BNL-62835

INFORMAL REPORT

The Carnol Process for CO_2 Mitigation From Power Plants and The Transportation Sector

by

Meyer Steinberg
Engineering Research & Applications Division
Department of Advanced Technology
Brookhaven National Laboratory
Upton, NY 11793

December 1995

Abstract

A carbon dioxide (CO_2) mitigation process is developed which converts waste CO_2, primarily from coal-fired power plant stack gases, to methanol for use as a liquid fuel and a coproduct carbon for use as a materials commodity. The Carnol process chemistry consists of methane decomposition to produce hydrogen which is catalytically reacted with the recovered waste CO_2 to produce methanol. The carbon is either stored or sold. A process design is modelled, and mass and energy balances are presented as a function of reactor pressure and temperature conditions. The Carnol process is a viable alternative to sequestering CO_2 in the ocean for purposes of reducing CO_2 emissions from coal burning power plants. Over 90% of the CO_2 from the coal burning plant is used in the process which results in a net CO_2 emission reduction of over 90% compared to that obtained for conventional methanol production by steam reforming of methane. Methanol, as an alternative liquid fuel for automotive engines and for fuel cells, achieves additional CO_2 emission reduction benefits. The economics of the process is greatly enhanced when carbon can be sold as a materials commodity. The process design and economics could possibly be achieved by developing a molten metal (tin) methane decomposition reactor and a liquid phase, slurry catalyst, methanol synthesis reactor directly using the solvent saturated with CO_2 scrubbed from the power plant stack gases. The application of CO_2 mitigation technologies, such as the Carnol process, depends to some extent, on how serious the country and the world takes the global greenhouse gas warming problem.

I. INTRODUCTION

The evidence for greenhouse gas CO_2 warming causing global climate change is continuing to mount, and international agreements are being sought to limit CO_2 emissions (1). The CO_2 emissions are primarily due to fossil fuel combustion (principally coal, oil, and gas) in the industrial, commercial, and transportation sectors. Although much effort in the U.S. has gone into the science of climate change, relatively little effort has been expended for technologies that mitigate greenhouse gas emissions. Improvement in efficiency of energy production and utilization is recognized as a cost effective method for reducing CO_2 emission to a limited degree(2). Fuel substitution, utilizing more natural gas and oil versus coal, is recognized to further reduce CO_2 emission. The use of biomass for energy production is also effective in CO_2 reduction. A more aggressive manner for reducing CO_2 emissions is the removal, recovery, and then disposal of CO_2 from central power plants, which primarily burn coal. A fair amount of research has gone into disposal and sequestering of CO_2 in the ocean and in depleted gas wells (3). However, CO_2 sequestration presents some formidable, technical, and economic problems. Much less effort has gone into precombustion fuel processing to significantly reduce CO_2 emission. Coal gasification combined cycle is one limited step in that direction but still requires CO_2 sequestration (3). The concept of extraction and disposal of carbon from fossil fuels and utilization of the hydrogen enriched fractions has been introduced with the idea that carbon is much less difficult to store and sequester than CO_2(4). The coprocessing of fossil fuels with biomass by the Hydrocarb process(5), producing methanol as a liquefied fuel, can achieve zero CO_2 emission. The use of methanol as an efficient automotive fuel can further reduce CO_2 emission from the transportation sector(6). To maximize methanol production and reduce development effort, the Hynol process which coprocesses biomass with natural gas has been introduced(7) and avoids carbon sequestration while still obtaining significant CO_2, emission reduction in a cost effective manner. In this paper we describe and develop an alternative process which converts waste CO_2, primarily recovered from coal-fired power plant stack gases, using natural gas to produce methanol as a liquid fuel and carbon as a storable materials commodity coproduct.

II. THE CARNOL PROCESS DESCRIPTION

The Carnol process grew out of a preliminary investigation of alternative processes for using CO_2(8). The Carnol process relies on two basic chemical reactions: the thermal decomposition of methane and the catalytic synthesis of methanol from hydrogen with CO_2

Methane decomposition: $3CH_4 = 3C + 6H_2$

Methanol synthesis: $2CO_2 + 6H_2 = 2CH_3OH + 2H_2O$

Overall Process: $3CH_4 + 2CO_2 = 2CH_3OH + 2H_2O + 3C$

Thus 1 mole of methanol is produced from the utilization of 1 mole of CO_2 which results in a net zero CO_2 emission when the methanol is burned. It takes 1.5 moles of CH_4 to produce 1 mole of methanol or to react with 1 mole of CO_2 by means of hydrogen. The CO_2 mitigation comes about by removing 1 mole of CO_2 from power plant stack gas (primarily coal fired) and producing but not burning the 1.5 moles of carbon per mole of methanol produced.

Both reactions are known to take place and have been practiced in different forms on a commercial scale. Methane decomposition to form carbon black is known as the Thermal Black process(9). The hydrogen is not recovered in this process but is used as fuel. From an energy point of view the Thermal Black process as commercially practiced is very inefficient. A continuous catalytic methane cracking process called Hypro has been operated for hydrogen production for hydrocracking oil in a refinery; however, in this case the carbon was not recovered but was used as fuel in the process(10).

The catalytic methanol synthesis from CO_2 and hydrogen has also been practiced commercially; however, only on a limited scale, mainly because of the lack of cost effective CO_2 feedstock(11). Most methanol produced currently is made by the catalytic synthesis of CO and hydrogen which is produced by the steam reforming of natural gas(12). There is no reduction in CO_2 emission by the use of the conventional methanol synthesis process using natural gas. In fact when coal is used to produce the synthesis gas, there is a large increase in CO_2 emission.

The Carnol process development is based on the following considerations.

1. Much chemical engineering development effort has recently gone into removal and recovery of CO_2 from power plant stack gases. Through the use of hindered amine absorption solvents, the energy requirement for CO_2 removal and recovery has been significantly reduced(3).
2. In principle, hydrogen production by methane decomposition requires the least amount of energy compared to other means of hydrogen production, such as steam reforming of methane and electrolysis of water(14). It only takes 18 kcal* to decompose 1 mole of methane. Thus the production of 1 mole of hydrogen requires only 5% of the energy of combustion of natural gas. The kinetics of methane decomposition has been further studied(15) and has become better understood. High surface area carbon itself can act as an autocatalyst for improving rates of decomposition at lower temperatures..
3. Much catalyst development work has lately gone into the synthesis of methanol from CO_2 and hydrogen resulting in the development of improved catalysts (16).
4. Methanol as an alternative fuel has a number of benefits: (1) it is a liquid fuel which can be used on a large scale, (2) it can be transported and stored in accordance with the present infrastructure, (3) it can be used in stationary and automotive engines as a substitute for petroleum based fuel, thus reducing imports and improving the balance of payments, (4) when used in internal combustion engines, it is 30% more efficient than gasoline which results in lower CO_2 emission(6) in the transportation sector, and (5) it has

---

[*] Readers more familiar with metric units may use the factors listed at the end of the front matter of this report to convert to this system.

potential as an ideal fuel supply for efficient fuel cell power systems now under development.

