BNL-63316

THE CARNOL PROCESS SYSTEM FOR CO_2 MITIGATION AND METHANOL PRODUCTION

Meyer Steinberg
Engineering Research and Applications Division
Department of Advanced Technology
Brookhaven National Laboratory
Upton, N.Y. 11973-5000

Abstract - The feasibility of an alternative CO_2 mitigation system and a methanol production process is investigated. The Carnol system has three components: (i) a coal-fired power plant supplying flue gas CO_2, (ii) the Carnol process which converts the CO_2 with He from natural gas to methanol, (iii) use of methanol as a fuel component in the automotive sector. For the methanol production process alone, up to 100% CO_2 emission reduction can be achieved; for the entire system, up to 65% CO_2 emission reduction can be obtained. The Carnol system is technically feasible and economically competitive with alternative CO_2-disposal systems for coal-fired power plants. The Carnol process is estimated to be economically attractive compared to the current market price of methanol, especially if credit can be taken for carbon as a marketable coproduct.

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.[1,2] CO_2 emissions are primarily due to fossil-fuel combustion in the commercial, industrial and transportation sectors. In the U.S., about one-third of the CO_2 comes from the industrial sector (mainly from central power stations which are largely fueled by coal). About an equal amount of CO_2 is emitted in each of the other two sectors. In this paper, we describe and develop the Carnol system, which converts CO_2 from coal-fired power-plant stack gases with natural gas (NG) to produce methanol as a liquid fuel for use in automotive engines. Carbon is produced as a coproduct and is a storable commodity. The carbon from coal is used twice and, therefore, the CO_2 is greatly reduced compared to conventional systems.

THE CARNOL SYSTEM-CONFIGURATION DEVELOPMENT

The basis for the Carnol system depends on integration of the following four developments: (i) A significant amount of effort and improvement has gone into the removal of CO_2 from the stack gas of fossil-fuel-burning plants, particularly for recovery and disposal of CO_2 in the ocean.[3,4] In the Carnol configuration, it is proposed to utilize the CO_2 rather than dispose and sequester it. (ii) To provide H_2 to reduce the CO_2 to methanol, it is proposed to decompose methane (from abundant NG) thermally to H_2 and C. In order to produce H_2 without generation of CO_2, it is proposed not to burn the C produced but to use it instead as a materials commodity.[5] An alternative H_2-production process without net CO_2 generation is gasification of biomass (wood).[6] (iii) The synthesis of methanol has been significantly improved by using liquid-phase slurry catalysts.[7,8] It is proposed to react the CO_2-saturated monoethanolamine (MEA) solvent used in the recovery of CO_2 from coal-fired power-plant stack gases to produce methanol. (iv) It is proposed to use the methanol produced in the Carnol system as an alternative fuel in automotive internal combustion engines in the transportation sector. It is recognized that in order to make an impact on CO_2 reduction, a large market must be available for the methanol product. The automotive fuel market provides that possibility. It is shown that methanol is 30% more efficient in IC engines than conventional gasoline, thus providing further incentives for reducing CO_2 emissions.[9]

Figure 1 shows a schematic of the overall Carnol configuration for achieving the CO_2-emission mitigation in the industrial and transportation sectors. Each of the process operations will be discussed and further developed.

H_2 PRODUCTION WITH ZERO CO_2 GENERATION

An investigation[5] of the basic energy requirements and CO_2 emission for various methods of H_2 production has indicated that methane decomposition can produce H_2 with the least CO_2 emission and with the least basic energy requirements.[5] This evaluation has been extended to include steam reforming of coal and biomass in Table 1. The latter shows that only thermal decomposition of methane and steam reforming of biomass can achieve zero CO_2 emission. Of these two, the process energy requirement is less for methane decomposition; however, the total energy requirement per unit of H_2 is less for biomass gasification because, in the thermal decomposition of methane, the C is not used to achieve zero CO_2 emission. In biomass gasification, zero net CO_2 emission is achieved because solar photosynthesis removes CO_2 from the atmosphere. Although the present conventional method for hydrogen production, by steam reforming of methane, has a higher energy efficiency than the thermal decomposition of methane, it generates considerable greater amounts of CO_2. Thus, thermal decomposition of methane competes with biomass gasification. From an economic point of view, natural gas, at present, is less expensive than biomass. However, a balance of not using the carbon and a lower thermal efficiency compensates somewhat for the higher cost of biomass from energy farms. Since the gasification of biomass is much better developed than the thermal decomposition of natural gas, the latter is chosen for further development.

