = \frac{0.687}{1.24} \times 100 = 55.4\%$$

The CO_2 required to be photosynthesized for methanol production and the combustion of wood is calculated as follows: (based on heat of combustion of methanol taken as 10,000 BTU/Lb methanol or 320,000 BTU/Lb mol):

$$\text{lb CO}_2/\text{MMBTU} = \frac{1.80 \times 44 \times 10^6}{32 \times 10^4} = 248 \text{ lbs/MMBTU of methanol energy}$$

The thermal efficiency including a 90% process carbon conversion efficiency (heating value of wood being 8500 BTU/Lb or 204,000 BTU/Lb mol)

$$= \frac{0.687 \times 10,000 \times 32 \times 0.9}{1.24 \times 204,000} = 78.2\%$$

3. Higher Temperature Pyrolysis of Wood

This process consists of pyrolyzing the wood to near thermodynamic equilibrium values of gas composition. A calculation was made at 50 atm pressure and for temperatures of 800°C, and 1100°C, and at 1 atm and 1000°C, for the five gaseous components. This can be obtained from the equilibrium Figure 1. A detailed flow sheet has not been developed for this process, however, the basic energy and mass needs can be arrived at as follows:

For $\text{CH}_{1.44}\text{O}_{0.66}$, the $\text{H/O} = 2.18$ and the $\text{C/O} = 1.52$, so that the gas composition at 800°C and 50 atm at equilibrium is:

H_2	27 Vol%
CO	15
CH_4	15
H_2O	27
CO_2	<u>16</u>
	100

From a mass balance, the reaction equation becomes:

The heat of reaction is then $\Delta H = +1.8$ Kcal/mol of wood, which means the reaction is almost in balance, thermally.

The methanol formation process reactions are then as follows:

and by reforming the methane with the water, additional CO and H_2 is formed which is then converted to methanol.

The overall reaction is:

Thus the total, CH₃OH formed is about 0.27 moles of CH₃OH (including some CO₂ conversion) from one mole of wood. Therefore:

$$\text{Photosynthesis of CO}_2 = \frac{1 \times 44 \times 10^6}{0.27 \times 32 \times 10^4 \times 0.9}$$

$$= 566 \text{ LbsCO}_2/\text{MMBTU of CH}_3\text{OH.}$$

$$\text{Thermal efficiency} = \frac{0.27 \times 320,000 \times 0.9 \times 100}{204,000} = 38.1\%$$

$$\text{The carbon efficiency} = \frac{0.27 \times 100}{1} = 27\%$$

Now, if the carbon is stored and only the methanol used for fuel, the removal of CO₂ from the atmosphere is found to be as follows:

$$\frac{(-1.00 + 0.27) \times 44 \times 10^6}{0.27 \times 32 \times 10^4 \times 0.9} = 413 \text{ LbCO}_2/\text{MMBTU of methanol}$$

Repeating the calculation at 1100°C and 50 atm

for CH_{1.44}O_{0.66}, where H/O = 2.18 and CO = 1.52, then

H ₂	45 Vol%
CO	45
CH ₄	4
H ₂ O	4
CO ₂	<u>2</u>
	100

From a mass balance, the reaction equilibrium results in the following reaction:

The heat of reaction for the previous reaction which produces CO then amounts to ΔH = +8.6 Kcal/mol of wood. Since the heat of combustion of wood is ΔH_c = -113 Kcal/mol, we then need to burn another $\frac{8.6}{113.0} = 0.076$ moles of wood for the energy required to produce the 0.56 moles of CO which is subsequently converted to CH₃OH shown by the following equation.

Recombining the CO with H₂ to produce methanol and neglecting the small amount of CO₂:

The remaining 0.28 mol CO is shifted with H₂O and converted to methanol for the overall reaction

Thus the total amount of CH₃OH formed is 0.09 + 0.28 = 0.37 moles.

$$\text{The Photosynthesis of CO}_2 = \frac{1.076}{0.37} \times \frac{44 \times 10^6}{32 \times 10^4 \times 0.9} = \frac{445 \text{ Lb CO}_2}{\text{MMBTU of CH}_3\text{OH}}$$

$$\text{Thermal efficiency} = \frac{0.37 \times 32 \times 10^4 \times 0.9}{1.076 \times 204,000} = 48.5\%$$

$$\text{Carbon efficiency} = \frac{0.37 \times 100}{1.085} = 34.1\%$$

By storing the carbon and using only the methanol as fuel, the removal of CO₂ from the atmosphere per unit of methanol energy then becomes:

$$= \frac{(-1.076 + 0.37 + 0.19 + 0.076) \times 44 \times 10^6}{0.56 \times 32 \times 10^4 \times 0.9} = -120 \text{ Lb CO}_2/\text{MMBTU methanol}$$

