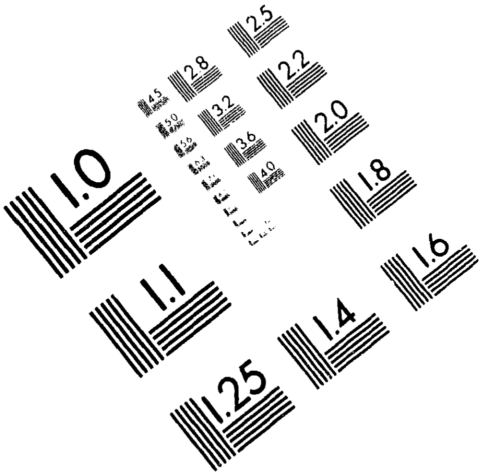

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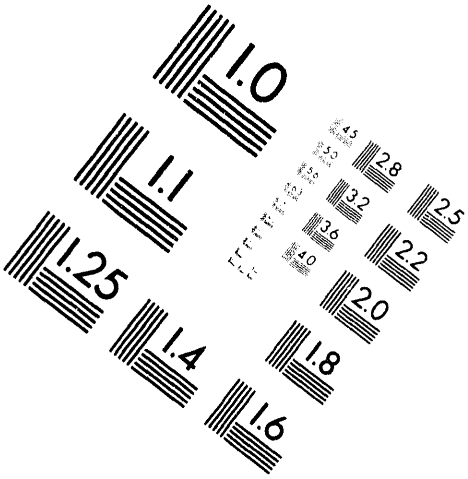

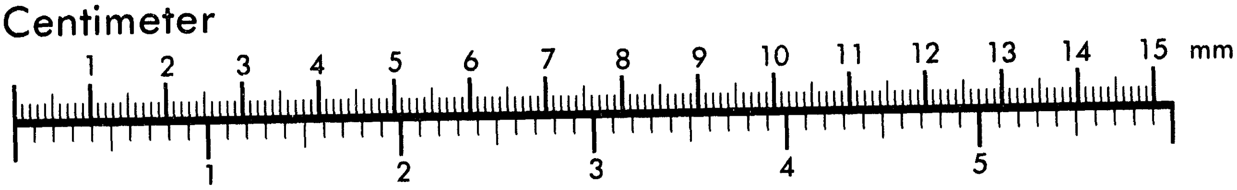

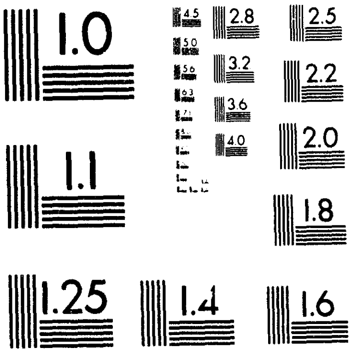

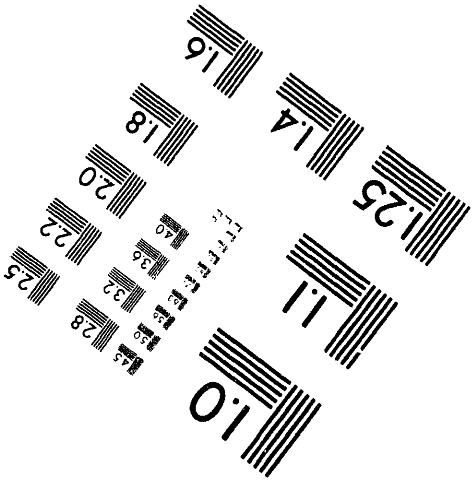

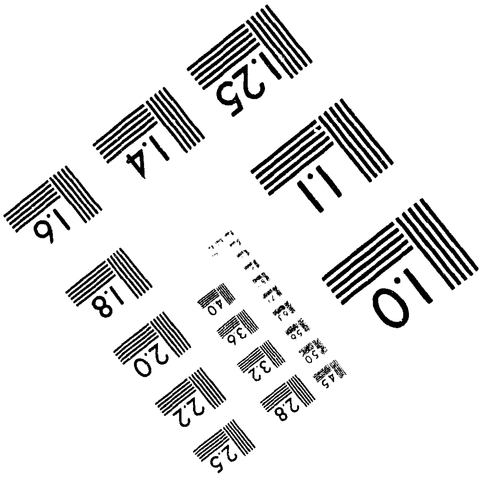

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ABSTRACT

A first order comparative mass and energy analysis is made of alternative processes for the production and utilization of methanol. Conventional reforming of natural gas with steam and CO_2 indicates a yield of approximately 1 mol of methanol per mol of methane and a net emission of 1 mol of CO_2 per mol of methanol. Three new processes called Carnol I, Carnol II and Carnol III utilize CO_2 as a feedstock in conjunction with hydrogen produced from the thermal decomposition of methane can reduce CO_2 emission compared to the conventional process by 35%, 88%, and 100% respectively while reducing methanol production by 11%, 35%, and 39% respectively. The carbon from methane decomposition can be sequestered or sold as a commodity. The methanol can be used in the transportation sector as an alternative efficient fuel. A preliminary economic estimate indicates the equivalent cost for reduction of CO_2 to be less than estimates for removal, recovery, and disposal of CO_2 from power plant stack gas. The Carnol process leverages the CO_2 reduction both from central fossil fuel fired power plants and the transportation sector. The Carnol process assists in the reduction of CO_2 emission from an otherwise impossible collection of CO_2 from highly dispersed heat engine and small scale fuel users.

INTRODUCTION

Methanol is an environmentally preferred alternative transportation fuel and also can serve as a clean stationary power plant fuel. It can be produced from a number of carbonaceous feedstocks including natural gas, oil, coal, biomass (wood), and other agricultural products as well as municipal solid waste (MSW). Because of its abundance, relatively low cost, and processability, the preferred feedstock currently is natural gas (methane). There is also presently great interest in the direct utilization of CO_2 for purposes of reducing CO_2 emissions in order to mitigate the global greenhouse warming problem. One possibility is the utilization of large quantities of CO_2 for the production of such potentially large scale fuel and chemical commodities as methanol.