5. The Carnol process converts CO_2 from power plant stacks to another useful fuel product and thus the carbon from the power plant is essentially used twice. Furthermore, the methanol fuel can obtain additional CO_2 reduction when used in the dispersed automotive sector of the economy. CO_2 emission from automotive engines emits about 30% of the total emission of CO_2 in the U.S. which is about the same quantity of CO_2 emitted from central power plant stacks.
6. It is possible to obtain low net CO_2 emission without the use of biomass. Instead of using waste CO_2 from the atmosphere through biomass, Carnol uses waste CO_2 directly from coal burning power plant stacks.
7. It is possible to consider the large scale application of Carnol because next to coal, natural gas is abundantly available at low cost.

Based on thermodynamic principles, a first order simplified analysis of Carnol can be made using the simplified two reactor flow diagram shown in Figure 1 and given in Table 1(8). Hydrogen is used to provide the endothermic heat of reaction (by indirect heat transfer) for the thermal decomposition of methane so as to obtain zero CO_2 emission. The catalytic CO_2/H_2 reaction for methanol synthesis is exothermic and can produce some process steam. Table 1 indicates that there is a 61% reduction in methanol yield by the Carnol process compared to the conventional methanol process by steam reforming of methane using the same simplified procedure. However, the CO_2 emission is completely eliminated compared to conventional methanol production. Although the thermal efficiency is 49.7% compared to 81.5%(12) by the conventional process, there is available a significant quantity of carbon coproduct which can be sold as a useful material on the commodity market to offset methanol costs in competing with conventional methanol cost. Because the potential production of carbon from the process can exceed the current market for carbon, new markets for carbon can be made available as an alternative to just sequestering (storage) of the carbon. Thus, thermal efficiency is not the only criterion by which to judge the Carnol process.

III. CARNOL PROCESS DESIGN

A process design and analysis has been made taking into account process temperature and pressure conditions. A computer simulation program was used to make a detailed mass and energy balance. The assumptions in the model are:

1. Close approach to equilibrium is assumed in the methane decomposition reactor (MDR) and the methanol synthesis reactor (MSR). The equilibrium data for methane decomposition are graphically shown in Figure 2.
2. A fluidized bed MDR is assumed using an indirectly heated circulating alumina heat transport system. The rate of methane thermal decomposition is adequate, for a reasonable reactor design, at temperatures of 800°C and above(15).

3. The MSR is a conventional Imperial Chemical Industries, Inc. (ICI) type gas-phase methanol catalytic converter operating at 50 atm pressure and 260°C with a 4 to 1 recycle ratio to achieve close to 100% conversion of the CO_2 feed to the MSR system.
4. A multistage compressor increases the pressure of the process gas from the MDR to the MSR. The compressor is driven by steam generated from the MDR combustor exhaust gas.
5. A condenser-fractionator separates the product methanol from the water, and the exothermic energy from the MSR provides the steam for the fractionator.
6. Residual gas from the MSR is recycled to the MDR for either process gas or as fuel in the combustor.
7. CO_2 is supplied as gas at 1 atm from the power plant stack gas recovery system.

A number of recycled and heat transfer configurations and process variables were explored. Table 2 gives the results of 11 computer runs for the process flow sheet configuration shown in Figure 3 (designated as Carnol III) varying the MDR pressure and temperature from 1 to 50 atm and the temperature from 800 to 1100°C respectively. Increasing temperature in the MDR decreases CO_2 emission, and increasing pressure in the MDR increases CO_2 emission. Decreasing pressure in the MSR also increases CO_2 emission. Table 2 indicates that, at 1 atm pressure in the MDR and temperatures from 800 to 1100°C, the yield (thermal efficiency) of MeOH remains at 41.1% while the CO_2 emission is reduced by 87% and higher compared to the combustion of methanol produced by the conventional steam reforming process. From a materials point of view, temperatures on the order of 800 to 900°C for the MDR are preferable. The flow sheet of Figure 3 is based on an MDR temperature of 800°C. A summary of the mass and energy balances for Carnol III is given in Table 3 and the stream compositions in Figure 3. The decrease in thermal efficiency from the simplified analysis of 49.7% indicates the inefficiencies when taking into account detailed mass and energy balances.

The CO_2 feed to the Carnol process is provided by removal and recovery from coal fired power plant stack gases by a monoethanolamine (MEA) solvent absorption-stripping system. The amine system has been used for CO_2 removal and recovery from process gases in ammonia and methanol plants in the U.S. for a number of decades. Recently published papers from Japan(13) have shown that hindered amine solvents and improved absorption column packing can decrease the pressure drop across the column. That system, with the power plant, has decreased energy requirements so that there is only an 8% loss in power from a coal burning plant when recovering 90% or better of the CO_2 from its stack gases.

IV. PRELIMINARY ECONOMIC ANALYSIS

The assumptions made are:

1. CO_2 is removed and recovered from a 600 MW(e) coal burning plant (40% efficiency) using amine solvent at 90% CO_2 recovery, 90% plant factor, and 10% additional capacity to make up for avoidance loss.

$$CO_2\ rate = \frac{215\ lb}{MMBtu\ coal} \times 6 \times 10^5\ kW(e) \times \frac{8500Btu}{kW(e)} \times 7884\ \frac{hr}{yr} \times \frac{ton}{2000lb} = 4.34 \times 10^6\ T/yr$$

The Carnol plant capacities are shown at the bottom of Table 4 requires 400,000 MSCF/D of natural gas. The methanol production rate is 8460 T/D or 61,100 bbl/D and the carbon produced is 5800 T/D.