Alternate methane decomposition reactor (MDR) designs have been considered. However, it appears that a molten metal bath which has been proposed for waste processing[10] has a number of advantages for a MDR design. For example, bubbling methane through a bath of a low melting metal, such as tin, heated to temperatures in the order of 800-1000° C could decompose over 90% of the methane. The carbon could be trapped and separated from the top of the molten metal bath due to the great density difference between carbon (1.8 gm/cc) and tin (7.3 gm/cc). The partial pressure of tin at 1000° C is less than 10^{-6} atm so that there would be no loss of tin or contamination of the hydrogen gas stream with tin. The low viscosity of tin would allow good gas/liquid contact resulting in good heat transfer between the tin and the methane gas. A reactor and process design is shown on the right hand side of Figure 2 which is based on the tin MDR reactor

operating at 900° C and 7.5 atm and heat and mass balances for producing a 90% H_2 - 10% CH_4 stream which after pressure swing absorption (PSA) produces a 100% H_2 stream. If the hydrogen is used to produce methanol, the 90% H_2 - 10% CH_4 stream can be used directly and the PSA operation can be eliminated.

THE SYNTHESIS OF METHANOL WITH ZERO CO_2 EMISSION

The hydrogen produced by methane decomposition is used to react with CO_2 recovered from coal fired power plant.

$$CO_2 + 3H_2 = CH_3OH + H_2O$$

If one mole of CO_2 is removed from the stack gases to produce 1 mole methanol, then when, the methanol is combusted as fuel, one mole of CO_2 is produced. Therefore, the net generation of CO_2 for production of methanol is zero.

Using MEA solvent gases, it is reported that it requires at least 25% of the capacity of the power plant to remove and recover CO_2 from the stack gases of the power plant.[11] With improvement in absorber packing, the pressure drop for feeding flue gas through the absorber using a hindered amine solvent the fraction loss of power to recover 90% of the CO_2 from a coal burning plant is reduced to 12%[4]. About 92% of the energy is needed in the stripper portion of the recovery system which is obtained from the low pressure side of the turbine and reduces the net power output of the plant. However, if the CO_2 is reacted with hydrogen, methanol is produced in an exothermic reaction and that energy can be used to strip out the CO_2 from the MEA and therefore it becomes unnecessary to take steam from the power plant for this purpose. Furthermore, if a liquid phase slurry catalyst system is used with an MEA solvent, the heat of reaction resulting from the synthesis of methanol is sufficient to distill out the methanol from the MEA solvent. The synthesis of methanol has an exothermic heat of reaction of 33 Kcal/gm mol CO_2 (or MeOH), which is more than enough to provide the heat of vaporization of methanol which is only 9 Kcal/mol.

Another important point is that the equilibrium concentration of methanol produced by the reaction of CO_2 with H_2 is favored at lower temperatures. Equilibrium calculation indicates that the concentration of methanol at 120° C is 5.8 and 3.4 times that at 260° C for pressure of 30 atm and 50 atm, respectively. The higher equilibrium methanol concentration results in a lower recycle ratio around the methanol synthesis steps and a higher thermal efficiency. The equilibrium partial pressure of CO_2 can be obtained from the phase equilibrium diagram for the amine H_2O - CO_2 given by Suda, et al.[4] The liquid phase methanol slurry catalysts are under investigation by several investigators.[7] The liquid phase synthesis is favored because its heat transfer characteristics are better than the gas phase heat transfer synthesis.

THE INTEGRATED CARNOL PROCESS SYSTEM

The methane decomposition molten metal reactor process can be integrated with the liquid phase synthesis of methanol, using CO_2 removed from a fossil fuel fired power plant. Figure 2 shows the integrated Carnol process. A computer simulation model of the entire process has been developed to obtain material and energy balances over a range of MDR and methanol synthesis reactor (MSR) conditions. A summary of one of the computer runs of the process including the performance parameters are shown in the summary of Table 2. The thermal efficiency reaches up to 50% while the total efficiency for both carbon and methanol is up to

90%. The CO_2 emission is reduced by 83% compared to that of the conventional methanol process based on steam reforming of natural gas.

