THE CARNOL SYSTEM FOR METHANOL PRODUCTION AND CO_2 MITIGATION FROM COAL FIRED POWER PLANTS AND THE TRANSPORTATION SECTOR

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ABSTRACT

The Carnol System consists of methanol production by CO_2 recovered from coal fired power plants and natural gas and the use of the methanol as an alternative automotive fuel. The Carnol process produces hydrogen by the thermal decomposition of natural gas and reacting the hydrogen with CO_2 recovered from the power plant. The carbon produced can be stored or used as a materials commodity. A design and economic evaluation of the process is presented and compared to gasoline as an automotive fuel. An evaluation of the CO_2 emission reduction of the process and system is made and compared to other conventional methanol production processes is including the use of biomass feedstock and methanol fuel cell vehicles. The CO_2 for the entire Carnol System using methanol in automotive IC engines can be reduced by 56% compared to conventional system of coal plants and gasoline engines and by as much as 77% CO_2 emission reduction when methanol is used in fuel cells in automotive engines. The Carnol System is shown to be an environmentally attractive and economically viable system connecting the power generation sector with the transportation sector which should warrant further development.

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 CO_2 greenhouse gas emissions, several approaches can be taken. The CO_2 emission from central power stations can be removed, recovered and disposed of in deep ocean [(1)]. 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 CO_2 emissions while storing the carbon [(2)]. Because of its physically properties, carbon is much easier to dispose of either by storage or used as a materials commodity than sequestering CO_2 [(1)]. A third alternative CO_2 mitigation method is to utilize the stack gas CO_2 from coal burning plants with hydrogen obtained from natural gas to produce methanol, which is a well-known liquid automotive fuel. In this paper, we describe and evaluate the Carnol process [(3)], which connects the power generation sector with the transportation sector resulting in an overall CO_2 mitigation system.

THE CARNOL PROCESS

The Carnol Process is composed of three unit operations described in the following.

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 CO_2 recovery and has recently been significantly improved upon for

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use in extracting CO_2 from power plant stack gases.[4] The power required to recover CO_2 from an integrated coal fired power plant to recover 90% of the CO_2 from the flue gas can be reduced to about 10% of the capacity of the power plant. However, this energy requirement can be reduced to less than 1% when the CO_2 recovery operation is integrated with a methanol synthesis step described in plant 3 below.

2. The hydrogen required to react with CO_2 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 $CH_4 + 2H_2O = CO_2 + 4H_2$. This process produces CO_2 and, thus, CO_2 emission is increased. However, hydrogen can be produced without CO_2 emission by the non-conventional method of thermally decomposing methane to carbon and hydrogen, $CH_4 = C + 2H_2$.

The energy requirement in conducting this process 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 [5]. The carbon is separated and either stored or can be sold in the market 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 10 atm and preferably about 1 atm.

3. The third step in the process consists of reacting the hydrogen from step 2 with the CO_2 from step 1 in a conventional gas phase catalytic methanol synthesis reactor, $CO_2 + 3H_2 = CH_3OH + H_2O$.

This is an exothermic reaction so that the heat produced in this operation can be used to recover the CO_2 from the absorption/stripping operation described in step 1, thus reducing the energy required to recover the CO_2 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 CO_2 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 zinc catalyst at lower temperature of 120 ˚C and 30 atm of hydrogen pressure.

CARNOL PROCESS DESIGN

A computer process simulation equilibrium model has been developed for the Carnol Process based on the flow sheet shown in Figure 1. A material and energy balance is shown in Table 1 selected from a number of computer runs. This run shows that 112.1 kg of methanol can be produced from 100 kg of natural gas (CH_4) and 171.1 kg CO_2 with a net emission of only 25.8 lbs CO_2/MMBTU of methanol energy including combustion of the methanol. This is an 85.7% reduction in CO_2 emission compared to the conventional emission from a steam reforming methanol plant which emits 182 lbs CO_2/MMBTU which includes the CO_2 from combustion of the methanol. The power plant at the same time has a 90% reduction in CO_2 because only 10% of the CO_2 from the MEA solvent absorption plant remains unrecovered and is emitted to the atmosphere.

Methanol As An Automotive Fuel

The Carnol Process can be considered as a viable coal CO_2 mitigation technology because the resulting large production capacity of liquid methanol can be used in the large capacity automotive fuel market. Most processes which utilize CO_2 produce chemical products which 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%. Methanol can also be used either directly or indirectly in fuel cells at several times higher efficiency for automotive use. 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 CO_2 emission from methanol in IC engines is 40% less.

It should also be pointed out that removal and ocean disposal of CO_2 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 CO_2 reduction by supplying liquid methanol fuel to these smaller diverse CO_2 emitting sources.

