

BNL- 65454
Informal Report

CO₂ Mitigation and Fuel Production

Prepared by:
Meyer Steinberg

RECEIVED
MAY 11 1998
OSTI

July 7, 1997

Engineering Technology Division
Department of Advanced Technology, Brookhaven National Laboratory
Upton, New York 11973

Prepared for the U.S. Department of Energy
Washington, DC
Contract No. DE-AC02-98CH10886

DTIC QUALITY INSPECTED 1

19980529 007

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, or any of their contractors, subcontractors, or their employees, makes any warrantee, expressed or implied, or assumes any legal liabilities or responsibility for the accuracy, completeness, or usefulness of an information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency, contractor, or subcontractor thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency contractor or subcontractor thereof.

CO₂ Mitigation and Fuel Production

Prepared by:

Meyer Steinberg
Brookhaven National Laboratory
Engineering Technology Division
Department of Advanced Technology
Upton, New York 11973

July 7, 1997

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

This work was performed under the auspices of the U.S. Department of Energy

ABSTRACT

Methanol as an alternative transportation fuel appears to be an effective intermediate agent, for reducing CO₂ from the utility power and the transportation sectors. On the utilization side, methanol as a liquid fuel fits in well with the current infrastructure for storage and delivery to the automotive sector with better efficiency. On the production side, CO₂ from fossil fuel plants together with natural gas and biomass can be used as feedstocks for methanol synthesis with reduced CO₂. Over the past several years, processes have emerged which have varying degrees of CO₂ emission reduction depending on the feedstocks used for methanol synthesis process. This paper reviews the methanol processes from the point of view of production efficiency and CO₂ emissions reduction. The processes include (1) the Hydrocarb Process which primarily utilizes coal and natural gas and stores carbon, and (2) the Hynol Process which utilizes biomass (including carbonaceous wastes, municipal solid waste (MSW)) or coal and natural gas, and (3) the Carnol Process which utilizes natural gas and CO₂ recovered from fossil fuel fired powered plant stacks, especially coal fired plants. The Carnol System consists of power generation, methanol production and methanol utilization as an automotive fuel. The efficiency and CO₂ emissions for the entire system are compared to the conventional system of petroleum derived automotive fuel (gasoline) and coal fired power generation plants. CO₂ reduction by as much as 56% and 77% can be achieved when methanol is used in internal combustion and fuel cell automotive vehicles, respectively.

CONTENTS

	<u>Page</u>
ABSTRACT	iii
LIST OF FIGURES	vi
LIST OF TABLES	ix
1 INTRODUCTION	1
2 THE HYDROCARB PROCESS	1
3 THE HYNOL PROCESS	2
4 THE CARNOL PROCESS	3
5 CARNOL PROCESS DESIGN	4
6 METHANOL AS AN AUTOMOTIVE FUEL	4
7 ECONOMICS OF CARNOL PROCESS	4
8 CO ₂ EMISSION EVALUATION OF ENTIRE CARNOL SYSTEM	5
9 CONCLUSIONS	7
10 REFERENCES	8

LIST OF FIGURES

		<u>Page</u>
Figure 1	Hydrocarb Process Block Diagram	11
Figure 2	A Block Diagram of the Hynol Process	11
Figure 3	Carnol III Process for Producing Methanol from Natural Gas and CO ₂ for Zero CO ₂ Emission	11
Figure 4	Carnol VI Process: Methanol Production From Power Plant CO ₂ and Natural Gas .	12
Figure 5	Carnol System Configuration for CO ₂ Emission Mitigation	12

LIST OF TABLES

		<u>Page</u>
Table 1	Methanol Production with Reduced CO ₂ Emissions	9
Table 2	Advanced Carnol VI Preliminary Process Economics	9
Table 3	Methanol Production and CO ₂ Emission Process Comparison	10
Table 4	CO ₂ Emission Comparison for Systems Consisting of Coal Fired Power Plant, Fuel Process Plant and Automotive Power Plant	10