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The following first reviews the conventional methods of reforming natural gas in Parts I, II, and III, and then the new Carnol processes are developed in Parts IV, V, and VI.

I. Conventional Method for Methanol Production - Steam Reforming

The conventional method for methanol production essentially consists of the steam reforming of natural gas to form carbon monoxide and hydrogen synthesis gas.[1] The synthesis gas is then sent to a methanol catalytic synthesis reactor for conversion to methanol. The excess hydrogen can be used in the reformer to provide the endothermic heat of the reforming operation. The reaction sequence is as follows:

1. Steam reforming: $H_2O + CH_4 = CO + 3H_2$
2. Methanol Synthesis: $CO + 2H_2 = CH_3OH$

Overall reaction: $H_2O + CH_4 = CH_3OH + H_2$

The endothermic heat of reaction[2]

$\Delta H = -26 + 0 -(-68)-(-18) = + 60$ Kcal/mol

The excess mol of hydrogen after the methanol synthesis can supply the energy for the steam reforming by combustion with air.

$H_2 + \frac{1}{2} O_2 = H_2O$; $\Delta H = -68$ Kcal/mol.

Additional methane for generating the steam must be used.

1 mol steam requires 10 Kcal/mol.

Moles CH_4 required by combustion $= \frac{10}{212} = 0.05$ moles

The total CO_2 emissions per mol of CH_3OH produced and used as fuel =

$$\frac{1.0\ (CH_4) + 0.05\ (CH_4)}{1.0\ (CH_3OH)} = 1.05 \text{ moles } CO_2/\text{mol } CH_3OH$$

Moles CH_3OH per mol of $CH_4 = \frac{1.00}{1.05} = 0.952$

A simplified block flow diagram of the conventional process is shown in Figure 1.

II. Gasification with CO_2 Reforming

The conventional method of reforming methane with steam can also be conducted instead with CO_2. The resulting synthesis gas can be shifted and the CO and H_2 can then be converted to methanol.

The reaction sequence is represented by the following reactions:

1. Reforming: $CO_2 + CH_4 = 2CO + 2H_2$
2. Shift: $0.67\ CO + 0.67\ H_2O = 0.67\ CO_2 + 0.67\ H_2$
3. Removal and Release of CO_2: $-0.67CO_2$
4. Methanol Synthesis: $1.33\ CO + 2.67\ H_2 = 1.33\ CH_3OH$

Overall Net Reaction: $0.33\ CO_2 + 0.67\ H_2O + CH_4 = 1.33\ CH_3OH$

The reforming reaction requires the following amount of energy:

in Kcal/mol, $\Delta H = 2(-26) + 2(0) + 94 + 18 = +\ 60$ kcal/mol

CH_4 required for combustion to provide the energy to the reformer =

$$= \frac{60}{212} = 0.28\ moles\ CH_4$$

The CO_2 emissions per mol CH_3OH when burned as fuel

$$= \frac{-0.33(CO_2) + 1.33(CH_3OH) + 0.28(CH_4)}{1.33\ (CH_3OH)}$$

$$= \frac{1.28}{1.33} = 0.962\ moles\ CO_2\ per\ mol\ CH_3OH$$

$$Moles\ CH_3OH\ produced\ per\ mol\ CH_4 = \frac{1.33}{1.28} = 1.039$$

A simplified block flow diagram of the conventional process with CO_2 reforming is shown in Figure 2.

III. Reforming with Steam and CO_2 Reforming

Reforming of CH_4 can take place both with steam and with CO_2 to produce a 2:1 mixture of H_2 and CO which is required by methanol synthesis. The reactions in the reformer are as follows:

$$CH_4 + H_2O = CO + 3H_2$$

and $$0.5\ CH4 + 0.5\ CO_2 = CO + H_2$$

---

1. Total Reforming: $1.5\ CH_4 + H_2O + 0.5\ CO_2 = 2CO + 4H_2$
2. Methanol Synthesis: $4H_2 + 2CO = 2CH_3OH$

Overall Net Reaction $1.5\ CH_4 + 0.5\ CO_2 + H_2O = 2CH_3OH$

The energy requirement for reforming can be calculated as follows:

$$\Delta H = 1.5(18) + 68 + 0.5(94) + 2(-26) = 90 \text{ kcal}$$

This energy is provided by burning additional CH_4. The CH_4 required for combustion is:

$$\frac{90}{212} = 0.42 \text{ moles } CH_4$$

Additional methane is required to raise the steam for use in gasifier.

$$= 0.05\ CH_4/CH_3OH$$

$$CO_2 \text{ emission} = \frac{-0.5(CO_2) + 2(CH_3OH) + 0.42\ (CH_4) + 0.05(CH_4)}{2\ (CH_3OH)}$$

$= 0.99$ moles CO_2 per mol CH_3OH used as fuel

The methane required per unit methanol.

$$CH_4/MeOH = (1.5 + 0.42 + 0.05)\ /2 = 0.99 \text{ mol/mol}$$

Moles of MeOH produced per mol CH_4 consumed $= \frac{1}{0.99} = 1.01$ mol/mol

A simplified block diagram is shown in Figure 3.