PRELIMINARY ECONOMICS

A preliminary estimate of the methanol production cost and CO_2 credit is summarized in Table 3 for various production cost factors including natural gas and CO_2 cost. The estimate is based on 90% recovery and utilization of CO_2 (feed) from a 600 MW(ϵ) coal fired power plant. The capital investment is based on an equivalent current steam reforming plant estimated at $100,000 per daily ton of methanol. Labor, maintenance and utilities are lumped into the fixed charge of 25% of the capital investment. At a natural gas cost of $2/MSCF, $10/ton storage of carbon with no income from carbon and if methanol is sold at the historic cost of $0.45/gal (in the U.S.), the cost of reducing CO_2 by this Carnol process amounts to $25/ton CO_2. At $3/MSCF natural gas, the cost of reducing CO_2 increases to $55/ton. This range of CO_2 emission reduction credit is less than the maximum cost estimated for sequestering CO_2 in the ocean, ~$60/ton[11] not counting the transport of liquid CO_2 from beyond 10 Km inland from the ocean. If the carbon can be sold for $58 to $120/ton, the methanol can be produced for $0.45/gal. However, recently due to the mandated use of methanol for MTBE oxygenation of gasoline, the price of methanol has increased to as high as $1.30/gal and has then dropped back to about $0.70/gal. At these prices, the Carnol process can easily meet these market costs, even when charging for CO_2 from the power plant at a rate of as high as $108/ton. The general conclusion is that the Carnol process is potentially competitive with conventional methanol prices while significantly reducing CO_2 emissions.

COMPARISON OF CO_2 EMISSION FOR THE CARNOL PROCESS AND FOR THE ENTIRE CARNOL SYSTEM

Since there are other competitive processes for methanol production using alternative feedstocks, a comparison of CO_2 emissions must be made between processes. Table 4 makes such a comparison. Taking the current conventional process for methanol production by steam reforming of natural gas as the base case, the Carnol process and the BCL biomass steam gasification process are compared[6]. Biomass is a feedstock of choice because it removes CO_2 from the atmosphere by photosynthesis. The Carnol process obtains an 83% reduction in CO_2 emission with a penalty of only 24% in production capacity of methanol when methane is used to heat the methane decomposition reactor. The CO_2 emission can be eliminated in the Carnol process when hydrogen is used to heat the reactor, in which case the production capacity is reduced by 29%. The steam gasification of biomass process also eliminates CO_2 emission, however, a further reduction in methanol production to 35% is obtained.

While the Carnol process emission reduction can be compared on a methanol production basis as referred to above, it is necessary to estimate the CO_2 emission for the entire system which includes (1) the coal-fired power plant, (2) the Carnol methanol production process and (3) the use of methanol as an automotive IC engine fuel, as shown in Figure 1. The total CO_2 emission for the system, must be based consistently on the HHV of the various feedstock energy inputs to the system including (a) electricity from the power plant, (b) liquid methanol fuel from the Carnol plant and (c) mechanical energy from the automotive IC engines. This was done in Table 7 for 4 systems: 1) current conventional coal fired power plant, and gasoline driven automobiles; 2) coal fired power plant with conventional natural gas steam reforming for methanol production and methanol fueled vehicles; 3) coal-fired power plant with Carnol process for methanol production and use of methanol fueled vehicles, and 4) coal-fired power plant with biomass gasification methanol production and with methanol fueled vehicles. Several assumptions must be made for a valid comparison. These are: (i) The oil refinery produces gasoline at 90% efficiency; the equivalent of 10% C is lost as CO_2. (ii) The thermal efficiency for steam reforming of methane to methanol is 64%. (iii) The Carnol thermal efficiency is 90%. (iv) The net CO_2 emission based on biomass gasification is zero. (v) The methanol-fueled vehicle is 30% more efficient than the gasoline-powered vehicle.[9]

The results shown in Table 5 indicate that the CO_2 emission reduction is reduced by 18% using conventional steam reforming of natural gas for methanol production and its use in vehicles. The CO_2 is reduced by 63% for the Carnol methanol process and 65% reduction when biomass gasification is used. The latter two thus achieves significant reductions in CO_2 emission for the entire system. From an economic point of view, the biomass feedstock is currently more expensive than natural gas in the U.S. and, therefore, for about equal CO_2 emission reduction, the Carnol natural gas process presently should be more economical.