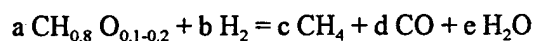
1 INTRODUCTION

Coal and natural gas are abundant fuels. Because of their physical and chemical properties, coal and natural gas are difficult to handle and utilize in mobile as well as stationary engines. The infrastructure is mainly geared to handle clean liquid fuels. In order to convert coal to liquid fuel, it is generally necessary to increase its H/C ratio either by increasing its hydrogen content or decreasing its carbon content. On the other hand, in order to convert natural gas to liquid fuels, it becomes necessary to decrease its hydrogen content. Thus, by coprocessing the hydrogen-rich natural gas with hydrogen deficient coal, it should be possible to produce liquid fuels in an economically attractive manner. For environmental purposes of decreasing CO₂ greenhouse gas emissions, several approaches can be taken. The CO₂ emission from central power stations can be removed, recovered and disposed of in deep ocean.⁽¹⁾ Efficiency of fossil fuel conversion for power generation and transportation can be increased.⁽²⁾ Alternatively, carbon can be extracted from coal and natural gas and only the hydrogen-rich fractions can be utilized from both of these fuels to reduce CO₂ emissions while storing the carbon.⁽³⁾ Because of its physical properties, carbon is much more easily disposed of either by storage or used as a materials commodity than sequestering CO₂. Another alternative CO₂ mitigation method is to utilize the stack gas CO₂ from coal burning plants with hydrogen obtained from natural gas to produce methanol, which is a well-known liquid automotive fuel. In this paper, in addition to reviewing the Hydrocarb⁽³⁾ and Hynol⁽⁴⁾ Processes, which involves the carbon separation processes, we describe the Carnol Process⁽⁵⁾ which connects the power generation sector with the transportation sector and results in an overall system for CO₂ mitigation.

2 THE HYDROCARB PROCESS ⁽³⁾

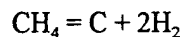
The Hydrocarb Process is based on the following three integrated chemical reaction steps:

1. Hydrogasification of Coal



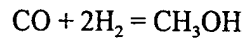
This reaction is exothermic and can take place efficiently at temperature of 800 to 900° and at pressures of 30 to 50 atm. A fluidized bed reactor is indicated for hydrogasification of solid carbonaceous feedstocks including coal and biomass. Limestone can be added to remove the sulfur.

2. Methane Decomposition

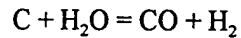


This reaction is endothermic, takes place efficiently at temperatures above 800°C and is favored by lower pressure. The methane produced by hydrogasification and additional feedstock methane provides the methane to be decomposed. This reaction produces the hydrogen for methanol synthesis in Step 3 and the excess is recycled to the hydrogasification reactor in Step 1.

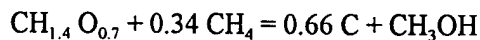
3. Methanol Synthesis



The synthesis of methanol from CO and H₂ is a well-known catalytic process which is usually practiced industrially at 260°C and 50 atm pressure. The CO is produced in the hydrogasification step from oxygen in the coal. The amount of CO formed depends on the water content of the coal according to the well-known gasification reaction:



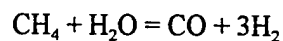
The Hydrocarb Process also works well with biomass as a co-feedstock because of its higher oxygen content. The overall reaction being:



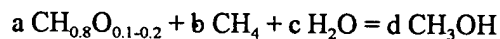
A generalized flow sheet of the Hydrocarb process is shown in Figure 1. A computer simulation model has been developed for the process which can determine the mass and energy balances when supplying various types of amounts of feedstocks. To reduce CO₂ greenhouse gas, the carbon produced in the Hydrocarb process can be sequestered or used as a materials commodity. Table I shows the methanol thermal efficiency and the degree of CO₂ emissions reduction compared to the production of methanol by conventional coal gasification and natural gas reforming processes. The addition of biomass can essentially reduce the net CO₂ emissions to zero because biomass uses CO₂ from the atmosphere in the production of methanol. The use of methanol as a liquid fuel in automotive engines improves the thermal efficiency by 30% compared to gasoline fuels. Thus, an additional 40% reduction in CO₂ emission can be realized using methanol instead of gasoline in automotive engines.⁽⁶⁾

3 THE HYNOL PROCESS⁽⁴⁾

For purposes of maximizing the methanol yield and simplifying the Hydrocarb process, the second step is changed from methane decomposition to the well-known reforming of methane with steam:



This is an endothermic process and can take place efficiently at temperatures above 900°C in the presence of a nickel catalyst. Additional methane feedstock produced in the hydrogasification step significantly improves the methanol yield. In this process, only liquid methanol is produced and there is no need to sequester carbon. The overall reaction involving the co-feedstocks coal and natural gas is:



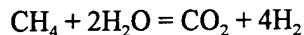
Biomass and municipal solid waste can also be used as co-feedstocks in addition to coal. Figure 2 shows a generalized flow sheet of this process. Hynol cannot reduce CO₂ emissions to zero, as shown in Table 1; however, the yield of methanol by Hynol is greater by as much as 20% than producing methanol by two separate conventional plants, i.e., (1) steam gasification of coal alone, and (2) methane reforming alone. Thus, by maximizing methanol production, the Hynol plant becomes economically attractive.