2. Since, the Carnol plant has two reaction steps (MDR and MSR) and the conventional plant has two steps (steam reforming of methane and MeOH synthesis), the capital investment is based on an equivalent conventional methanol world size plant estimated at \$100,000/ton MeOH/day(17). Thus, the total investment is \$100,000 x 8460 T/D = $\$846 \times 10^6$. Production cost is estimated based on factors of capital investment as follows: 19% for financing (depreciation & interest), 1% for labor, 3% for maintenance and 2% for power and miscellaneous, resulting in a total of 25% of the capital investment on an annual basis for the production cost.
3. Natural gas prices are assumed to vary between \$2 and \$3/MSCF (\$95 to \$142/ton). Note that natural gas prices in the U.S. were as low as \$1.50/MSCF (\$71/ton) in 1994.
4. The carbon is assumed to be stored at \$10/ton. Carbon can also result in income since it has a market in tires, pigments, newsprint inks, etc. Depending on grade, carbon can sell for from \$100 to \$1000/ton. In Table 4, carbon price balanced production cost at less than \$20/ton.
5. The cost of CO_2 to Carnol recovered from the power plant can be a highly variable quantity depending on whether there is a carbon tax, in which case Carnol can charge the power plant for disposing of the CO_2. At full cost recovery, it is estimated that \$5/ton would cover the cost of CO_2 recovery, assuming 8% reduction in power plant output charged at \$0.06/kWh(e). Other CO_2 cost charges were also assumed varying from zero to \$108/ton as the market income of MeOH varied.
6. The market price of MeOH has been historically around \$0.45/gal (\$136/ton) depending on stable natural gas feed stock costs. Recently, the MeOH market price increased to \$1.30 gal (\$394/ton) due to a supply shortage in its use for production of methyltertiary butyl ether (MTBE) mandated as a gasoline oxygenation agent (18). This huge increase in price has a profound effect on the economics of the Carnol process. However, as soon as new MeOH capacity comes on line in the next several years, it is expected that the price will drop back to historical levels(18). At \$0.45/gal MeOH competes with gasoline at a production cost of \$0.69/gal based on a 30% improvement in internal combustion (IC) engine efficiency (1.54 gal MeOH is equivalent to 1 gal gasoline)(6). No credit is taken in this paper for the use of methanol as a transportation fuel which would result in an additional 30% reduction in CO_2 emission compared to gasoline.

In Table 4, production cost factors were equated to income factors and the CO_2 credit was determined in the last column and evaluated as the figure of merit for the process. The conclusions drawn from this analysis are:

1. When operating the MDR at 900°C and above and the MSR at 50 atm, the CO_2 emission reduction is greater than 90% compared to CO_2 emission for methanol production by the conventional process.
2. With no cost for feedstock CO_2 to Carnol, natural gas at \$2/MSCF, no credit for carbon, and methanol at \$0.45/gallon, the cost of reducing CO_2 emission is \$25/ton (listed as negative credit). This is less than the average International Energy Agency (IEA) estimate for removal, recovery and sequestering CO_2 in the ocean at \$37/ton neglecting transportation (pipelining) costs to the ocean. At \$3/MSCF the CO_2 reduction cost using Carnol increases to \$55/ton which is the upper limit for ocean disposal of CO_2 neglecting pipelining to the ocean.
3. By selling the carbon as a commodity at \$58 and \$126/ton when natural gas costs \$2 and \$3/MSCF respectively, the CO_2 reduction cost is reduced to zero. Since the carbon is very pure this carbon price of \$0.06/lb or less would have an easy market to compete with current prices of carbon black of up to \$0.50/lb. The U.S. market for tire carbon amounts to 2×10^6 tons/yr. and there are other uses for carbon at a low cost price, for example as a filler in construction materials.
4. If the power plant wants to recover its cost for recovering CO_2 up to as high as \$10/ton, at a natural gas cost of \$3/MSCF, carbon produced by Carnol would have to sell for \$170/ton (\$0.085/lb) to achieve zero CO_2 reduction cost, which is still a very reasonable possibility.
5. If the methanol can continue to demand \$1.30/gal or almost 3 times the historical price, at \$3/MSCF for natural gas and CO_2 feedstock cost recovered from the power plant of \$5/ton (recoverable cost) and assuming no carbon sales, a CO_2 credit of \$103/ton for reducing CO_2 emission can be realized. On the other hand, if the CO_2 credit for reducing emissions is reduced to zero, the power plant could charge as much as \$108/ton for feeding its CO_2 to the Carnol plant. Obviously the charges and profits could be negotiated between the power plant and the Carnol plant.

It can be pointed out that the production of carbon using all the CO_2 from a 600 MW(e) coal fired power plant for feedstock to the Carnol plant will produce approximately 2×10^6 T/Yr of carbon black which is equivalent to the current market capacity of the carbon black. Thus, new markets for carbon black must be developed - if cost offset to methanol is needed - an alternative to just sequestering the carbon. At a low cost of carbon, as offered by the Carnol process, a new market should be possible, for example, for carbon as a filler in construction material.

V. ADVANCED CARNOL VI PROCESS

Two recent developments have been uncovered that could significantly improve the basic Carnol process. One is methane decomposition and the other is methanol synthesis.

1. The design of an efficient methane decomposition reactor (MDR) can be difficult because high temperature energy must be provided to decompose the methane, and the particulate carbon must be recovered and removed in a continuous manner. As mentioned earlier,

intermittent reheat batch reactors and fluidized bed reactors have their drawbacks. Recently, we have found that molten metal technology is being applied to decompose liquid and solid carbonaceous waste material to produce simple gaseous compounds using a molten iron (Fe) bath at temperatures from 1400 to 1650°C(19). The advantage of using a molten metal bath to decompose waste material can be readily applied to the decomposition of methane. Molten metal is a good liquid phase direct contact heat transfer media through which gaseous methane can be bubbled. The large density differences between solid carbon and the molten metal could allow efficient capture from the gas phase and separation of the carbon particles from the liquid phase by flotation. Although molten iron at temperatures up to 1600°C could completely decompose methane to its elements, carbon and hydrogen, as indicated by the equilibrium diagram in Figure 2, the use of such extreme temperatures is a disadvantage when it becomes necessary to design a thermally efficient heat recovery system. Molten tin (Sn) at a lower temperature appears to be a suitable molten metal media for an MDR for the following reasons:

a) The liquid range for Sn is much wider than for Fe; Mpt = 236°C to Bpt 2260°C.
b) Density of liquid Sn = 7.31 g/cm^3
c) Partial pressure of Sn at 1000°C = < 10^{-6} atm (< 1 ppm)
d) Molten tin in the range of 800 to 1000°C should be sufficient to decompose methane to a high degree.
e) The molten metal Sn bath may also be catalytic for decomposing methane.
f) Carbon does not react or dissolve in liquid Sn.
g) Surface nitrided refractory metal (titanium or molybdenum) can provide adequate corrosion resistant materials for heat transfer and containment of the molten tin.
h) The viscosity of the molten Sn is low which provides for good mixing between the gaseous and liquid phases.