Repeating the calculation at 1000° and 1 atm (taken from other thermodynamic equilibrium curves), the gas composition is:

H ₂	52 Vol%
CO	48
CH ₄	0
H ₂ O	0
CO ₂	<u>0</u>
	100

From a mass balance, the stoichiometric reaction for the pyrolysis of wood becomes:

Since there is not enough hydrogen to combine with all the CO to form CH_3OH , some of the CO will be shifted with water to produce hydrogen and CO_2 and the remaining H_2 and CO are combined to produce methanol. The overall reaction of CO can then be stated as follows:

Thus the moles of CH_3OH produced per mole of wood,

$$= \left(0.66 - \frac{0.72}{2}\right) \frac{1}{3} + \frac{0.72}{2} = 0.46$$

The energy required to drive the pyrolysis reactions in terms of the combustion of wood is

$$= \frac{+ 12.8 \text{ Kcal}}{113 \text{ Kcal}} = 0.11 \text{ moles of wood}$$

The photosynthesis of CO_2 per MMBTU of methanol energy

$$\frac{(1 + 0.11) \times 44 \times 10^6}{0.46 \times 32 \times 10^4 \times 0.9} = 369 \text{ Lb CO}_2/\text{MMBTU}$$

$$\text{The carbon efficiency} = \frac{0.46}{1.11} \times 100 = 41.4\%$$

$$\text{Thermal efficiency} = \frac{0.46 \times 32 \times 10^4 \times 0.9 \times 100}{1.11 \times 204 \times 10^3} = 58.5\%$$

By storing the C and only using the methanol, the removal of CO_2 from the atmosphere per unit of methanol energy then becomes:

$$\frac{(-1.11 + 0.46 + 0.11) \times 44 \times 10^6}{0.46 \times 32 \times 10^4 \times 0.9} = -179 \text{ Lb CO}_2/\text{MMBTU methanol}$$

4. Coprocessing of Biomass With Fossil Fuel Using the Hydrocarb Process

The fourth series of processes refers to the processing of biomass (lignocellulose or wood) alone or with fossil fuel by the clean carbon Hydrocarb process which is shown in a general manner in Figure 2. It consists of the hydropyrolysis of the wood with excess hydrogen forming methane followed by thermal decomposition of methane to carbon and hydrogen. The hydrogen gas is recycled. Between the two steps the CO formed is converted to methanol in the excess hydrogen.

4.1. Processing Biomass Alone And Producing H₂ As A Fuel Using Hydrocarb Process

wood → carbon + water + hydrogen

Burn H₂ as fuel and store carbon

$$\text{Energy efficiency} = \frac{0.06 \times 68 \text{ Kcal/mol}}{113 \text{ Kcal/mol}} \times 100 = 3.6\%$$

$$\text{Removal of CO}_2/\text{MMBTU} = \frac{1.0 \times 44 \times 10^6}{0.06 \times 68 \times 10^3 \times 1.8} = -6000 \text{ Lbs CO}_2/\text{MMBTU H}_2 \text{ energy}$$

4.2. Co-Processing Biomass With Natural Gas Using Hydrocarb Process

The general scheme for the Hydrocarb Process is shown on Figure 3. A detailed flow sheet has been developed for coal and can be extended to other feedstocks including biomass and other fossil fuels either alone or in combination.

The overall stoichiometry is as follows:

wood + Nat. gas → carbon + methanol

Store the carbon and burn only methanol as fuel.

$$\text{CO}_2 \text{ removed from atm} = \frac{(-1.00 + 0.66) \times 44 \times 10^6}{0.66 \times 32 \times 10^4 \times 0.9} = -78 \text{ Lb CO}_2/\text{MMBTU of methanol}$$

$$\text{Efficiency} = \frac{\text{MMBTU CH}_3\text{OH}}{\text{MMBTU Feedstock}} = \frac{0.66 \times 32 \times 10^4 \times 0.9 \times 100}{0.3 \times 212 \times 10^3 \times 1.8 + 204 \times 10^3} = 59.8\%$$