4 THE CARNOL PROCESS

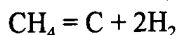
An interesting process which can be applied to coal burning power plants to reduce CO₂ emissions has been developed as follows:

The Carnol Process is composed of three unit operations described as follows:

1. Carbon dioxide is extracted from the stack gases of coal fired power plants using monoethanolamine (MEA) solvent in an absorption-stripping operation. The technology for this operation is well known in the chemical industry for CO₂ recovery and has recently been significantly improved for extracting CO₂ from power plant stack gases.⁽⁷⁾ The power required to recover CO₂ from an integrated coal fired power plant to recover 90% of the CO₂ from the flue gas has been reduced to about 10% of the capacity of the power plant. However, this energy requirement can be further reduced to less than 1% when the CO₂ recovery operation is integrated with a methanol synthesis step described in Item 3 below.
2. The hydrogen required to react with CO₂ for producing methanol can be obtained from either of two methods involving natural gas. In the conventional method for producing hydrogen, natural gas is reformed with steam.



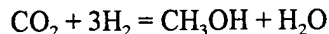
This process produces CO₂ and, thus CO₂ emission is increased. However, hydrogen can be produced without CO₂ emission by the non-conventional method of thermally decomposing methane to carbon and hydrogen.



The energy requirement in conducting this process per unit of hydrogen is less than that required by the above conventional process. A fluidized bed reactor has been used to thermally decompose methane and more recently we are attempting to improve reactor design by utilizing a molten metal bath reactor.⁽⁸⁾

The carbon is separated and either stored or can be sold as a materials commodity, such as in strengthening rubber for tires. The temperatures required for this operation are 800°C or above and pressures of less than 10atm.

3. The third step in the process consists of reacting the hydrogen from Step 2 with the CO₂ from Step 1 in a conventional gas phase catalytic methanol synthesis reactor.



This is an exothermic reaction so that the heat produced in this operation can be used to recover the stack gas CO₂ from the absorption/stripping operation described in Step 1, thus, reducing the energy required to recover the CO₂ from the power plant to less than 1% of the power plant capacity. This is an advantage compared to the energy cost in terms of derating the power plant when CO₂ is disposed of by pumping into the ocean in which case more than 20% of the power

plant capacity is consumed. The gas phase methanol synthesis usually takes place at temperatures of 260°C and pressure of 50 atm using a copper catalyst. The synthesis can also be conducted in the liquid phase by using a slurry of zinc catalyst at a lower temperature of 120°C and 30 atm of hydrogen pressure.

In its simplest form, the Carnol Process is a two-step operation as shown in Figure 3. When hydrogen is used to supply the energy for the thermal decomposition of methane, then the CO₂ emission for methanol production is reduced to zero as given in Table 1. A more detailed evaluation of the Carnol Process is given below.

5 CARNOL PROCESS DESIGN

A computer process simulation equilibrium model has been developed for the Carnol Process based on the flow sheet shown in Figure 4. A material and energy balance selected from a number of computer runs indicates that 112.1 kg of methanol can be produced from 100 kg of natural gas (CH₄) and 171.1 kg CO₂ extracted from the coal fired power plant with a net emission of 25.8 lbs CO₂/MMBTU of methanol energy including combustion of the methanol. The power plant at the same time is credited with a 90% reduction in CO₂ because only 10% of the CO₂ from the MEA solvent absorption plant remains unrecovered and is emitted to the atmosphere.

6 METHANOL AS AN AUTOMOTIVE FUEL

The Carnol Process can be considered as a viable coal-fired CO₂ mitigation technology because the resulting large production capacity of liquid methanol resulting from the large amount of CO₂ emitted can be utilized in a large capacity automotive fuel market. Those processes which utilize CO₂ to produce products for the chemical market such as carbonates and organic chemicals will tend to swamp the market and, thus, cannot be used. Methanol as an alternative automotive fuel has been used in internal combustion (IC) engines as a specialty racing car fuel for a long time. More recently, the EPA has shown that methanol can be used in IC engines with reduced CO and HC emissions and at efficiencies exceeding gasoline fuels by 30%.⁽⁶⁾ Methanol can also be used either directly or indirectly in fuel cells at several times higher conversion efficiency for automotive use.⁽¹³⁾ A great advantage of methanol is that, as a liquid, it fits in well with the infrastructure of storage and distribution compared to compressed natural gas and gaseous or liquid hydrogen which are being considered as alternative transportation fuels. Compared to gasoline, the CO₂ emission from methanol in IC engines is 40% less.