2. Recently liquid-phase catalytic synthesis of methanol has been shown to improve production of methanol because of improvement in transferring the exothermic heat of the synthesis reaction(20). The catalyst is in a slurry form in an organic solvent carrier such as an oil or glycol. For application in the Carnol process it then becomes possible to practice liquid-phase methanol synthesis by reacting hydrogen with CO_2 when it becomes absorbed in the MEA solvent during recovery from the power plant stack gases. A methanol synthesis catalyst would be carried in slurry form in the MEA absorbent. The conditions for the synthesis can be estimated from the phase diagram shown in Figure 4 using a hindered amine solvent(13). For example, absorbing flue gas CO_2 from a coal burning plant, at equilibrium at 40°C, produces a solution having a CO_2 to amine ratio of 0.58. Heating this solution to 120°C gives an equilibrium partial pressure of CO_2 above this solution of 100 psia (6.8 atm). By pressurizing this solution with hydrogen up to about 30 atm pressure, thus providing a 3 to 1 H_2 to CO_2 partial pressure ratio in the presence of the slurry catalyst, methanol should be formed. Table 5 estimates the equilibrium concentration of methanol at 30 and 50 atm and at 120 and 260°C, respectively, when feeding a 3 to 1 ratio of H_2 to CO_2 mixture. These data indicate a

much improved yield of methanol at the lower temperature, which results in a lower recycle ratio and improved economics of the process[21].

Applying the above two developments, a Carnol VI process flowsheet is designed and is shown in Figure 5. The heat recovery around the molten tin reactor and the separation of hydrogen from the unreacted methane by pressure swing adsorption (PSA) to produce a pure H_2 stream are shown in Figure 6. A heat and mass balance for Carnol VI indicates that the overall thermal efficiency for production of methanol is 49.7%. By storing the carbon or using it as a materials commodity, the net CO_2 emission, taking credit for CO_2 from the power plant, is 13.0 kgCO_2/GJ (30.2 lb CO_2/MMBtu) which represents an 83% reduction in CO_2 emission compared to the production of methanol by conventional process; i.e., the steam reforming of natural gas. When methanol is used in IC engines an additional 30% reduction in CO_2 emission is obtained compared to the use of gasoline as automotive fuel.

VI. CONCLUSION

The Carnol process, which produces methanol as a liquid fuel, can effectuate a very significant net decrease in CO_2 emission from coal-fired power plants. The economic value is significantly improved when the coproduct carbon can be sold as a materials commodity. Two research and development efforts which can significantly improve the process are (1) developing a molten metal methane decomposition reactor and (2) developing a liquid-phase MEA slurry catalyst reactor for directly converting CO_2 scrubbed from power plant fuel gas with hydrogen from methane decomposition to produce methanol as a liquid fuel for the automotive industry. Further development of the Carnol process is required to realize the full benefits of the process. Serious consideration of the applicability of the Carnol process depends on how serious the country and the world takes the global greenhouse gas warming problem and CO_2 mitigation technologies.

REFERENCES

[1] W.K. Stevens, "Scientists Warn of Effect of Rise in Greenhouse Gases," New York Times, The Environment, p.C4 (April 11, 1995).

[2] E. Mills, D. Wilson, T. Johanssen, "Getting Started. No Regrets Strategies for Reducing Greenhouse Gas Emissions," Energy Policy, July/August (1991).

[3] U.S. Department of Energy, "The Capture, Utilization and Disposal of CO_2 from Fossil Fuel-Fired Power Plants," Vols. I and II, Washington, D.C. (1993).

[4] M. Steinberg, "Biomass and Hydrocarb Technology for Removal of Atmospheric CO_2," BNL-44410, Brookhaven National Laboratory, Upton, NY (March 1990).

[5] M. Steinberg, Y. Dong , R.H. Borgwardt, " The Coprocessing of Fossil Fuels and Biomass for CO_2 Emission Reduction in the Transportation Sector," Energy Convers. Mgmt. 34, No. 9-11, p. 1015-1022 (1993).

[6] EPA Report, "An Analysis of the Economic and Environmental Effects of Methanol as an Automotive Fuel," EPA Report No. 0730, (NTIS PB90-225806), Motor Vehicle Emissions Laboratory, Ann Arbor, Michigan (September, 1989).

[7] M. Steinberg, Y. Dong, "Hynol, an Economic Process for Methanol Production from Biomass and Natural Gas with Reduced CO_2 Emission," BNL-49733, Brookhaven National Laboratory, Upton, NY (October 1993).

[8] M. Steinberg, Y. Dong, "The Carnol Process for Methanol Production and Utilization with Reduced CO_2 Emissions," BNL-60575, Brookhaven National Laboratory, Upton, NY (June 1994).

[9] J.P. Donnet, A. Voet, Carbon Black, pp. 16-18, Marcel Dekker, New York, NY (1976).

[10] "Hypro Process Cleaves Hydrogen from Hydrocarbon," Chem. Eng. 69, p. 90-91 (1962).

[11] Faith, Keyes, Clarke, Industrial Chemicals 4th Edition, p.526, John Wiley and Sons, New York, NY (1975).

[12] L.E. Wade et al., "Methanol ," Kirk-Othmer Encyclopedia of Chemical Technology 15, 3rd Ed., p. 398-415, Wiley-Interscience and Sons, New York, NY (1981).

[13] Suda et al., "Development of Fuel Gas Carbon Dioxide Recovery Technology," Chapter in Carbon Dioxide Chemistry: Environmental Issues, Ed. by Jon Paul and Claire-Marie Pradier, p. 222-35, The Royal Society of Chemistry, Sweden (1994).

[14] M. Steinberg, "The Hy-C Process (Thermal Decomposition of Natural Gas) Potentially the Lowest Cost Source of Hydrogen with the Least CO_2 Emission," BNL-61364, Brookhaven National Laboratory, Upton, NY (December 1994).

[15] A. Kobayashi, M. Steinberg, "The Thermal Decomposition of Methane," BNL-47159, Brookhaven National Laboratory, Upton, NY (January 1992).

[16] H. Arakawa et al., "Effective Conversion of CO_2 to Methanol and Dimethyl Ether by Catalytic Hydrogenation Over Heterogeneous Catalysts," International Conference on Carbon Dioxide Utilization, p. 95-102, University of Bari, Italy (Sept. 26-30, 1993).

[17] J. Korchnak, John Brown Co. A/E Houston, TX, Personnel Communication (1994).

[18] G. Peaff, "Methanol Transformation to Commodity Status Stretchers Supply," Chem. & Eng. News, p. 13-15 (October 24, 1994).

[19] P. Nahass, P.A. Moise, C.A. Chanenchuk, "Quantum CEP for Mixed Waste Processing," Molten Metal Technology, Inc., Waltham, MA (1994).

[20] S. Lee, Methanol Synthesis Technology, p. 198-224, CRC Press, Inc., Boca Raton, FL (1990).