IV. The CARNOL I Process for Methanol Synthesis for Reducing CO_2 Emission

There is, however, another method of utilizing CO_2 and CH_4 for the production of methanol which could reduce CO_2 emissions significantly but with a small reduction in methanol production per unit of methane. This process involves the gasification of carbon with CO_2 to produce CO and the production of carbon and hydrogen by the thermal decomposition of methane. Half of the carbon is then sequestered or sold and not burned and half is used in the gasification with CO_2. Finally, the CO from the gasification reaction is combined with the hydrogen from the decomposition of methane reaction to form methanol. The reaction sequence is as follows:

1.	Gasification	$0.5\ CO_2 + 0.5C = CO$
2.	Methane Decomposition	$CH_4 = C + 2H_2$
3.	Remove and Sequester or sell as Carbon	$-0.5C$
4.	Methanol Synthesis	$CO + 2H_2 = CH_3OH$

Overall Net Reaction $0.5CO_2 + CH_4 = 0.5C + CH_3OH$

Energy requirements for gasifications and methane decomposition:

Gasification: $\Delta H = (-26)-0.5(-94) = +\ 21$ Kcal/mole

Methane Decomposition : $\Delta H = -(-18) = +18$

Total methane required for combustion to provide the endothermic energy for the above energy requirement:

$$= \frac{21 + 18}{212} = 0.184 \text{ moles } CH_4 \text{ per mol of } CH_3OH$$

$$CO_2 \text{ emission per mol } CH_3OH = \frac{-0.5(CO_2) + 1.0\ (CH_3OH) + 0.184\ (CH_4)}{1.00\ (CH_3OH)}$$

$$= 0.684 \text{ moles } CO_2 \text{ per mole } CH_3OH \text{ used as fuel}$$

Moles CH_3OH produced per mol CH_4 utilized

$$= \frac{1.00}{1.00 + 0.184} = 0.845$$

A simplified block flow diagram of the CARNOL I process is shown in Figure 4.

Alternate Carnol IA Process for Methanol Synthesis

An alternate Carnol I process is also possible which yields very similar results to the above Carnol I process, deals with the reforming of methane with CO_2 instead of the gasification of part of the carbon from methane decomposition. The reaction sequence then is as follows:

1. Thermal decomposition $0.5\ CH_4 = o.5\ C + H_2$
2. Remove, store, or sell carbon $-0.5C$
3. Reform methane with CO_2 $0.5CH_4 + 0.5CO_2 = CO + H_2$
4. Methanol synthesis $CO + 2\ H_2 = CH_3OH$

Overall net reaction $1CH_4 + 0.5CO_2 = 0.5C + CH_3OH$

Energy requires for methane decomposition and reforming is as follows:

Methane decomposition $\Delta H = -0.5\ (-18) = +\ 9$
Methane reforming $\Delta H = (-26)\ -0.5(-94)\ -0.5(-18)$
$= +\ 30$ Kcal

Total methane required for combustion to provide endothermic energy for above energy requirements is:

$$\frac{30+9}{212} = 0.184\ moles\ CH_4\ per\ mol\ CH_3OH$$

CO_2 emission per mol CH_3OH

$$= \frac{-0.5(CO_2+\ +\ 1.0\ (CH_3OH)\ +\ 0.184\ (CH_4)}{1.0\ (CH_3OH)}$$
$$= 0.684\ moles\ CO_2\ per\ mole\ CH_3OH$$

A simplified field block diagram of the Carnol IA process is shown in Figure 5.

V. Carnol II Process for Methanol Synthesis for Reducing CO_2 Emission

A more efficient process for CO_2 emission reduction and production of methanol is devised as follows. Methane is first decomposed to carbon and hydrogen. The carbon is not burned; it can be stored or sold as a commodity like carbon black. The hydrogen is then reacted with CO_2 to form methanol. The CO_2 can come from scrubbing and recovery CO_2 from power plant stacks, wells, and ammonia plants. Methane is used to provide the endothermic energy for the thermal decomposition of methane for hydrogen production.

The reaction sequence is as follows:

1.	Methane Decomposition	$3CH_4 = 3C + 6H_2$
2.	Methanol Synthesis	$2CO_2 + 6H_2 = 2CH_3OH + 2H_2O$

The overall net reaction $3CH_4 + 2CO_2 = 2CH_3OH + 2H_2O + 3C$

It should be noted that the methanol synthesis from CO_2 and $3H_2$ instead of the conventional CO and $2H_2$ is not unusual. There are catalysts available to accomplish this and indeed there are several commercial plants operating with CO_2 currently[1].

The energy requirements for methane decomposition:

$$\Delta H = -3(-18) = +54\ Kcal$$

The methane required for combustion to provide the endothermic energy for the decomposition of methane is as follows:

$$= \frac{54}{212} = 0.254\ moles\ CH_4\ per\ mol\ CH_3OH$$

$$CO_2\ emission = \frac{-2.0(CO_2) + 2.0(CH_3OH) + 0.254(CH_4)}{2.0\ CH_3OH}$$

= 0.127 moles CO_2 per mole CH_3OH when used as fuel.

Moles CH_3OH produced per mole CH_4 utilized:

$$= \frac{2.0}{3.0 + 0.254} = 0.615$$

A simplified block flow diagram of the CARNOL II process is shown in Figure 5.

VI. Carnol III Process for Methanol Synthesis for Zero CO_2 Emission

A final version of the Carnol process with zero CO_2 emission is designed as follows. Methane is decomposed to carbon and hydrogen. Part of the hydrogen is used to provide the endothermic energy for decomposition of methane. Thus, there is no generation and emission of CO_2. The larger remaining part of the hydrogen is reacted with CO_2 from external sources to produce the methanol. The reaction sequence for Carnol III is the same as for Carnol II as follows:

1.	Methane decomposition	$3CH_4 = 3C + 6H_2$
2.	Methanol Synthesis	$2CO_2 + 6H_2 = 2CH_3OH + 2H_2O$
	Overall Net Reaction	$3CH_4 + 2CO_2 = 2CH_3OH + 2H_2O + 3C$

The energy requirement for methane decomposition:

$$\Delta H = -3(-18) = +54 \text{ Kcal}$$

The methane decomposition required to produce the hydrogen used for combustion to provide the endothermic heat of decomposition of the methane is calculated as follows:

Heat of combustion of hydrogen

$$H_2 + 1/2O_2 = H_2O$$

$$\Delta H = -68 \text{ Kcal/mol}H_2$$

Since 1 mol of CH_4 produces 2 mols of hydrogen, the amount of methane needed to provide the hydrogen for its own decomposition is:

$$\text{moles } CH_4 \text{ decomposition for hydrogen energy} = \frac{18}{68x2} = 0.132 \frac{mol\ CH_4}{mol\ CH_4}$$

per mol CH_4 decomposition

Since by the above overall reaction it is necessary to decompose 3 moles of methane to produce 2 moles of methanol, the methane required to produce the combustion hydrogen is calculated and iterated because each time methane is decomposed for hydrogen energy, additional methane must be decomposed to provide additional hydrogen.