It should also be pointed out that removal and ocean disposal of CO₂ is only possible for large central power stations. For the dispersed domestic and transportation (industry and automobiles) sectors the Carnol Process provides the capability of CO₂ reduction in this sector by supplying liquid methanol fuel to these smaller dispersed CO₂ emitting sources.

7 ECONOMICS OF CARNOL PROCESS

A preliminary economic analysis of the Carnol process has been made based on the following assumptions:

1. 90% recovery of CO₂ from a 600 MW(e) coal fired power plant.
2. Capital investment based on an equivalent 3 step conventional steam reforming plant which amounts to \$100,000/ton MeOH/day.⁽¹⁰⁾
3. Production cost which includes 19% financing, 1% labor, 3% maintenance, and 2% process catalyst and miscellaneous adding up to a fixed charge of 25% of the capital investment (IC) on an annual basis.
4. Natural gas varies between \$2 and \$3/MSCF.
5. Carbon storage is charged at \$10/ton. Market value for carbon black is as high as \$1000/ton.
6. Methanol market price is \$0.45/gal, but has varied historically from \$0.45/gal to \$1.30/gal in the last few years.

At \$18/bbl oil and 90% recovery as gasoline and \$10/bbl for refining cost, gasoline costs \$0.78/gal, and methanol being 30% more efficient than gasoline competes with gasoline at \$0.57/gal methanol.

Table 2 summarizes the economics of production cost factors and income factors for a range of cost conditions. In terms of reducing CO₂ cost from power plants, with \$2/MSCF natural gas, and a \$0.55/gal methanol income CO₂ reduction cost is zero. At \$3/MSCF natural gas and \$0.45/gal income from methanol, the CO₂ disposal cost is \$47.70/ton CO₂, which is less than the maximum estimated for ocean disposal.⁽⁹⁾ More interesting, without any credit for CO₂ disposal from the power plant, methanol at \$0.55/gal can compete with gasoline at \$0.76/gal (~ \$18/bbl oil) when natural gas is at \$2/MSCF. Any income from carbon makes the economics look even better.

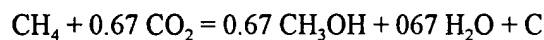
8 CO₂ EMISSION EVALUATION OF ENTIRE CARNOL SYSTEM

The Carnol system consists of a coal-fired power plant, a Carnol process methanol conversion plant and the use of methanol as a liquid automotive fuel.

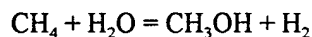
Although we can show 90% or more CO₂ emission reduction for the coal fired power plant, the other two parts of the system, methanol production and automotive emissions, have relatively less CO₂ emission reduction compared to conventional systems. Therefore, the entire Carnol System, as shown in Figure 5, must be evaluated and compared to alternative methanol production processes.

For purposes of comparison, the overall stoichiometry for the Carnol Process is given in the following together with the conventional processes, and with CO₂ addition.

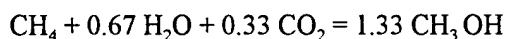
Carnol Process



Conventional Steam Reforming Methane

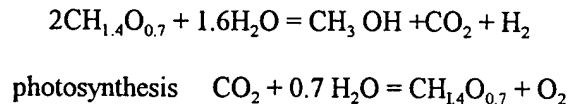


Conventional Steam Reforming of Methane With CO₂ Addition



Methanol can also be produced using biomass and since the net CO₂ emission is zero with CO₂ being converted to biomass by solar photosynthesis, the biomass process must also be included in the evaluation.

Biomass Steam Gasification Process for Methanol Synthesis



The alternative methanol production processes are evaluated in Table 3. The yield of methanol per unit of methane feedstock is shown for the following processes:

1. Conventional process in two parts;
 - A. Steam reforming, of natural gas process, and
 - B. CO₂ addition in steam reforming of natural gas.
2. Carnol process, in two parts;
 - A. Using methane combustion to decompose methane for hydrogen in MDR, and
 - B. Hydrogen combustion to decompose the methane in MDR
3. Steam gasification of biomass process.

The Carnol Process with H₂ and the biomass process (solar energy) reduces CO₂ to zero emission compared to conventional, but with a loss of 35% and 47% methanol yield respectively. The Carnol process when using methane combustion in the decomposer reduces CO₂ emission by 43% while the production yield is only reduced by 26% compared to conventional. The conventional process with CO₂ addition (IB) is interesting because there is an increase of 32% in production although the CO₂ emission is only reduced by 23%. It is noted that in the Carnol process a maximum amount of CO₂ is utilized and an excess of carbon is produced. In the conventional process, no CO₂ is used and an excess of hydrogen is produced. With CO₂ addition to the conventional process, no excess of carbon or hydrogen is formed and methanol per unit natural gas is maximized.