[21] S. Okyama, "Evaluation of Low Temperature Methanol Synthesis in the Liquid Phase," ACS Division of Fuel Chemistry, 200th ACS National Meeting 39 No. 4, p. 1182-6, Washington, D.C. (Aug. 20-25, 1994).

This work was done under the auspices of the U.S. Dept. Of Energy under Contract No. DE-AC02-76CH00016.

Table 1
SIMPLIFIED THERMODYNAMIC ANALYSIS OF CARNOL PROCESS

Unit Operations	Reaction	Enthalpy, ΔH
Decomposition:	$3CH_4 = 3\ C + 6H_2$	$+ 18$ kcal/mol CH_4
MeOH Synthesis:	$2CO_2 + 6H_2 = 2CH_3OH + 2H_2O$	$- 22$ kcal/mol MeOH
Combustion:	$H_2 + \frac{1}{2}O_2 = H_2O$	$- 68$ kcal/mol H_2

Carnol Process Analysis

Moles CH_4 to produce 2 moles MeOH		= 3.000
Moles CH_4 to produce combustion H_2 for heat transfer to CH_4		= 0.455
Moles MeOH per total mole CH_4	= 2.00/3.455	= 0.579
Higher heat of combustion of MeOH		= 182,000 kcal/Mol
Higher heat of combustion of CH_4		= 212,000 kcal/Mol
Carnol MeOH thermal efficiency		= 49.7%
Carbon produced per mol MeOH	= 3.455/2.0	= 1.728

CO_2 emission=-2 mol CO_2 (from stack gas) $+2$ mol CO_2 from MeOH combustion = 0

Conventional Process Analysis(12)

Moles MeOH produced per mol CH_4	= 0.95
Thermal efficiency	= 81.5%
Moles CO_2 produced per mol CH_4	= 1.05

Relative to Conventional Methanol

Carnol process CO_2 reduction	= 100%
Yield of Carnol MeOH to conventional	= 61%

Table 2
METHANOL PRODUCTION EFFICIENCY AND CO_2 EMISSION REDUCTION AS A FUNCTION OF PROCESS REACTOR CONDITIONS

CARNOL III+ PROCESS CONFIGURATION FOR METHANOL PRODUCTION FROM CO_2 AND METHANE

Methane Feed = 100 kg

Computer Run No.	MDR P atm/T°C	MSR P atm/T°C	CO_2 Feed Stock kg	MeOH Thermal Eff. %	MeOH Carbon Eff. %	CO_2 Emission $\frac{\text{lb}}{\text{MM Btu}}$ HHV MeOH	CO_2* Emission Reduction
1	1/800	50/260	156.6	41.1	50.3	22.7	87.4
5	1/900	50/260	147.1	41.1	50.4	10.2	94.3
6	1/1000	50/260	143.1	41.1	50.4	5.0	98.2
10	1/1100	50/260	142.5	41.5	50.8	2.7	98.5
11	1/800	30/260	163.1	27.7	34.0	33.7	81.3
2	1/800	30/120	150.1	44.3	54.2	21.1	88.3
3	1/800	6.8/120	163.1	40.7	49.9	23.0	87.3
4	10/900	50/260	133.3	28.8	35.3	99.3	44.8
8	10/900	10/120	133.3	31.5	38.6	90.9	49.5
7	30/100	50/260	122.2	30.3	145	Increase in Emission	
9	10/1000	10/260	-- NO BALANCE OBTAINED --				

*Emission reduction is compared to production of methanol by conventional steam reforming of natural gas which produces 180 lb CO_2/MM Btu of methanol energy (HHV). Thermal efficiency for a conventional steam reforming plant for methanol production=64%

Table 3

CARNOL PROCESS III DESIGN
PROCESS SIMULATION - MASS AND ENERGY BALANCES

UNIT	CARNOL III+ H_2 - RICH GAS FUEL FOR MDR
MDR	
Pressure, atm	1
Temperture, °C	800
CH_4 Feedstock, kg	100
Preheat Temp, °C	640
CH_4 Fuel for MDR, kg	0
CH_4 Conversion, %	91.9
Carbon Produced, kg	68.8
Heat Load, kcal	82,091
Purge Gas for Fuel, kmol	2.4
MSR	
Pressure, atm	50
Temp., °C	260
CO_2 Feedstock, kg	156.6
CO_2 Conversion, %	90.9
Methanol Produced, kg	100.6
Water Condensed kg	58.7
Energy for Gas Compression to MSR	
Energy, kcal	75,114
Performance	
Ratio, MeOH/CH_4, kg/kg	1.01
Carbon Efficiency MeOH, %	50.3
Thermal Efficiency MeOH, %	41.1
Thermal Efficiency C + MeOH, %	81.8
CO_2 Emission, lb/MM Btu	22.7
CO_2 Emission, kg/GJ	9.8

Table 4

PRELIMINARY CARNOL PROCESS ECONOMICS
Costs shown in $\$10^8$/yr and (Unit Costs)

Investable Capital Cost (IC) = $8.46 x 10^8*

PRODUCTION COST FACTORS = INCOME FACTORS

0.25 IC	Natural Gas		C Storage		CO_2 Cost		C Income		MeOH Income		CO_2 Credit	
$\frac{\$10}{yr}$	$\frac{\$10^8}{yr}$	$\left(\frac{\$}{MSCF}\right)$	$\frac{\$10^8}{yr}$	$\left(\frac{\$}{ton}\right)$	$\frac{\$10^8}{yr}$	$\left(\frac{\$}{ton}\right)$	$\frac{\$10^8}{yr}$	$\left(\frac{\$}{ton}\right)$	$\frac{\$10^8}{yr}$	$\left(\frac{\$}{gal}\right)$	$\frac{\$10^8}{yr}$	$\left(\frac{\$}{ton}\right)$
2.12	2.60	($2)	0.19	(10)	0	(0)	0	(0)	3.78	(0.45)	-1.10	(-25)
2.12	3.90	($3)	0.19	(10)	0	(0)	0	(0)	3.78	(0.45)	-2.40	(-55)
2.12	2.60	($2)	0.19	(10)	0	(0)	1.10	(58)	3.78	(0.45)	0	(0)
2.12	3.90	($3)	0.19	(10)	0	(0)	2.18	(126)	3.78	(0.45)	0	(0)
2.12	2.60	($2)	0.19	(10)	0.42	(10)	0	(0)	3.78	(0.45)	-1.53	(-35)
2.12	3.90	($3)	0.19	(10)	0.84	(20)	3.25	(170)	3.78	(0.45)	0	(0)
2.12	3.90	($3)	0.19	(10)	0.23	(5)	0	(0)	10.95	(1.30)	+4.47	+103
2.12	3.90	($3)	0.19	(10)	0.23	(5)	0	(0)	6.48	(0.77)	0	(0)
2.12	3.90	($3)	0.19	(10)	4.69	(108)	0	(0)	10.95	(1.30)	0	(0)