Methane to provide hydrogen to decompose process methane

$$= 3 \times 0.132 = 0.396$$

Additional methane = $0.396 \times 0.132 = 0.052$
Additional methane = $0.052 \times 0.132 = 0.007$

Total methane for H_2 combustion = 0.455
Methane for process H_2 = 3.000
TOTAL METHANE = 3.455

The methanol produced per mol of total methane

$$= \frac{2}{3.455} = 0.579 \ \frac{moles\ CH_3OH}{mol\ CH_4}$$

The carbon yield per mol of methanol which can be either sold as a commodity or sequestered:

$$= \frac{3.455}{2} = 1.728$$

A simplified block flow diagram of the Carnol III process is shown in Figure 6.

Comparative Analysis

A comparative analysis can now be made of the six systems described above and summarized in Table 1 and Table 2. The three conventional reforming systems: (I) steam, (II) CO_2, and, (III) steam and CO_2 reforming yield approximately 1 mol methanol produced per mol of methane consumed and each emits a net of approximately 1 mol CO_2 per mol of methanol produced and eventually consumed as fuel.

In the new CARNOL I or IA processes, when the methanol is used as fuel, the CO_2 emission can be reduced by 35% from that produced by the conventional reforming processes. This CO_2 reduction, however, is obtained with an 11% decrease in methanol production per unit of methane compared to the reforming processes. The CO_2 fixed for Carnol I is only 0.42 mol CO_2 per mole of CH_4 feedstock and the carbon yield is 0.5 mole per mol of methanol produced.

In the new CARNOL II process the CO_2 emission can be reduced by as much as 88%. However, this larger reduction is obtained at the expense of reducing methanol production per unit of natural gas by 35%, compared to conventional reforming. The amount of CO_2 feedstock for Carnol II is 0.61 moles CO_2 per mol CH_4 feedstock and the carbon yield is increased to 1.5 moles per mol of methanol produced.

In the new Carnol III process the CO_2 emission is completely eliminated. The penalty for achieving zero CO_2 emission is the reduction of methanol production per unit of natural gas by 39% compared to conventional reforming. The amount of CO_2 fixed for Carnol III is 0.58 moles CO_2 per mole CH_4 feedstock and the carbon yield is increased to 1.73 moles C per mole of methanol product.

It should be pointed out that in this first order analysis the additional energy due to inefficiency of energy recovery in the reformer and decomposer combustors and the energy for compression is not accounted for in the above estimates. These energy requirements in terms of fuel methane relative to the methane requirement for the process gas are relatively small and should not alter the general comparative conclusions of this fundamental first order assessment.

ECONOMIC CONSIDERATIONS

A preliminary economic evaluation of the new Carnol III process in terms of the cost of eliminating or reducing CO_2 emissions can be made with the following assumptions:

1. Real market U.S. selling price (SP) of Methanol = \$0.45/gal(3)
2. Capital cost of a conventional natural gas - steam reforming methanol production plant is calculated from current selling price and fixed charges.
3. Fixed charges including return on investment = 21%
4. Natural gas cost (gulf cost) = \$2.00/MSCF
5. Labor, maintenance and supplies included in above charges
6. Plant life 20 years. Plant on-line factor = 90%
7. Assume cost of CO_2 recovery from flue gas is charged to the power plant so there is zero cost to the Carnol process. Later on we will show the effect of CO_2 if it is charged to the Carnol III process

For Conventional Plant:

Cost of Natural gas/gal CH_3OH =

$$\frac{mol\ CH_4 \times 380\, ft^3 \times 6.6\ Lbs \times \$2.00}{0.95\ mol\ CH_3OH \times mol\ CH_4 \times 32\ Lbs/gal\ 1000\ ft^3} = \$0.165/gal\ CH_3OH$$

$$\text{Fixed charges/gal } CH_3OH = \frac{0.21 \times U.C.}{365 \times 0.9} = \$2.1 \times 10^{-4} U.C.$$

Where U.C. = Unit Capital Investment

Thus,

S.P. of methanol = natural gas cost + fixed charges

$\$0.45 = \$0.165 + 2.1 \times 10^{-4}$ U.C.

The Unit Capital Investment, U.C. = $136,700/ton/day.

Actually, the unit capital cost in 1991 was quoted (Reference 4) at $100,000/ton/day and this unit value is assumed in this report. This unit capital investment is applied to the Carnol Process III (zero CO_2 emission) where the methanol yield is 0.579 moles CH_3OH/mol CH_4 compared to the conventional steam reforming it is 0.95. The natural gas cost per unit methanol increases to:

$$\text{Cost natural gas/gal } CH_3OH = \$0.165 \times \frac{0.95}{0.579} = \$0.271$$

It is assumed that the unit capital investment of the Carnol III plant is similar to the conventional plant because each has basically two units, however, because of the lower production the unit capital investment must be increased by the 0.66 power rule for the lower capacity CARNOL III plant.

$$U.C. = \$100,000 \times \left(\frac{0.95}{0.579}\right)^{0.66} = \$139,000/ton/day$$

The cost of the methanol for the Carnol III process:

$$\begin{aligned} \text{Methanol cost} &= 0.271 + 2.1 \times 10^{-4} \times 139,000 \\ &= \$0.56/\text{ gal-}CH_3OH \end{aligned}$$

To this must be added the cost of sequestering the carbon which we estimate at $15/ton (based on coal mining cost) and converting to per gallon MeOH cost.