Economics of Carnol Process

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

1. 90% recovery of CO_2 from a 900 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[8].
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 CO_2 cost from power plants, with \$2/MSCF natural gas., and a\$0.55/gal methanol income CO_2 reduction cost is zero. At \$3/MSCF natural gas and \$0.45/gal income from methanol, the CO_2 disposal cost is \$47.70/ton CO_2, which is less than the maximum estimated for ocean disposal [7]. More interesting, without any credit for CO_2 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.

CO_2 Emission Evaluation of Entire Carnol System

Although we can show 90% or more CO_2 emission reduction for the coal fired power plant, the other two parts of the system, methanol production and automotive emissions, have relatively less CO_2 emission reduction compared to conventional systems. Therefore, the entire Carnol System must be evaluated as shown in Figure 2.

Alternative methanol production processes are evaluated in Table 3. The yield of methanol per unit of methane feedstock is shown for 1) conventional process in two parts; A) steam reforming of natural gas process, and B) using CO_2 addition in conventional steam reforming process; 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, and 3) a steam gasification of biomass process. The Carnol Process with H_2 and the biomass process (solar energy) reduces CO_2 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 CO_2 emission by 43% while the production yield is only reduced by 26% compared to conventional. The conventional process with CO_2 addition (1B) is interesting because there is an increase if 32% in production although the CO_2 emission is only reduced by 23%

For purposes of comparison and clarificatiton, the overall stoichiometry for the Carnol Process is shown in the following together with the conventional processes, and with CO_2 addition.

Carnol Process $CH_4 + 0.67\ CO_2 = 0.67\ CH_3OH + 0.78\ H_2O + C$

Conventional Steam Reforming Methane $CH_4 + H_2O = CH_30H + H_2$

Conventional Steam Reforming of Methane With CO_2 Addition

$$CH_4 + 0.67\ H_2O + 0.33\ CO_2 = 1.33\ CH_3\ OH$$

It is noted that in the Carnol process a maximum amount of CO_2 is utilized and an excess of carbon is produced. In the conventional process, no CO_2 is used and an excess of hydrogen is produced. With CO_2 addition to the conventional process, no excess of carbon or hydrogen is formed and methanol per unit natural gas is maximized.

Methanol can also be produced using biomass and since the net CO_2 emission is zero with CO_2 being converted to biomass by solar photosynthesis, the biomass process must also be included in the evaluation.

Biomass Steam Gasification Process for Methanol Synthesis

$$2CH_{1.4}O_{0.7} + 0.6H_2O = CH_3\ OH + CO_2$$

photosynthesis $CO_2 + 0.7\ H_2O = CH_{1.4}\ O_{0.7} + O_2$

The entire Carnol System is evaluated in table 4 in terms of CO_2 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 engine is also evaluated. All the cases are normalized to emissions from 1MMBTU of coal fired power plant which produces CO_2 for a Carnol methanol plant equivalent to 1.27 MMBTU 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 CO_2 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 CO_2 recovered from the coal fired power plant to the conventional methanol process, the CO_2 from the power plant is reduced by about 25% (161 lbs/MMBTU compared to 215 lb CO_2/MMBTU) and the CO_2 emissions for the entire system is reduced by 24%. It should be pointed out that the CO_2 can also be obtained from the flue gas of the reformer furnace of the methanol plant and does not need to be obtained from the coal fired plant.
3. The Carnol Process reduced the coal fired power plant CO_2 emission by 90% and the overall system emission is reduced by 56%.
4. Since the use of biomass is a CO_2 neutral feedstock, there is no emission from the power plants because the production of biomass feedstock comes from an equivalent amount of CO_2 in the atmosphere which has been generated from the coal fired power plant. Thus, the only net emission comes only from burning methanol in the automotive IC engine and thus, the CO_2 emission for the entire system is reduced by 57%, only slightly more than the Carnol System. However, the main point is that 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 [11]. Applying the Carnol process to produce methanol for fuel cell engines reduces the CO_2 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 CO_2 emissions from the coal burning power plant.

CONCLUSIONS

The Carnol Process can reduce CO_2 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 CO_2 emission for the entire Carnol System is reduced by 56%. Compared to the conventional system, steam reformed natural gas with CO_2 addition from the power plant, reduces CO_2 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 CO_2 by 57%. The development of methanol fuel cell engines can reduce CO_2 emissions by 77% for the entire system with a large increase in production capacity. The use of methanol as an automotive fuel produced from coal fired power plant CO_2 emissions and natural gas appears to be an environmentally attractive and economically viable system connecting the power generation sector with the transportation sector and, therefore, should warrant further development effort.

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