The entire Carnol System is evaluated in table 4 in terms of CO₂ emissions and compared to the alternative methanol processes and to the base line case of conventional coal fired power plant and gasoline driven automotive IC engines. Methanol in fuel cell engines is also evaluated.⁽¹³⁾ All the cases are normalized to emissions from 1MMBTU of coal fired power plant which produces CO₂ for a Carnol methanol plant equivalent to 1.27 BTU for use in an automotive IC engine. The assumptions made are listed at the bottom of Table 4. The conclusions drawn from table 4 are as follows:

1. The use of conventional methanol reduces CO₂ by 13% compared to the gasoline base case and is mainly due to the 30% improved efficiency of the use of methanol in IC engines.
2. By addition of CO₂ recovered from the coal fired power plant to the conventional methanol process, the CO₂ from the power plant is reduced by about 25% (161 lbs/MMBTU compared to 215 lb CO₂/MMBTU) and the CO₂ emissions for the entire system is reduced by 24%. It should be pointed out that part of the CO₂ can also be obtained from the flue gas of the reformer furnace of the methanol plant.

3. The Carnol Process reduced the coal fired power plant CO₂ emission by 90% and the overall system emission is reduced by 56%.
4. Since the use of biomass is a CO₂ neutral feedstock, there is no emission from the power plants because the production of biomass feedstock comes from an equivalent amount of CO₂ in the atmosphere which has been generated from the coal fired power plant. Thus, the only net emission comes from burning methanol in the automotive IC engine and thus, the CO₂ emission for the entire system is reduced by 57%, only slightly more than the Carnol System. However, at present the cost of supplying biomass feedstock is higher than that of natural gas feedstock.
5. Another future system involves the use of fuel cells in automotive vehicles. The efficiency of fuel cells is expected to be 2.5 times greater than gasoline driven engines.⁽¹³⁾ Applying the Carnol process to produce methanol for fuel cell engines reduces the CO₂ emission for the entire system by a maximum of 77%. Furthermore, because of the huge increase in efficiency, the capacity for driving fuel cell engines can be increased by 92% over that for Carnol Process using the same 90% of the CO₂ emissions from the coal burning power plant.

9 CONCLUSIONS

For coal-burning plants, the Hydrocarb Process is less efficient in the production of methanol, and the Hynol Process is the most efficient, but has higher CO₂ emission. The Carnol System can reduce CO₂ emissions from coal fired power plant while producing methanol for automotive IC engines with virtually no derating of the power plant. With natural gas at \$2/MSCF, the methanol cost appears to be competitive with gasoline for IC engines at \$18/bbl oil. The CO₂ emission for the entire Carnol System is reduced by 56%. Compared to the conventional system, steam reformed natural gas with CO₂ addition from the power plant, reduces CO₂ emissions by only 13%, but can have a higher production capacity per unit natural gas than the Carnol Process. Biomass as a methanol feedstock can reduce CO₂ by 57%. The development of methanol fuel cell engines can reduce CO₂ emissions by 77% for the entire system with a large increase in production capacity. Therefore, the use of methanol as an automotive fuel produced from coal fired power plant CO₂ emissions and natural gas appears to be an environmentally attractive and economically viable system connecting the power generation sector with the transportation sector, and, warrants further development effort.