Total methanol production and selling price =
0.56 + 0.03 = $0.59/gal CH_3OH

Thus, the incremental cost of producing methanol by Carnol III is (0.59 - 0.45) = $0.14 gal/$CH_3OH$.

If the natural gas cost increases to $3.00/MSCF the production cost increases to $0.73/gallon and the incremental cost increases to $0.28/gal CH_3OH.

Translating this to the cost of CO_2 emission reduction for Carnol III, using the \$2.00/MSCF natural gas, the following calculation can be made.

The total CO_2 reduction from Carnol III is equivalent to the carbon sequestered.

Gallons of CH_3OH per ton of CO_2 reduction =

$$\frac{moles\ CH_3OH \times 32 Lb \times 2000\ Lbs}{1.73\ mol\ CO_2 \times 44\ Lbs \times 6.6\ Lbs/gal}$$

$$= 127\ gal\ CH_3OH/ton\ CO_2\ reduction$$

Thus, the incremental cost due to reducing CO_2 for the \$2.00/MSCF case,

$$= \frac{\$0.14}{gal\ CH_3OH} \times 127 = \$18/ton\ CO_2$$

To put this cost of reducing CO_2 in perspective, the minimum estimated cost for CO_2 emission reduction by removal, recovery and disposal in depleted gas wells and the ocean, from stationary sources such as power plants is estimated to be in the range of \$18 to \$45/ton of CO_2 (References 5, 6). Thus, at an average cost of CO_2 reduction of \$32/ton CO_2 the above Carnol III CO_2 reduction cost of \$18/ton CO_2 is 44% lower.

If a value can be placed on the carbon black to be sold as a marketable commodity not only can the cost of avoiding emission of CO_2 be reduced, but also a credit can be applied to the methanol cost to reduce its selling price. This is not unreasonable. For example, carbon black demands anywhere from \$0.10/lb (\$200/ton) to \$0.50/lb (\$1000/ton) depending on the use and grade. The large markets for carbon are for rubber tire vulcanization, pigments in paints and for, water purification. For Carnol III the carbon production per unit of methanol is:

$$Lbs.\ C/gal\ CH_3OH = \frac{1.73\ molC \times 12 \times 6.6}{mol\ CH_3OH \times 32}$$

$$= 4.28\ Lb.C/gal\ CH_3OH$$

If the carbon can be sold at \$0.10/lb, then the income from the carbon = \$0.10 x 4.28 = \$0.43/gal CH_3OH. Since the cost of methanol from Carnol III was found to be \$0.59/gal. and applying this credit of carbon sales to methanol, the selling price of methanol becomes \$0.16/gal., which is 65% lower than the current selling price of \$0.45/gal. By selling the carbon at \$0.05/lb.

(which is the fuel oil equivalent energy value at \$20/bbl oil) then the income from carbon is 0.05 x 4.28 = \$0.21/gal CH_3OH and the methanol can sell \$0.38/gal. Furthermore, if the efficiency of methanol claimed by EPA is 30% greater for methanol cars than for gasoline cars (i.e., 1.54 gallons methanol is equivalent to 1 gallon gasoline)$^{(7)}$, at a selling price of \$0.45/gal the equivalent gasoline cost for methanol is \$0.73/gal. The 1992 refining price for gasoline with oil at \$20/bbl amounted to about \$0.73/gal. The conclusion is that not only can Carnol III reduce CO_2 emission at an equivalent competitive price compared to other means of CO_2 avoidance, but can supply the transportation market at a price competitive with petroleum based fuel. Table 3 summarizes the above economic arguments for Carnol III.

It is interesting to note that a coal fired power plant can remove and recover CO_2 for supply to a Carnol III plant to produce methanol which in turn can be used in the transportation sector, as well as other dispersed smaller users of fuel. One mol of natural gas (CH_4) in the Carnol III plant removes one mol of CO_2 produced from 1 mol of coal ($CH_{0.8}\ O_{0.1}$) from a coal fired power plant which is sequestered or sold as carbon. The methanol can then be used as a fuel in the automotive industry which gains another 39% reduction in CO_2 emissions. Furthermore, this is obtained from a highly dispersed source for which there is no other easy means of removal and recovery. Thus, natural gas with Carnol, leverages the coal fired power plant and the automotive industry in obtaining a significant reduction in CO_2 emission.

An interesting question arises as to which sector should bear the cost of CO_2 reduction; the power plant, the methanol Carnol plant or the automotive methanol or smaller user? The answer to this question depends on whether there will be an environmental government regulation or taxation applied to CO_2 emissions from fossil fuel plants. If there is no regulation, then (1) the cost of CO_2 recovered from the power plant can be charged to the Carnol methanol plant, and (2) the carbon coproduct from the Carnol plant can be used or sold as fuel or as a material commodity.

If regulation or taxation becomes an economic requirement imposed by government rule, the Carnol process application will come about more quickly and then, (1) the Carnol plant can actually charge the power plant disposal costs because the Carnol plant will provide a service for the power plant in getting rid of the CO_2, and (2) the carbon will either be sequestered or sold as a commodity but prohibited as a fuel.

By the same token, the automotive industry should pay the Carnol plant for reducing the CO_2 emissions from vehicles by supplying more efficienct CO_2 reducing methanol.

One possible accounting can be made as follows and illustrated in Figure 8. As mentioned earlier, the CO_2 sequestering cost for the power plant is estimated to be \$32/ton CO_2 and the cost of recovery of CO_2 is estimated to be \$25/ton CO_2(6). Therefore, the power plant can pay the Carnol plant up to the sequestering cost of \$7/ton CO_2 or in terms of per unit of methanol (7/127) or \$0.06/gal methanol. Since the total cost of methanol by the Carnol process with \$2.00/MSCF methane is \$0.59/gal in order to bring it to conventional methane cost of \$0.45/gal, \$0.14/gal must be made up. Since the power plant has paid \$0.06 already, the automotive industry should pay the difference or \$0.08/gal, which is only \$10/ton of CO_2 avoided, which is fairly reasonable. Thus, the automotive industry will pay (0.45 + 0.08) or \$0.53/gal or the equivalent of \$0.82/gal of gasoline which is 11% higher than the 1990 refining price of \$0.73/gal, which is not too unreasonable. In the meantime, if the carbon can be sold for \$0.05/lb then the credit to the Carnol plant amounts to \$0.21/gal and an additional \$0.03/gal is credited since sequestering is avoided and the net methanol cost is reduced (0.45-0.24) to \$0.21/gal. Some of the savings can be returned to both the power plant and the automotive industry to reduce the cost. Furthermore, serious development work is progressing on the use of methanol in fuel cells in automobiles which is aimed at improving the efficiency of the use of methanol by more than a factor of 2. This would significantly reduce CO_2 emissions and make the use of methanol much more economical.