Note the heat of combustion of methane = 212 Kcal/mol.

$$\text{Carbon efficiency} = \frac{0.66 \times 0.9}{1.30} \times 100 = 45.7\%$$

$$\text{Lbs CO}_2 \text{ photosynthesized/MMBTU} = \frac{1 \times 44 \times 10^6}{0.66 \times 320 \times 10^3 \times 0.9} = 232 \text{ Lb/MMBTU}$$

Methanol efficiency based on natural gas only:

$$\text{Carbon efficiency} = \frac{0.66 \times 0.9}{0.3} \times 100 = 198\% \text{ on natural gas}$$

$$\text{Thermal efficiency} = \frac{0.66 \times 0.9 \times 32 \times 10^4}{0.3 \times 212 \times 10^3 \times 1.8} \times 100 = 167\% \text{ on natural gas}$$

4.3 Coprocessing Biomass With Oil Using Hydrocarb Process

wood + oil → carbon + methanol

Store the carbon and burn only the methanol as fuel

$$\text{CO}_2 \text{ removed from atm} = \frac{(-1.00 + 0.66) \times 44 \times 10^6}{0.66 \times 32 \times 10^4 \times 0.9} = -78 \text{ Lbs/MMBTU of methanol}$$

$$\text{Carbon efficiency} = \frac{0.66 \times 0.9}{1.70} \times 100 = 34.9\%$$

$$\text{Thermal efficiency} = \frac{0.66 \times 32 \times 10^4 \times 0.9 \times 100}{0.7 \times 13.7 \times 18,000 + 204 \times 10^3} = 50.4\%$$

$$\text{Lbs CO}_2 \text{ photosynthesized/MMBTU} = \frac{1.0 \times 44 \times 10^6}{0.66 \times 0.32 \times 10^6 \times 0.9} = 232 \text{ Lb/MMBTU}$$

Methanol efficiency based on oil only:

$$\text{Carbon efficiency} = \frac{0.66 \times 0.9}{0.7} \times 100 = 84.9\%$$

$$\text{Thermal efficiency} = \frac{0.66 \times 32 \times 10^4 \times 0.9 \times 100}{0.7 \times 13.7 \times 18,000} = 110\% \text{ on oil}$$

4.4 Coprocessing Biomass With Coal Using Hydrocarb Process

wood + bit. coal → carbon + methanol

Store carbon and use only the methanol as fuel.

$$\text{CO}_2 \text{ removed from atmosphere} = \frac{(-0.32 + 0.32)}{0.32} \times 100 = 0\%$$

$$\text{Carbon efficiency} = \frac{0.32}{1.32} \times 100 = 24.2\%$$

$$\text{Thermal efficiency} = \frac{0.32 \times 32 \times 10^4 \times 0.9 \times 100}{0.32 \times 204 \times 10^3 + 1.8 \times 116 \times 10^3} = 33.6\%$$

[Note heat of combustion of bit. coal = 116 Kcal/mol(MAF)].

$$\text{Lb CO}_2 \text{ photosynthesized/MMBTU} = \frac{0.32 \times 44 \times 10^6}{0.32 \times 32 \times 10^4 \times 0.9} = 153$$

Methanol efficiency based on coal alone:

$$\text{Carbon efficiency} = \frac{0.32 \times 0.9}{1.00} \times 100 = 28.8\%$$

$$\text{Thermal efficiency} = \frac{0.32 \times 32 \times 10^4 \times 0.9}{1.8 \times 116 \times 10^3} = 44.1\%$$

5. Displacement of Fossil Fuel With Biomass

A preliminary estimate of the displacement or savings of fossil fuel by utilizing biomass (wood) can be made by comparing the thermal energy efficiency of converting fossil fuel to methanol by conventional processes with the biomass process given herein. The thermal efficiencies for the various fuels based on the conventional steam reforming of natural gas under the best conditions for producing methanol are as follows:

<u>Fuel</u>	<u>Thermal Efficiency %</u>
Gas	82
Oil	60
Coal	42

The fossil fuel displacement per unit of new fuel

$$\% \text{ fossil fuel saved or displaced} = \frac{\text{Thermal efficiency of biomass process}}{\text{Thermal efficiency of conventional process}}$$

When biomass alone is processed then the percent displacement is direct. However, when coprocessing of fossil fuel with biomass then the displacement appears to be more meaningful if it is based only on the use of the fossil fuel.