*Based on the following plant capacities:

1) CO_2 rate, 90% recovered from a 600 MW(e) net [650 MW(e) gross] coal-fired power plant = 4.34 x 10^6 T/yr
2) CH_4 rate = 2.77 x 106 T/yr = 400,000 MSCF/D
3) MeOH produced = 2.78 x 10^6 T/yr = 61,100 bbl/D. = 8460 T/D
4) Carbon produced = 1.91 x 10^6 T/yr = 5800 T/D

Table 5

METHANOL SYNTHESIS EQUILIBRIUM

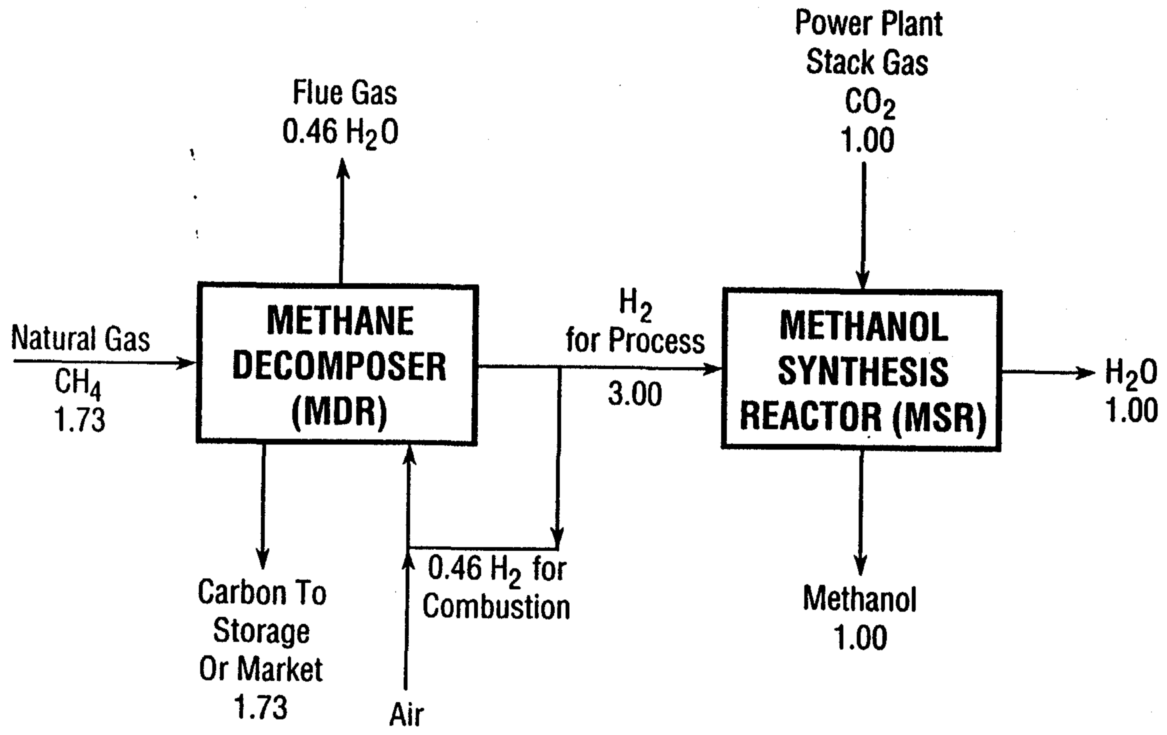
Input: H_2 3 moles
CO_2 1 mole

P (atm)	30	30	50	50
T (°C)	120	260	120	260
CO (mole)	0.0007	0.1365	0.0004	0.1089
CO_2 (mole)	0.4459	0.7686	0.3285	0.6865
H_2O (mole)	0.5541	0.2314	0.6715	0.3135
H_2 (mole)	1.3391	2.5787	0.9862	2.2773
MeOH (mole)	0.5534	0.0949	0.6711	0.2046
Total (mole)	2.8932	3.8101	2.6577	3.5908

Fig. 1

Simplified Carnol Process for Producing Methanol from Natural Gas and CO_2 for Zero CO_2 Emission