An important final point can be made concerning the Carnol process, and that is, it avoids the need for growing rapid rotational crop biomass in energy farms in order to capture CO_2. On the other hand, the addition of biomass can further reduce CO_2 emissions if it substitutes as an alternative fuel to fossil fuels in power plants.

Conclusion

The conclusion of this first order evaluation of alternative processes, appears to be that there is a decided benefit in pursuing the development of the CARNOL processes for purposes of utilizing CO_2 recovered from power plants and significantly reducing the net CO_2 emissions in the production and utilization of methanol as an alternative liquid fuel for the transportation fuel market, as well as, the stationary fuel user market.

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5. W.C. Turkenburg, "CO_2 Removal, Some Conclusions", Proceedings of the <u>First International Conference on Carbon Dioxide Removal</u> p. 821, Pergamon Press, Oxford, U.K. (1992).

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TABLE 1

COMPARATIVE ANALYSIS FOR METHANOL PRODUCTION

PROCESS	I. CONV. STEAM REF.	II. CONV. CO_2 REF.	III. CONV. STEAM AND CO_2 REF.	IV. & IVA. CARNOL I & IA PROCESS	V. CARNOL II PROCESS	IV. CARNOL III PROCESS
Energy for process (Kcal/mol MeOH)	60	45	45	39	27	31
Yield MeOH MeOH/CH_4 (mol/mol)	0.95	1.04	1.01	0.85	0.62	0.58
CO_2 Emission (mol CO_2/ mol MeOH)	1.05	0.96	0.99	0.68	0.13	0.00
Gasifier Shift or Reformer Reactor	YES	YES	NO	YES	NO	NO
Acid gas removal	NO	YES	NO	NO	NO	NO
Carbon yield Mol C/Mol MeOH	0	0	0	0.5	1.5	1.73
No. of Reactors	2	4	2	3	2	2
Percent CO_2 reduction from base %	BASE	-9	-6	35	88	100

TABLE 2

CARNOL PROCESSES FOR METHANOL PRODUCTION AND UTILIZATION FOR REDUCING CO_2 EMISSION REDUCTION

FEEDSTOCK - NATURAL GAS CO_2 FROM POWER PLANT STACKS SEQUESTER OR SELL CARBON -		
PROCESS	% REL.* MeOH PRODUCTION	REL.* CO_2 EMISSION REDUCTION
CARNOL I OR IA C GASIF. OR CH_4 REFORMING	89%	35%
CARNOL II CH_4 FOR REFORMING AND COMBUSTION	65%	88%
CARNOL III H_2 COMBUSTION	61%	~100%

*REL. means relative to a conventional natural gas to methanol plant

TABLE 3

ECONOMICS OF CO_2 REDUCTION FROM THE CARNOL III PROCESS

Current Selling Price MeOH	=	\$0.45/gal
Natural Gas Cost	=	\$2.00/MSCF
CO_2 Cost from Power Plant	=	\$0.00
Cost of Sequesting Carbon	=	\$15/ton
Plant Factor	=	90% on line
Unit Capital Cost	=	\$139,000/t day-methanol
Fixed Charges	=	21%
MeOH Production Cost	=	\$0.59/gal
at 3.00/MSCF NG	=	\$0.73/gal
Cost of Reducing CO_2 based	=	\$18/ton CO_2
on Increased MeOH Cost	=	(44% lower than \$32/ton CO_2)
Cost of Removal, Recover, & Disposal in Ocean Aquifer From PC Power Plants	=	\$32/ton CO_2
Taking Credit for 38% Reduction CO_2 Emission in MeOH Fueled Vehicles - S.P. MeOH	=	\$0.45/gal
If Carbon is sold, MeOH cost: with <u>no</u> MeOH vehicle <u>credit</u>:		
@ \$0.10/Lb C Credit	=	\$0.16/gal
@ \$0.05/Lb C Credit	=	\$0.38/gal
Equivalent Cost of Gasoline (1.54 gal MeOH = 1 gal Gasoline)	=	\$0.73/gal[*] (at \$0.45/Gal Methanol)

[*] \$0.73/gal is current (1992) refining price of gasoline based on \$20/bbl of oil.

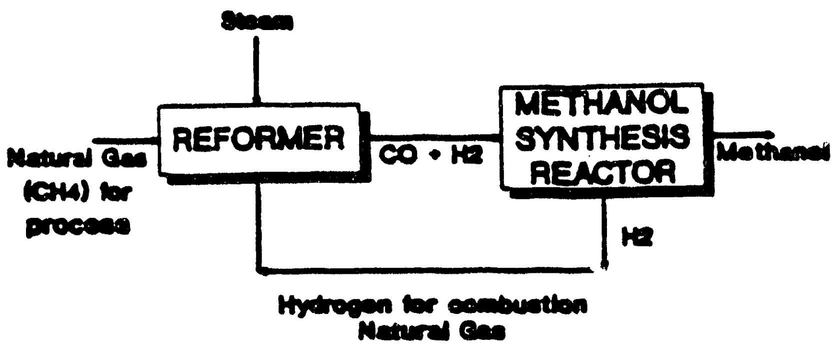


Figure 1. Conventional process for producing methanol by steam reforming of natural gas.