For example, under 4.2 coprocessing wood with natural gas by the Hydrocarb Process, the displacement of or the more efficient utilization of the natural gas compared to steam gasification of natural gas is

$$\% \text{ increased utilization or displacement of nat. gas} = \frac{167\%}{82\%} \times 100\% = 204\%$$

In other words, the natural gas produces more than twice the amount of methanol in the Hydrocarb biomass coprocessing system than in the conventional steam reforming of natural gas process. For every unit of natural gas used in the coprocess system two units are displaced by the conventional system.

The Effect of Carbon Conversion Efficiency on CO₂ Emission

The effect of carbon conversion efficiency and thermal efficiency are important in determining the net emission of CO₂. The processes can be operated in either of two modes. In one mode, the unconverted carbon in the feedstock can be burned to supply the insufficiency of energy in the system, in which case it adds to the CO₂ emissions. In the second mode the unconverted carbon from the process can be stored together with the coproduct carbon produced and the make-up of the energy balance (thermal energy efficiency) can be supplied by burning additional biomass in which case there is no effect on the CO₂ emission. What is affected is the amount of CO₂ that must be photosynthesized. The second mode is thus preferable from the CO₂ emission point of view and the effect of carbon conversion on CO₂ is analyzed as follows, taking for example the 4.2 Hydrocarb coprocessing of natural gas and biomass.

$$\text{CO}_2 \text{ removed from atm/MMBTU} = \frac{(-1.00 + 0.66 E) \times 44 \times 10^6}{0.66 E \times 32 \times 10^4}$$

where E is the carbon conversion efficiency. This is a more rigorous application of conversion efficiency than given earlier to compute CO₂ removal from the atmosphere. The values as a function of different conversion efficiencies are as follows:

<u>Carbon Conversion Efficiency E-%</u>	<u>CO₂ Removed/MMBTU Methanol Generated</u>
90	- 94
75	-140
60	-210

As the efficiency of carbon conversion decreases, the CO₂ removed from the atmosphere per unit of methanol increases. However, more biomass must be grown and the fraction of energy that is extracted from the fossil fuel becomes smaller. Thus, the optimum benefit for CO₂ removal must be evaluated as a function of both conversion and energy efficiency.

Discussion of Processes and Conclusion

A summary of the data generated in this report is given in Table 1. The primary purpose of this study is to determine the effect of biomass-based methanol processes on net CO₂ emission. It should be remembered that this is a preliminary analysis and that it can change with more detail. However, it is believed the comparison is basically sound, because it is based on first principles.

Reviewing the table, it appears that generating hydrogen from biomass, using the Hydrocarb Process (system 4.1) yields a huge removal in CO₂ per unit of hydrogen energy generated (-6000 LbCO₂/MMBTU). However, the thermal conversion efficiency is extremely low, only 3.6%. A better figure of merit, in this case, might be the product of the efficiency and the CO₂ removal per unit energy. Furthermore, the fuel is hydrogen which is not as convenient as methanol.

Using wood alone in conventional processes does not generate any net CO₂ emission. But then it does not allow the use of fossil fuel. The wood pyrolysis process system 3 is not too bad as far as CO₂ removal is concerned (-120 to -374 Lb CO₂/MMBTU). However, the process has not been worked out in detail so that there may be other process difficulties not taken into account here, such as heat transfer problems. The CO₂ photosynthesis requirements are high (296 to 527 Lb CO₂/MMBTU) compared to the coprocess systems (153 to 232 Lb CO₂/MMBTU). It also suffers from not utilizing fossil fuels. The Hydrocarb biomass and fossil fuel coprocesses 4.2, 4.3 and 4.4 all look interesting because, (1) with gas and oil there is still a

significant net reduction in CO₂ emissions (-78 Lbs/MMBTU), (2) the systems allow the use of fossil fuels, (3) the efficiency of utilization of fossil fuel is significantly enhanced compared to its use in conventional processes alone and (4) the requirement of CO₂ photosynthesis is less than the other wood conversion processes which determines the land area required to grow the biomass.

The conclusion is that the Hydrocarb coprocessing systems which use biomass and fossil fuel feedstocks to produce carbon and methanol liquid fuel, is worthy of further development from the point of view of improved methanol production as well as for CO₂ mitigation. Further process design data should be obtained and economic evaluation made.