10 REFERENCES

1. Cheng, H. and M. Steinberg, "A System Study for the Removal, Recovery and Disposal of Carbon Dioxide from Fossil Fuel Power Plants in the U.S.," DOE/CH-0016-2 TRO16, U.S. Dept. of Energy, Washington, D.C. (December 1984).
2. Cheng, H.C., Steinberg, M. and M. Beller, "Effects of Energy Technology on Global CO₂ Emissions," BNL 37947, Brookhaven National Laboratory, Upton, NY, November 1983.
3. Steinberg, M. and E.W. Grohse, "Production of a Clean Carbon Fuel and Byproduct Gaseous and Liquid Fuels from Coal by the Hydrocarb Process System," BNL 46490, Brookhaven National Laboratory, Upton, N.Y. (November 1990).
4. Steinberg, M., Y. Dong and R.H. Borgwardt, "The Coprocessing of Fossil Fuels and Biomass for CO₂ Emission Reduction in the Transportation Sector," BNL 49732, Brookhaven National Laboratory, Upton, NY (October 1993).
5. Steinberg, M., "The Carnol Process for Methanol Production and Utilization with Reduced CO₂ Emissions" BNL 60575, Brookhaven National Laboratory, Upton, N.Y. 11973 (October 1993).
6. Motor Vehicle Emissions Laboratory (MVEL), "An Analysis of the Economic and Environmental Effects of Methanol as an Automotive Fuel," EPA report No. 0730, Ann Arbor, Michigan (Sept. 1989).
7. Suda, O., et al., "Development of Fuel Gas Carbon Dioxide Recovery Technology," Chapter in Carbon Dioxide Chemistry Environment Issues, Eds, T. Paul and C.M. Pradies, pp. 222-35, the Royal Society of Chemistry, Hemovan, Sweden, (1994) and T. Mimura, Kansai Electric Power Co., Osaka, Japan, private communication (June 1995).
8. Steinberg, M., "The Carnol Process for CO₂ Mitigation from Power Plants and the Transportation Sector," to be published as EPA Report 606/R-96-003, USEPA, Research Triangle Park, N.C. 27711 (January 1996).
9. IEA Greenhouse Gas R and D Programs, "Greenhouse Issues," No. 7, Cheltenham, U.K. (March 1993).
10. Korchnak, J., John Brown Engineers Co., Houston, Texas, Private Communication (1994).
11. Wyman, C.E., et al., "Ethanol and Methanol from Cellulosic Biomass," pp. 866-923, in Renewable Energy, Eds., T.B. Johansson, et al., Island Press, Washington, D.C. (1993),
12. Larson, E.D., and R.E. Katofsky, "Production of Hydrogen and Methanol via Biomass Gasification," in Advance in Thermochemical Biomass Conversion, Elsevier Applied Science, London, U.K. (1992).
13. World Car Conference '96, Boums College of Engineering, Center for Environmental Research and Technology, University of California, Riverside, CA (January 21-24, 1996).

Table 1 METHANOL PRODUCTION WITH REDUCED CO₂ EMISSIONS

Process and Reactors	Feedstock	Products	MeOH Thermal Efficiency Based on Coal and Natural Gas - %	CO ₂ Emission from MeOH Combustion Lbs/MMBtu	CO ₂ - % Reduction from Conventional Processes
Hydrocarb HPR MPR MSR	Coal	MeOH+C	35%	130	60%
	Coal + Natural Gas	MeOH+C	40%	130	60%
	Coal + Natural gas + Biomass	MeOH+C	45%	~0	~100%
Hynol HPR SPR MSR	Coal + Natural gas	MeOH	65%	260	30%
Carnol MDR MSR	CO ₂ from Coal Fired Power Plant + Natural Gas	MeOH+C	50%	~0	~100%

* CO₂ emission from combustion of methanol produced by natural gas reforming = 170 lbs CO₂/MMBtu produced by coal gasification = 330 lbs CO₂/MMBtu

HPR - Hydrolysis Reactor
MPR - Methane pyrolysis Reactor
MSR - Methanol Synthesis Reactor
MDR - Methane Decomposition Reactor

Table 2 ADVANCED CARNOL VI PRELIMINARY PROCESS ECONOMICS

Plant Size - To Process 90% Recovery of CO₂ from 600 MW(e) Nominal Coal Fired Power Plant
90% Plant Factor, CO₂ Rate = 611 T/Hr. = 4.82 x 10⁶ Tons CO₂/Yr.
Feedstock: Natural Gas Rate = 2.82 x 10⁶ T/Yr. = 407,000 MSCF/D
Carbon Production = 2.03 x 10⁶ T/Yr.
Methanol Production = 3.16 x 10⁶ T/Yr. = 69,300 Bbl/D
Plant Capital Investment (IC) = 9607 T/D x \$10³ = \$961 x 10⁶