CONCLUSIONS

The Carnol process system configuration appears to be technically feasible and economically viable both as a CO_2 mitigation method for coal-fired power plants and as a methanol production process compared to the conventional method especially when considering credit for marketing the carbon coproduct. For process improvement, the development of a molten metal methane decomposition reactor and a CO_2 liquid phase catalytic slurry methanol synthesis reactor are recommended.

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.D. Mills, D. Wilson, and T. Johansson, Energy Policy Volume, FIRST PAGE (YEAR) (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. T. Suda, et al., *Development of Fuel Gas Carbon Dioxide Recovery Technology*, Chapter in Carbon Dioxide Chemistry: Environment Issues, Ed. By Jon Paul and Claire-Marie Pradier, The Royal Society of Chemistry, 1994 and private communication, p. 222-35 (June 1995).

5. 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, N.Y. (December 1994).

6. E.O. Larson, and R.E. Katofsky, *Production of Hydrogen and Methanol via Biomass Gasification*, in Advances in Thermochemical Conversion, Elsevier Applied Science, London (1992).

7. S. Lee, Methanol Synthesis Technology, CRC Press, Inc., Boca Raton, Florida, p. 198-224 (1990).

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

9. EPA Report, *An Analysis of the Economic and Environmental Effects of Methanol as an Automotive Fuel,* EPA Report No. 0730, Motor Vehicle Emissions Laboratory, Ann Arbor, Michigan (September, 1989).

10. P. Nahass, P.A. Moise and C.A. Chanenchuk, *Quantum CEP for Mixed Waste Processing*, Molten Metal Technology, Inc., Waltham, Mass. (1994).

11. IEA Greenhouse Gas R and D Programme Report, *Carbon Dioxide Capture From Power Stations*, Cheltenham, U.K. (1994).

Table 1 Hydrogen Production - Comparison of basic energy requirements for CO_2 emission

Process	Energy Efficiency		Process Fuel	Feedstock	Ratio mol H_2 mol CH_4	Energy-Kcal/mol H_2		CO_2 Emission mol CO_2 mol H_2
	Process Energy	Overall Fuel				Process	Total	
1. Methane Thermal Decomposition $CH_4 = C + 2H_2$	(A)80%(t)	53.3%(t)	H_2	CH_4	1.67	11.3	126.9	0.00
	(B)80%(t)	58.1%(t)	CH_4	CH_4	1.81	11.3	117.1	0.05
	(C)80%(t)	64.2%(t)	C	CH_4	2.00	11.3	106.0	0.12
Combined Cycle Power For Electrical Heating	(D)55%(t) 80%(t) 44%(t)	53.9%(t)	CH_4	CH_4	1.68	11.3	126.2	0.10
2. Methane Steam Reforming $CH_4+2H_2O=CO_2+4H_2$	80%(t)	94.6%(t)	CH_4	CH_4+H_2O	2.95	18.8	71.9	0.34
3. Coal Steam Reforming $CO_{0,8}0_{0.08}+1.92H_2O=CO_2+2.32H_2$	80%(t)	92.4%	Coal	Coal$+H_2O$	1.45 H_2/Coal	21.9	73.5	0.69
4. Biomass Steam Reforming $CH_{1.5}O_{0,6}+1.4H_20=CO_2+2.15H_2$	80%(t)	92.0%(t)	Biomass	Biomass$+$ H_2O	1.54 H_2/Biomass	20.3	73.9	0.00

Table 2 Carnol process design parameters - mass and energy balances

Unit	Process Data
MDR	
Pressure, atm	7.5
Temperture, °C	900.0
MSR	
Pressure, atm	30.0
Temperature, °C	120.0
PERFORMANCE	
Ratio, Methanol/CH_4,kg/kg	1.19
Ratio Carbon/Methanol, kg/kg	0.57
Thermal Efficiency of MeOH,	49.7%
Total Thermal Efficiency, C + MeOH	89.7%
CO_2 Emissions, LbCO_2/MMBTU	30.2%
KgCO_2/GJ	13.0
CO_2 Emission Reduction Compared to Conventional Steam Reforming Process	83.4%