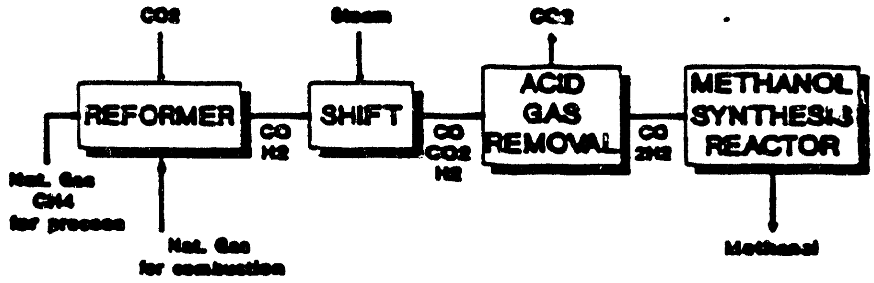


Figure 2. Conventional process for reforming natural gas to produce methanol using CO2 for reforming.

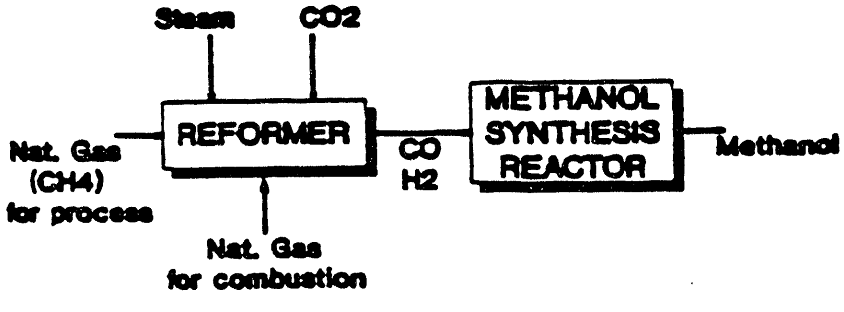


Figure 3. Conventional process for producing methanol by steam and CO2 reforming combined.

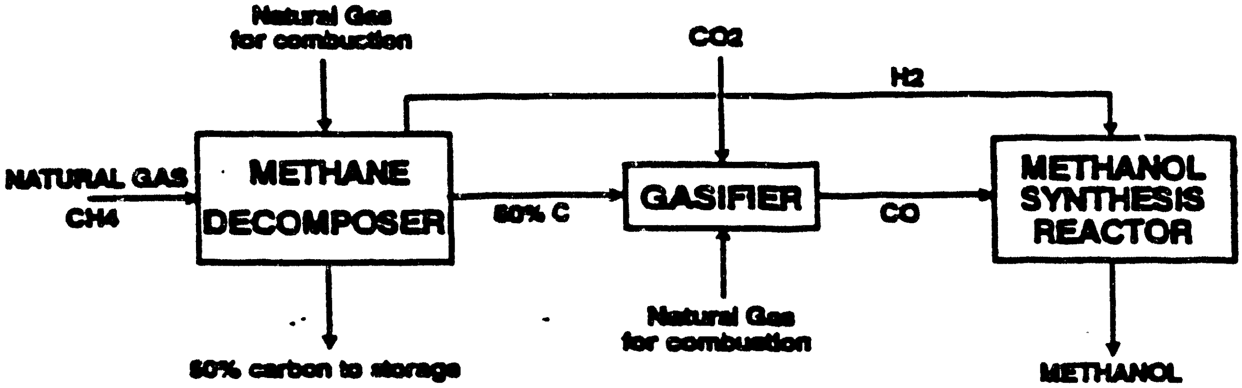


Figure 4. Carnol I process for producing methanol from natural gas and CO2 for reducing CO2 emission.

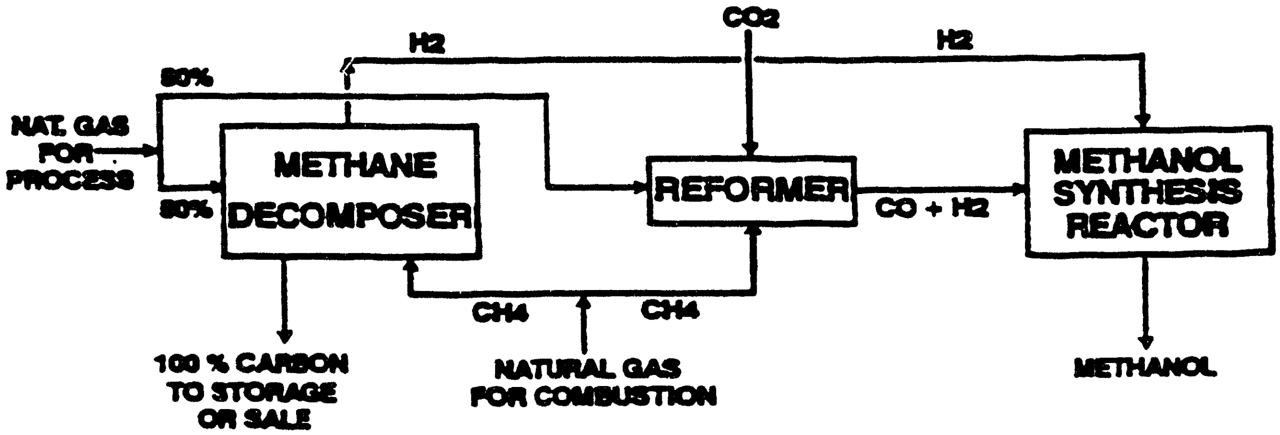


Figure 5. Carnol IA process for producing methanol from natural gas and CO2 for reducing CO2 emission.