0.25 IC	Production Cost Factors						Income Factors					
	Natural Gas			C Storage		CO ₂ Cost		C Income		MeOH Income		Cost for Reducing CO ₂
\$10 ⁶ /Yr	\$10 ⁶ /Yr	(\$/MSCF)	\$10 ⁶ /Yr	(\$/Ton)	\$10 ⁶ /Yr	(\$/Ton)	\$10 ⁶ /Yr	(\$/Ton)	\$10 ⁶ /Yr	(\$/Gal)	\$10 ⁶ /Yr	(\$/Ton)
2.40	2.67	(2)	0.20	(10)	0	(0)	0	(0)	5.27	(0.55)	0	(0)
2.40	4.00	(3)	0.20	(10)	0	(0)	0	(0)	5.27	(0.55)	-1.34	(-27.60)
2.40	2.67	(2)	0.20	(10)	0	(0)	0	(0)	5.27	(0.55)	0	(0)
2.40	4.00	(3)	0	(0)	0	(0)	1.13	(55.60)	5.27	(0.55)	0	(0)
2.40	2.67	(2)	0.20	(10)	0	(0)	0	(0)	4.30	(0.45)	-0.97	(-20.00)
2.40	2.67	(2)	0	(0)	0	(0)	0.77	(37.90)	4.30	(0.45)	0	(0)
2.40	4.00	(3)	0.20	(10)	0	(0)	0	(0)	4.30	(0.45)	-2.30	(-47.70)
2.40	4.00	(3)	0	(0)	0	(0)	2.10	(103.00)	4.30	(0.45)	(0)	(0)

**Table 3
METHANOL PRODUCTION AND CO₂ EMISSION
PROCESS COMPARISON**

PROCESS	PRODUCTION YIELD		CO ₂ EMISSION ⁴	
	Moles MeOH Mole Feedstock	% Reduction from Conventional	Lbs CO ₂ MMBTU (MeOH)	% Reduction from Conventional
1A Conventional Process Steam Reforming of CH ₄	0.76 ¹	0%	44	0%
1B Conventional Process with CO ₂ Addition	1.00	(32%) ²	34	23%
2A Carnol Process Heating MDR with CH ₄	0.56	26%	25	43%
2B Carnol Process Heating MDR with H ₂	0.50	35%	0	100%
3 Steam Gasification of Biomass	0.40 ³	47%	— 43	100%

1. Based on thermal efficiency of 64% (Ref. 11)
2. This represents a 32% increase in yield vs conventional
3. Based on BCL process (Ref. 12)
4. CO₂ emission only from fuel production plant

**Table 4 CO₂ EMISSION COMPARISON FOR SYSTEMS CONSISTING OF
COAL FIRED POWER PLANT, FUEL PROCESS PLANT AND AUTOMOTIVE POWER PLANT**

Basis 1 MMBTU for coal fired 600 MW(e) power plant
1.27 MMBTU of liquid fuel for IC engine - other fuel efficiencies proportions energy up and down
CO₂ Emission units in Lbs CO₂/MMBTU (multiply by 0.43 for KG/GJ)

System Unit	Coal Fired Power Plant	Fuel Process Plant	IC Automotive Power Plant	Total System Emission	CO ₂ Emission Reduction
Baseline Case: Coal Fired Power Plant and Gasoline Driven IC Engine	215	15	285	515	0%
Case 1A Coal Fired Power Plant With Conventional Steam Reformed Methanol Plant	215	56	175 ⁴	448	13%
Case 1B Coal Fired Power Plant With CO ₂ Addition to Conventional Methanol Plant	161 ⁴	54	175	390	24%
Case 2 Coal Fired Power Plant with CARNOL Process Methanol Plant	21 ¹	32	175	228	56%
Case 3 Coal Fired Power Plant with Biomass for Methanol Plant	0	43	175	219	57%
Case 4 Coal Fired Power Plant with CARNOL Methanol and Fuel Cell Automotive Power	11 ³	17	Fuel Cell 89 ³	117	77%

- 1) 90% recovery of CO₂ from coal fired plant.
- 2) Methanol is 30% more efficient than gasoline in IC engines.
- 3) Fuel cell as 2.5 times more efficient than conventional gasoline IC engine
Only 52% emissions of coal plant CO₂ is assigned to Carnol for fuel cells
- 4) Only 25% recovery of CO₂ from coal plant is necessary for supply CO₂ to conventional methanol plant