Table 3 Liquid phase - catalytic slurry methanol synthesis

Reaction	Heat of Reaction cal/g mol CO_2
CO_2 + Hindered Amine: $R\text{-}NH_3^+ + CHO_3 = R\text{-}NH_2 + CO_2 + H_2O_{(\ell)}$	$\Delta H_A = +16{,}500$
Methanol Synthesis: $CO_{2(aq)} + 3H_{2(g)} = CH_3OH_{(\ell)} + H_2O_{(\ell)}$	$\Delta H_R = -33{,}000$
Methanol Fractionation Heat of Vaporization of MeOH	$\Delta H_v = +9{,}000$ (MeOH)

Table 4 Methanol production and CO_2 emission process comparison

Process	Production Capacity		CO_2 Emission	
	Moles MeOH Moles Feedstock	% Reduction from Conventional	lbs CO_2 MMBTU	% Reduction from Conventional
Conventional Process Steam Reforming of CH_4	0.76	0%	180	0%
Carnol Process from CH_4 (and CO_2)	0.58[1] 0.54[2]	24% 29%	30 0	83% 100%
Steam Gasification of Biomass	0.50	35%	0	100%

[1] Heating methane decomposition reactor with CH_4

[2] Heating methane decomposition reactor with H_2

Table 5 CO_2 emission from system of coal-fired power and liquid HC fueled automative power

Emission Units in Lbs/MMBTU (HHV)
(Multiply by 0.43 to Convert to Kg/GJ)

System	Unit CO_2 Emission	CO_2 Emission From Combined System	% CO_2 Emission Reduction From Current System
COAL-FIRED POWER PLANT Gasoline[1] Fueled Automotive IC Engine (Current System)	215 196	205	0%
COAL-FIRED POWER PLANT Natural Gas to Methanol[2] by Conventional Reforming and with Methanol Fueled Automotive IC Engine[5]	215 139	169	18%
COAL-FIRED POWER PLANT Carnol MeOH Plant (Methane Decomp)[3] Plant with Methanol Fueled Automotive IC Engine[5]	215 117	76	63%
COAL-FIRED POWER PLANT Biomass MeOH[4] (Gasification) Plant with Methanol Fueled Automotive IC Engine	215 106	71	65%

Assumptions

[1] Oil Refinery is 90% efficient for gasoline production - 10% lost to CO_2

[2] Thermal efficiency is 64% for conversion of natural gas to MeOH - Conventional steam reforming plant

[3] Carnol plant for methanol is 90% efficient with respect to CO_2 obtained from coal-fired power plant

[4] Net CO_2 emission from biomass gasification to methanol is zero due to photosynthesis

[5] MeOH fueled IC automotive engine is 30% more efficient than gasoline driven IC engine