Mass Flows Are In Moles



EQUILIBRIUM DATA

$CH_4 = C + 2H_2$

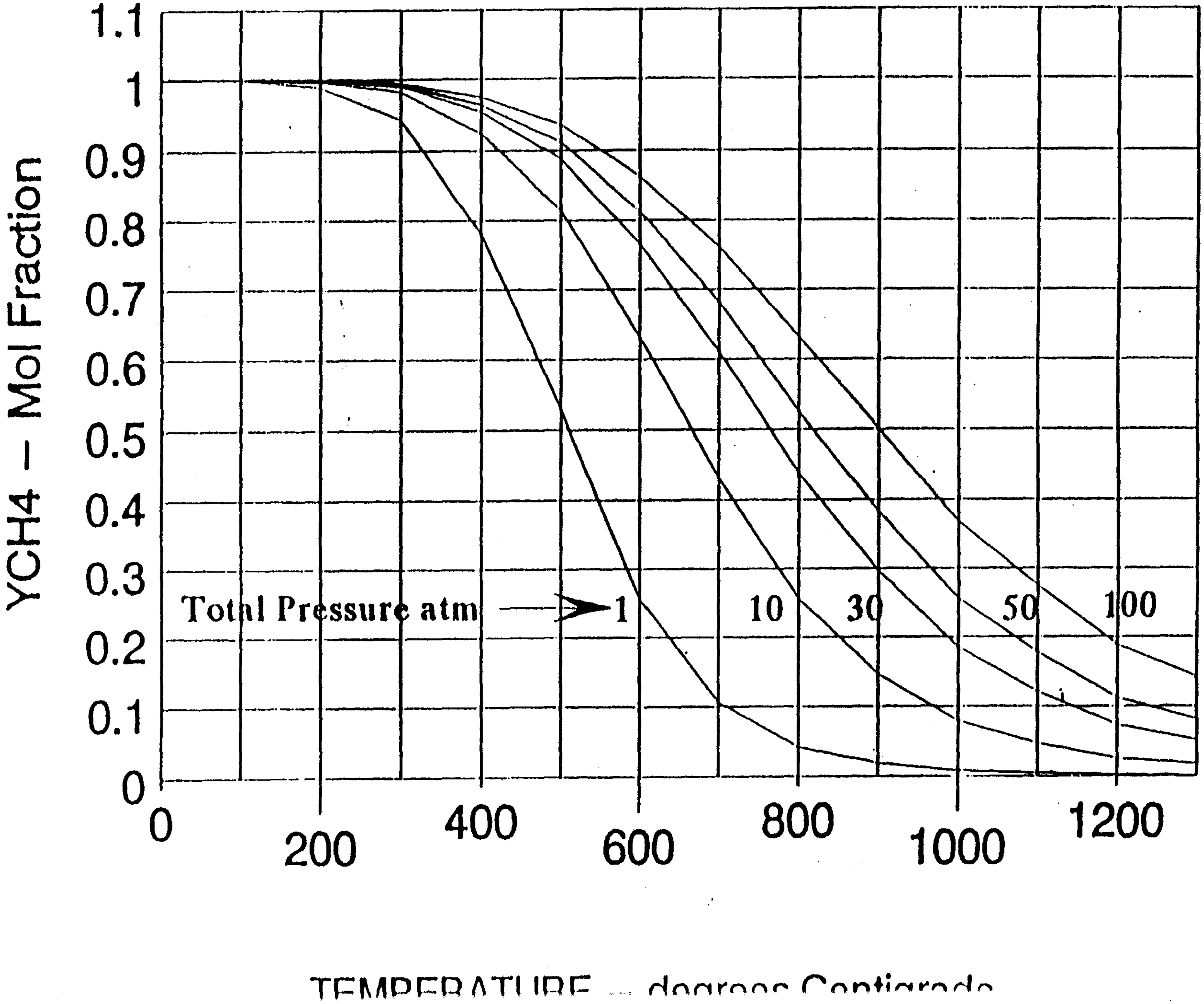
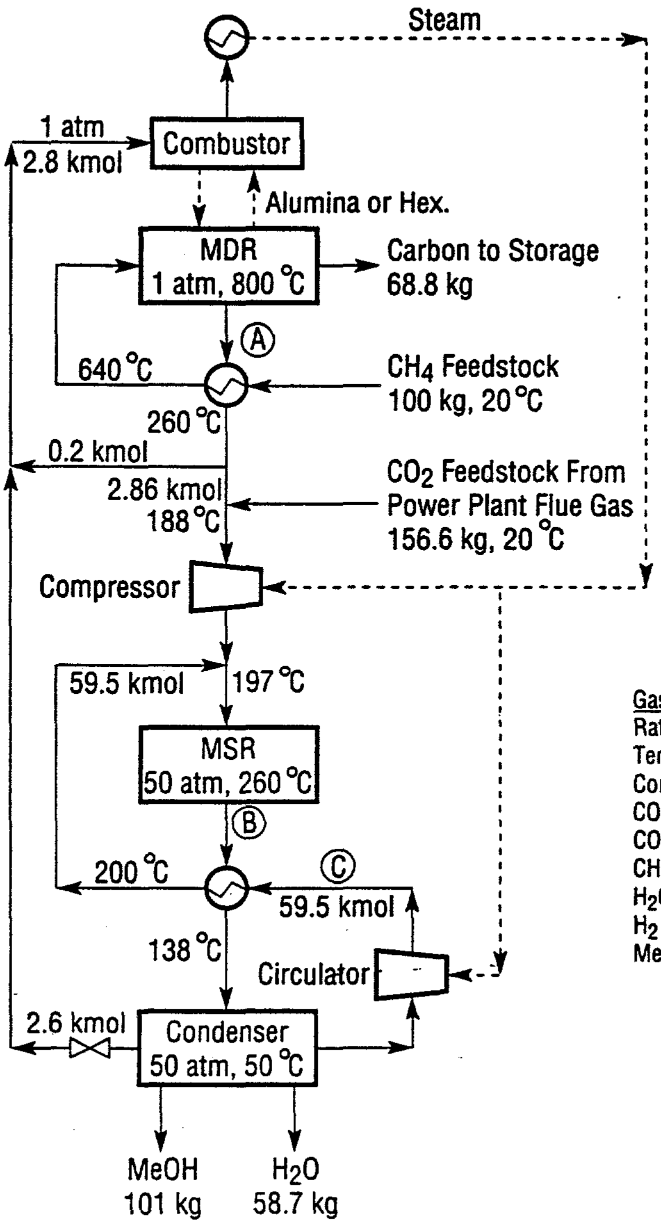


Fig. 3
CO_2 Mitigation Technology Carnol-III + Process



Carbon Efficiency 50.3%
Thermal Efficiency 41.1%
CO_2 Emission 22.7 lbs/MMBTU
Basis 100 kg CH_4 Feed

Gas Stream	A	B	C
Rate-Kmol	12.0	70.4	64.0
Temp-°C	800	260	50
Comp. mol%			
CO		3.35	3.68
CO_2		12.86	14.15
CH_4	4.25	17.34	19.08
H_2O		4.76	0.14
H_2	95.75	56.67	62.34
MeOH		5.02	0.60

Fig. 4

CO_2 - H_2O - Amine Phase Equilibrium

For Liquid Phase Methanol Synthesis
(Taken From Suda et al, Nov. 1993, Sweden)