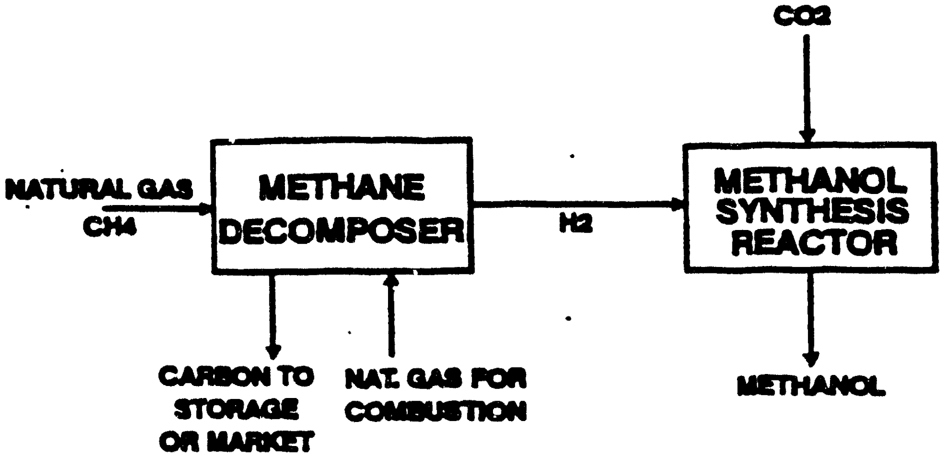


Figure 6. Carnol II process for producing methanol from natural gas and CO2 for reducing CO2 emission.

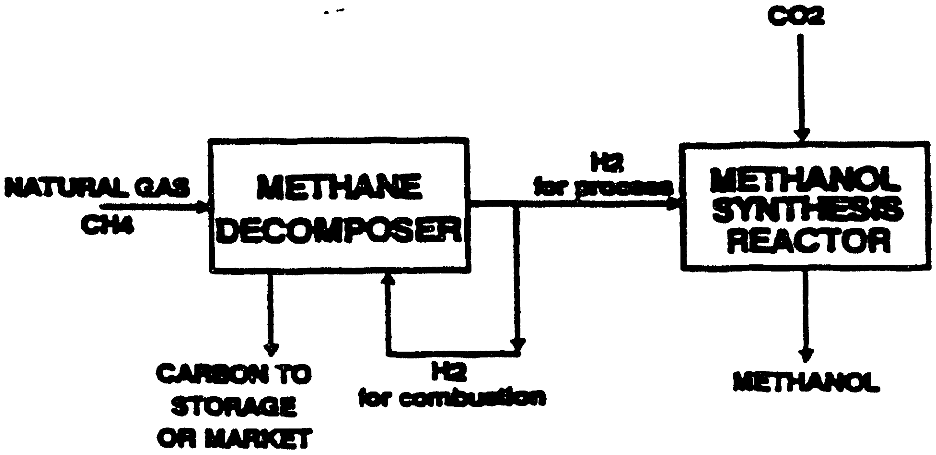
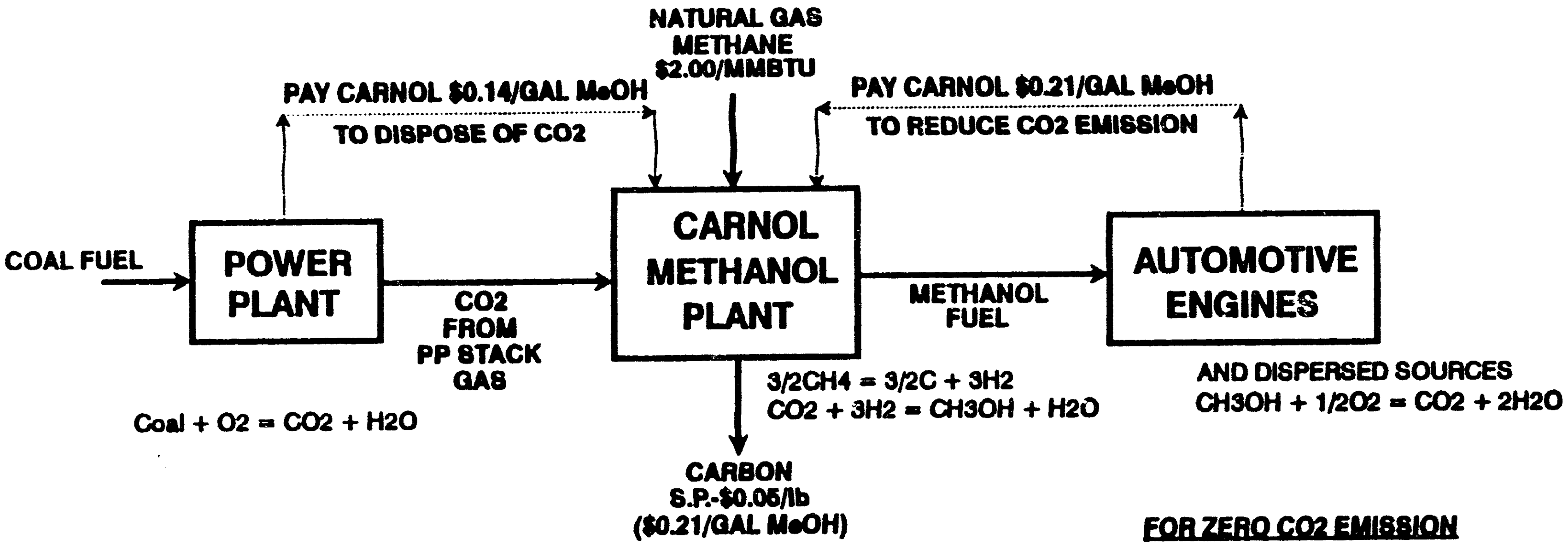


Figure 7. Carnol III process for producing methanol from natural gas and CO2 for zero CO2 emission.

Figure 8

CARNOL PROCESS FOR METHANOL PRODUCTION

TO REDUCE CO2 EMISSION FROM POWER PLANTS AND AUTOMOTIVE ENGINES



<u>FOR ZERO CO2 EMISSION</u>

- 1mol CH4 removes CO2 from 1 mol coal **<u>AND</u>**
- 1 mol CH4 removes CO2 from 1 mol CH4

DATE
FILMED
9/29/94

END