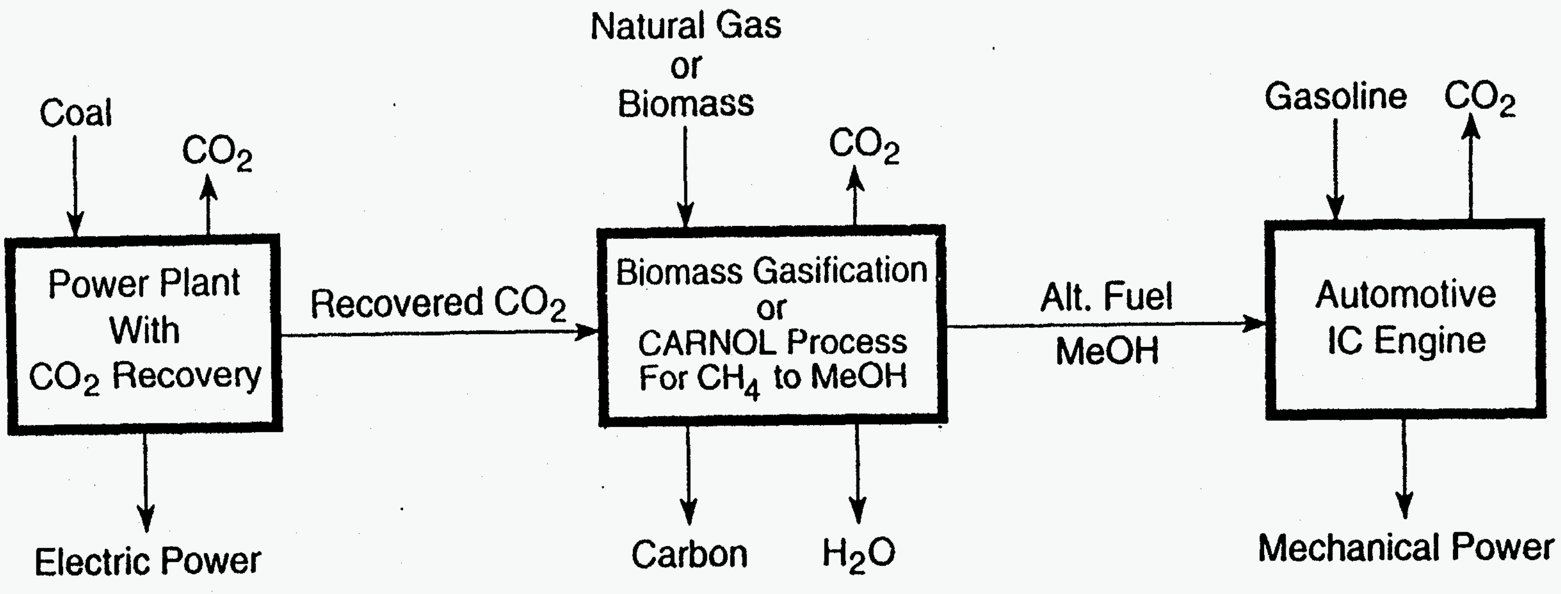

Fig. 1. The Carnol system configuration of CO_2-emission mitigation

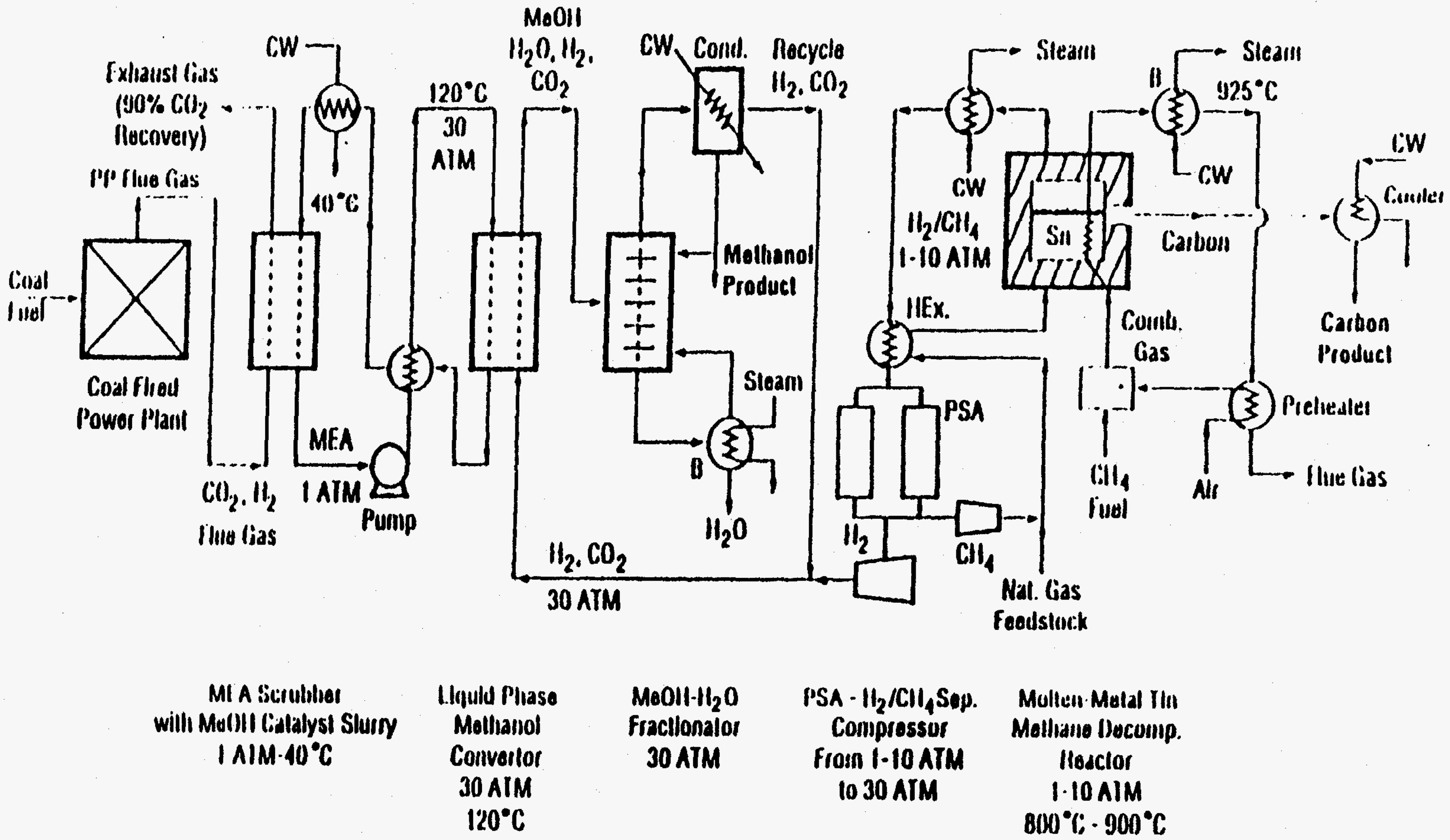

Fig. 2. Carnol VI process for CO_2 mitigation technology combining