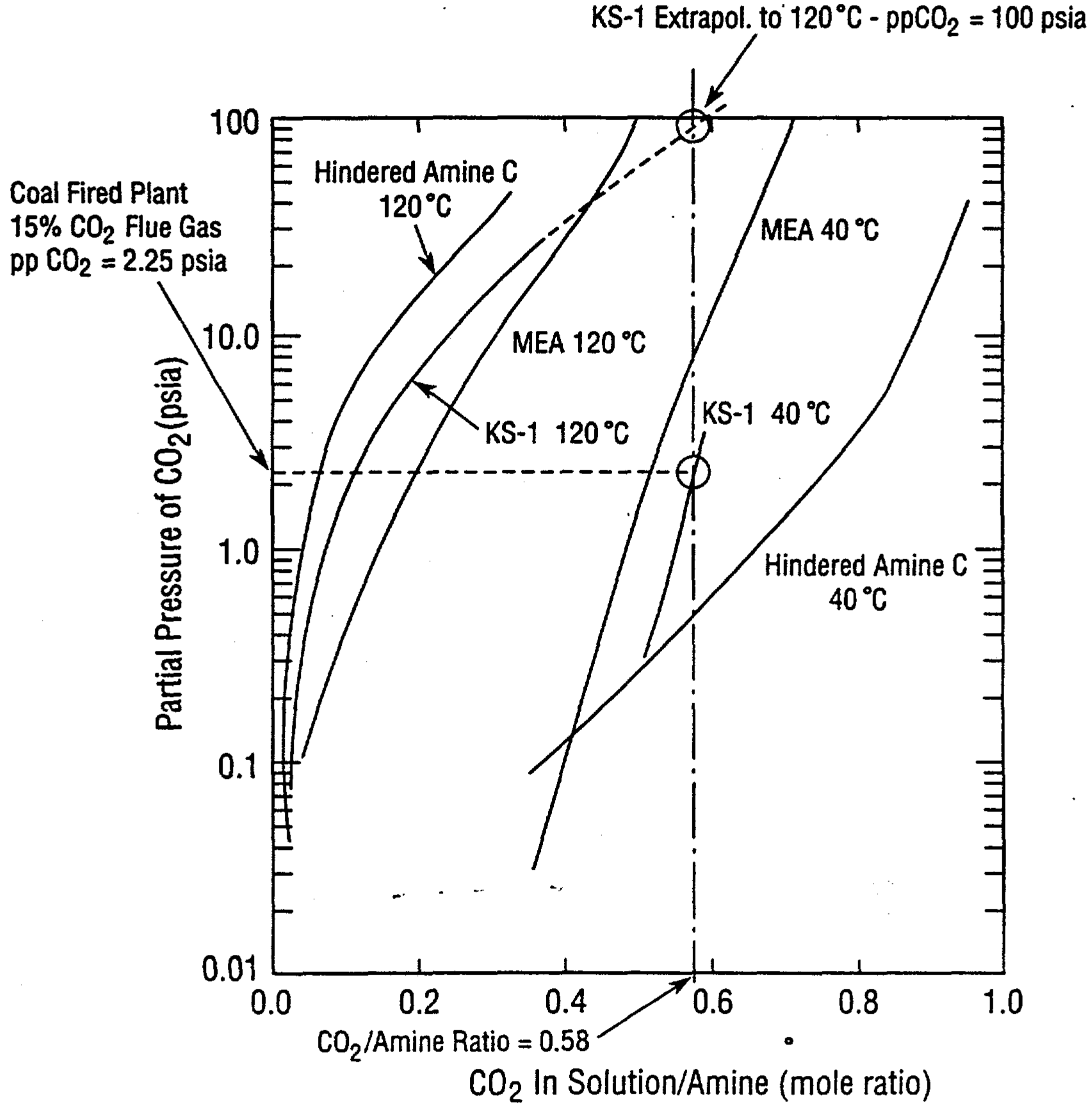
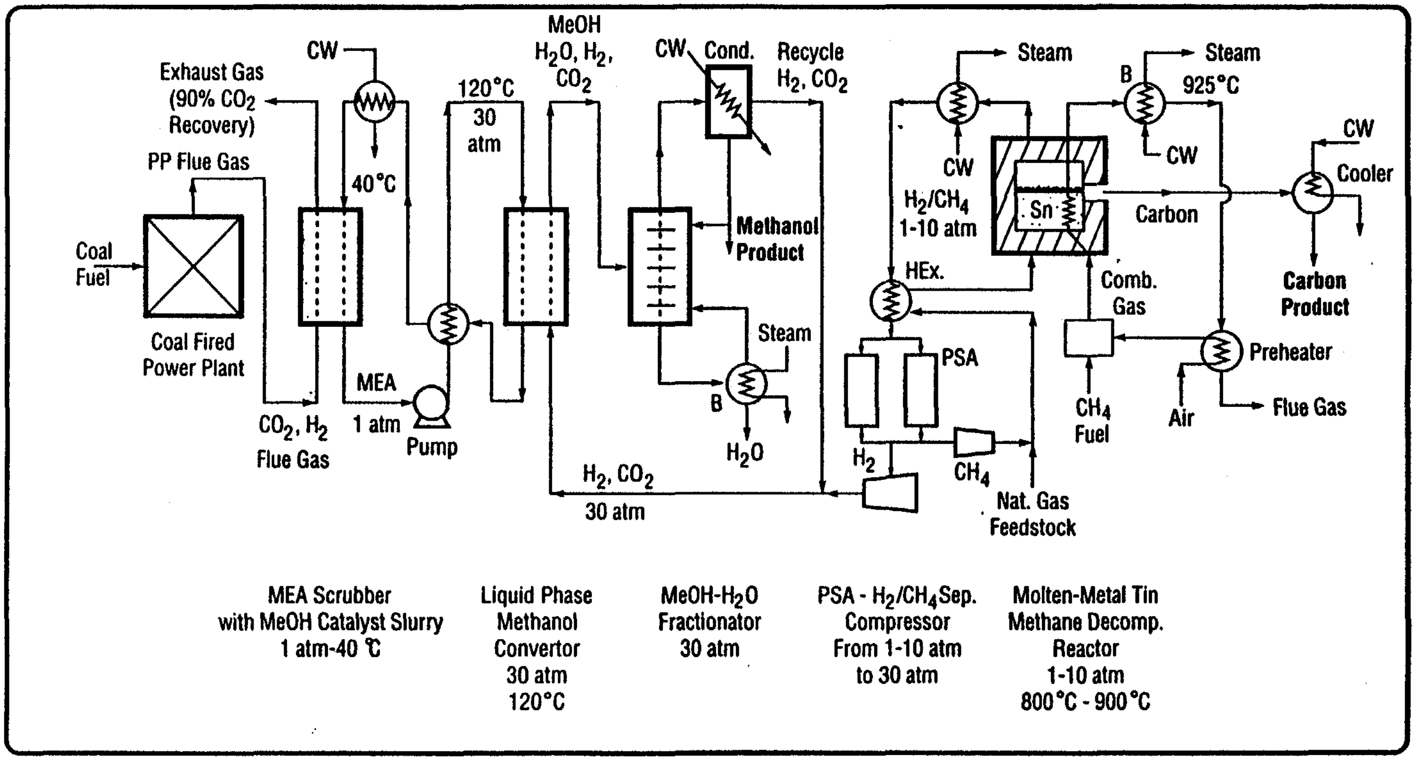


Fig. 5

Carnol VI Process for CO_2 Mitigation Technology

Combining CO_2 Recovery From Power Plants with Liquid Metal Methane Decomposition and Liquid-Phase Methanol Synthesis



Process Chemistry:

$$\overset{\text{Feedstock}}{\downarrow}\; 3/2\,CH_4 = 3/2\,C + 3H_2 \quad \overset{\text{Product}}{\ulcorner\!\!\rightarrow} \quad \longleftarrow \text{Nat. Gas, Decomp.}$$

$$\underset{\text{Flue Gas}}{\uparrow}\; 3\,H_2 + CO_2 = CH_3OH + H_2O \;\underset{\text{Product}}{\downarrow} \quad \longleftarrow \text{MeOH Synthesis}$$

Fig. 6

Molten Metal Methane Decomposition Reactor For Carnol VI Process

Basis 1.0 g-mol CH_4 Process Gas