Reference Literature

1. "Biomass Gasification", Edited by T.B. Reed, Noyes Data Corporation, Park Ridge, N.J. (1981).
2. Sunggyu, Lee, "Methanol Synthesis Technology" CRC Press, Inc, Boca Raton, Florida (1990).
3. E.W. Grohse and M. Steinberg, "Economical Clean Carbon And Gaseous Fuels From Coal And Other Carbonaceous Materials" BNL 40485, Brookhaven National Laboratory, Upton, N.Y. (December 1987).
4. M. Steinberg, "Biomass and Hydrocarb Technology For Removal Of Atmospheric CO₂" BNL 44410, Brookhaven National Laboratory Upton, N.Y. (March 1990).
5. M. Steinberg and E.W. Grohse, "Hydrocarb-M Process For Conversion Of Coal To Carbon-Methanol Liquid Fuel", (Carboline-M), BNL 43569, Brookhaven National Laboratory, Upton, N.Y. (January 1989).

Table 1
CONVERSION OF BIOMASS TO METHANOL
AND ITS EFFECT ON CO₂ EMISSIONS

Process System	Feedstock and Raw Material	Products	Methanol Efficiency		Net CO ₂ Emissions Lb CO ₂ /MMBTU MeOH Energy	Fossil Fuel Displacement			Photosynthesized Requirement Lbs CO ₂ /MMBTU
			C Eff. %	Thermal Eff. %		Gas - % 82†	Oil - % 60†	Coal - % 42†	
1. Destructive Distillation of Wood	Wood and Fuel Wood	Methanol and CO ₂	6.4	10	0	12	17	24	2150
2. Steam/Oxygen Gasification of Wood	Wood, Steam, Oxygen	Methanol and CO ₂	55.4	78	0	95	122	174	248
3. Pyrolysis of Wood at Hi-Temp and Pressure	Wood and Fuel Wood	Methanol and CO ₂	27.0 34 41.2	38 49 58	800°C/50 ATM -413 1100°C/50 ATM -120 1000°C/1 ATM -179	46 60 71	68 82 97	98 117 138	566 445 369
4.1. *Hydrocarb Process Biomass Alone	Wood	H ₂ Fuel only Carbon Stored	0.36	H ₂ eff. = 3.6%	-6000/MMBTU H _c Energy				6000
4.2. *Hydrocarb CoProcess Wood & Nat. Gas	Wood and Nat. Gas	Methanol Carbon Stored	45.7 198	60 167	-78 -78	204	278	398	232 **
4.3. *Hydrocarb CoProcess Wood & Oil	Wood and Oil	Methanol Carbon Stored	34.9 84.9	50 110	-78 -78	134	183	261	232 **
4.4. *Hydrocarb CoProcess Wood & Coal	Wood and Coal	Methanol Carbon Stored	24.2 28.8	34 44	0 0	54	73	105	153 **

Notes The above table makes the implicit assumption that to produce the biomass takes a small amount of energy, based on studies of energy farms (< 10% of the biomass energy is needed to produce the biomass).

* HYDROCARB Systems - assumes 90% Carbon conversion efficiency.

TOT - assumes efficiencies based on total biomass and fossil fuel feedstock.

FF - assumes efficiencies based only on fossil fuel part of the feedstock.

** Interesting Systems to Pursue - because: 1) Reduces CO₂ emission, 2) Reduces CO₂ photosynthesis requirements, 3) Allows the use of Fossil Fuel and, 4) Improves the use of Fossil Fuel for producing methanol, compared to conventional processes for conversion of fossil fuel to methanol.

† Efficiencies based on conventional methanol production from the fossil fuel indicated.

EQUILIBRIUM COMPOSITIONS IN C,H,O SYSTEMS

Figure 1

GENERAL HYDROCARB PROCESS

PRODUCTION OF A CLEAN CARBON FUEL AND CO-PRODUCTS

THREE METHODS OF HEAT TRANSFER - GAS, SOLID, OR STEAM
THREE REACTOR TYPES - FLUIDIZE BED, MOVING BED, ENTRAINED BED

Figure 2

CO-PROCESSING BIOMASS WITH FOSSIL FUEL VIA THE CLEAN CARBON PROCESS FOR REMOVAL OF ATMOSPHERIC CO₂ AND PRODUCTION OF METHANOL FUEL.

(1.15)

Figure 3

END

DATE FILMED

02 / 14 / 91