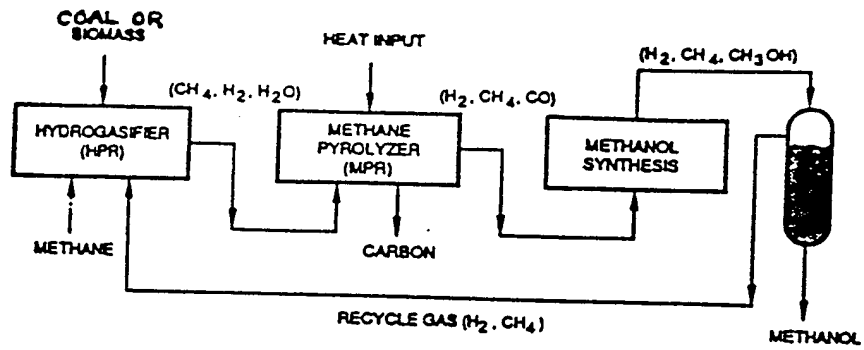


Figure 1 Hydrocarb process block diagram

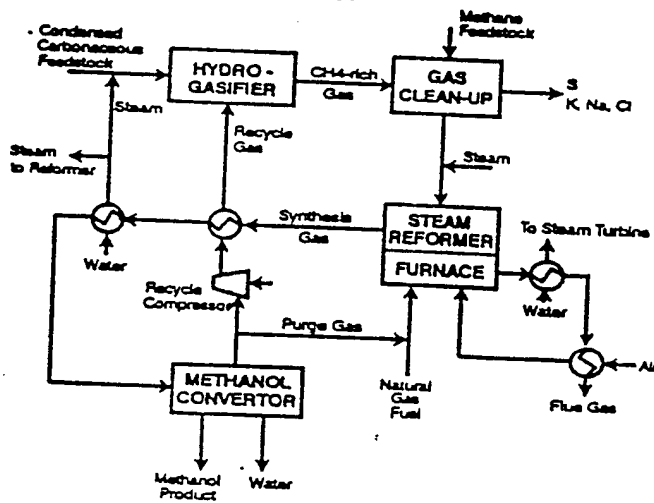


Figure 2 A block diagram of the Hynol process.

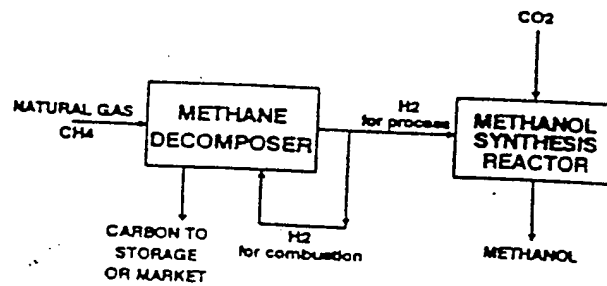


Figure 3 Carnol III process for producing methanol from natural gas and CO₂ for zero CO₂ emission.

Figure 4
Carnol VI Process
Methanol Production From Power Plant CO₂ and Natural Gas
Process Simulation

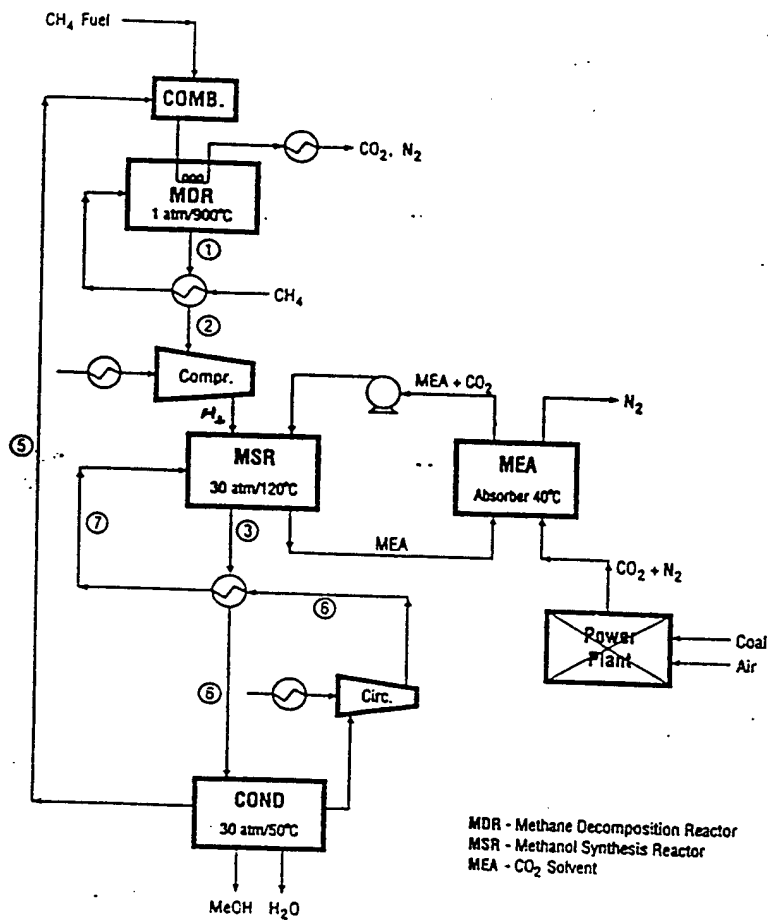


Figure 5

CARNOL System Configuration For CO₂ Emission Mitigation