CO_2 recovery from power plants with liquid metal methane decomposition and liquid phase methanol synthesis

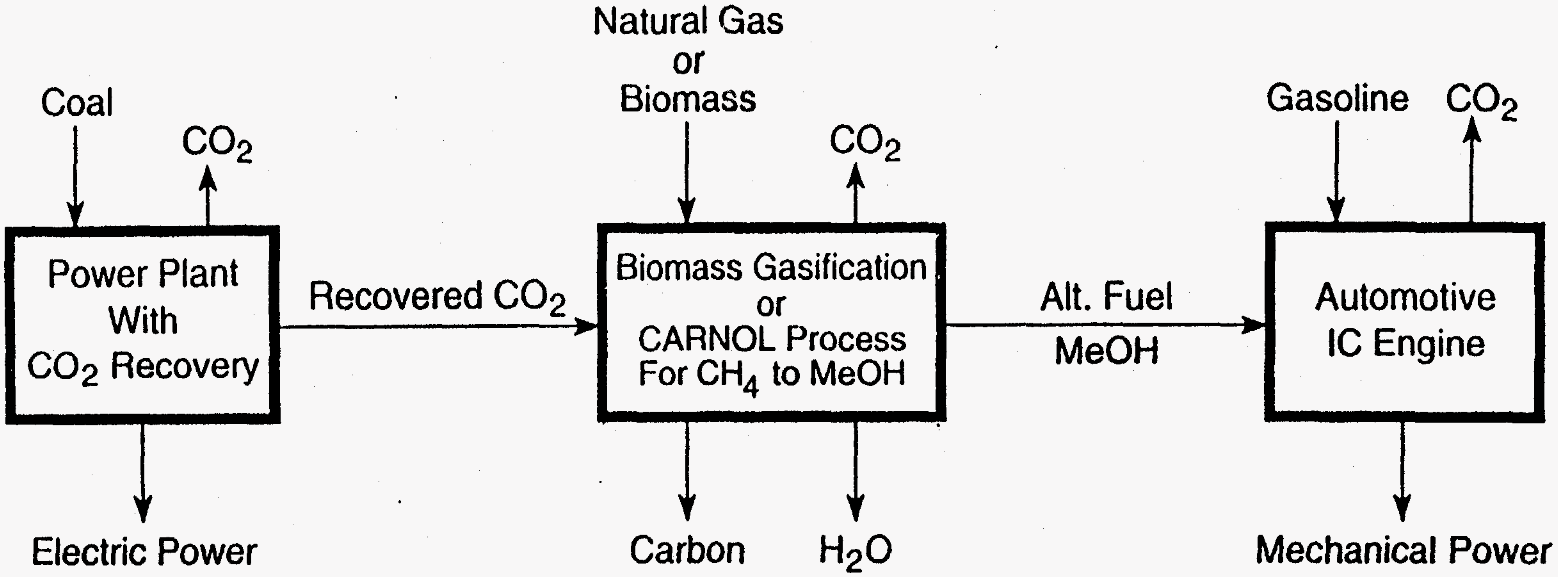

Fig. 1. The Carnol system configuration of CO_2-emission mitigation