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A PROCESS CONCEPT FOR UTILIZING FOSSIL FUEL RESOURCES WITH REDUCED CO_2 EMISSION

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INTRODUCTION

There is increasing evidence of the probability of a global carbon dioxide greenhouse warming effect. The concentration of CO_2 in the atmosphere at the turn of the century was 280 ppm; presently it is 345 ppm, an increase of 23%. This increase has resulted mainly from human activity in burning increasing amounts of fossil fuel - coal, oil, gas and from deforestation, the cutting down of forested areas. It is predicted that by the year 2050 the CO_2 concentration in the atmosphere could double, reaching over 600 ppm due to continuing combustion of fossil fuel and deforestation resulting in raising the temperature 1.5 to 4°C, melting the polar ice caps causing a significant rise in ocean levels (ref. 1). A competition arises between major energy supplies in attempts to reduce CO_2 emissions, i.e., CO_2 generating fossil energy and non-CO_2 generating non-fossil energy, nuclear, geothermal and solar.

Mitigating Options for the Coal Industry

Studies have been made dealing with reducing CO_2 emissions from coal burning power plants (ref.2) as follows. (1) CO_2 can be removed, recovered and stored in the deep oceans. This would result in at least a doubling in the cost of power and we would have to learn more about the effect on the ecology of the ocean. (2) Recover and utilize CO_2 as a commodity, however, there is a supply-demand mismatch and then nuclear energy will have to be utilized. (3) Large acreages of trees can be planted to photosynthetically absorb the CO_2 from fossil fuel plants. (4) Improve energy technology efficiency of existing and future power plants; by installing all the known improved efficient technologies by the year 2050 when a doubling in CO_2 is expected, the CO_2 concentration would be reduced by 60%. Furthermore, an economic incentive is realized in that a return on investment is obtained due to decreased fuel consumption. (5) Substituting natural gas as a fuel will produce half the amount of CO_2, compared to coal. However, the reserves of gas is limited and much smaller than coal. Furthermore, methane itself is a severe greenhouse gas.

The HYDROCARB Process for Reducing CO_2 Emissions

The HYDROCARB Process was primarily derived to produce a clean carbon fuel and co-product hydrogen-rich gas from coal (ref.3). The process is described in Table 1, and depends on two reaction steps: (1) the hydrogenation of coal to methane followed by (2) the thermal cracking of methane to carbon black and hydrogen. The hydrogen is recycled and the excess becomes a co-product hydrogen-rich gas. The process is thermodynamically controlled and equilibrium limited. A process flowsheet is shown in Figure 1. The process

essentially cracks the coal into its elements C and H_2 with the oxygen being removed as H_2O or alternatively as CH_3OH. If the objective is to limit CO_2 emission, then the hydrogen-rich fuel can be used and the carbon black returned to the mine for possible future use should the greenhouse effect not materialize. The HYDROCARB Process can be applied to all carbonaceous raw materials. In effect, we are proposing a "hydrogen economy" based on extracting hydrogen from fossil fuels without generating any CO_2. Previously, the hydrogen economy was only applied to non-fossil energy sources, nuclear or solar.

Analysis of Hydrogen Energetics from Fossil Fuels

All fossil fuels contain some amount of hydrogen in addition to carbon. Table 2 indicates the hydrogen content in the major fossil fuels found in nature. By cracking or decomposing the natural fossil fuels, elemental carbon and hydrogen can be produced. In the case of natural gas (methane), the thermal decomposition can take place at temperatures in the order of 1000°C. The minimum energy required to crack methane is equal to the heat of reaction of methane to carbon and hydrogen, which is 18 kcal/mol endothermic. The atomic content of hydrogen in methane is 80%. Two moles of hydrogen and one of carbon is formed from methane. Thus, 64% of the energy that is generated by combustion of the original methane resides in the hydrogen. The higher heat of combustion of methane is 212 kcal/mol. The fraction of energy needed to crack the methane is 18/212 = 8.5%, which reduces the energy available to the hydrogen. Subtracting this amount results in a net fraction of energy in the hydrogen of about 56%. Thus, a penalty of 44% lower energy results compared to the original natural gas fuel if one wants to utilize the natural gas without generating any CO_2. Similar calculations can be made for the other two fossil fuels, oil and coal. Petroleum contains basically two types of hydrocarbon types, the alkanes, stoichiometrically represented as CH_2, as in octane, and the aromatics, represented stoichiometrically as CH as in benzene. Table 2 indicates that on cracking these oil components to carbon and hydrogen, the net energy declines to 37% and 25%, respectively.

We then consider the cracking of coal, which has the lowest H to C ratio of the fossil hydrocarbons amounting to 0.8 of an atom of H to 1 atom of C, which is not trivial. Bituminous coal also contains oxygen with an average atomic ratio of 0.08 of an atom of O per atom of C. On cracking coal, the oxygen can combine with either hydrogen or carbon to form H_2O or CO_2. The maximum amount of hydrogen is formed when we allow the oxygen to be removed as a small amount of CO_2. An important factor in the HYDROCARB Process is that the net heat of cracking of coal is practically zero, so the net energy that can be derived from the hydrogen expressed as a fraction of the original heating value of coal can be as high as 24%. It may appear that this relatively low thermal efficiency seems to be a heavy price to pay for purposes of reducing CO_2 emission. However, a hydrogen economy based on a non-fossil energy source, i.e., nuclear or solar energy, yields the same efficiency. The generation of electrical energy from a nuclear reactor or a solar tower power is about 30% efficient, and the best water electrolysis cell is about 80% efficient, so that the overall thermal efficiency of energy to hydrogen is also 24%. Generating hydrogen from petroleum and natural gas is even higher than this value. By storing the clean carbon for future use, does not necessarily close out the possibility of utilizing the remaining carbon energy at a future date, should it prove allowable because the greenhouse effect may not take place. In this manner, we form a strategic monitored retrievable reserve of energy in the form of clean carbon.

Another dimension is that the process lends itself to altering the product mix in such a manner as to reduce the C/H ratio from the original feedstock. The CO_2 emissions per unit energy can be varied from zero emission for hydrogen alone up to a maximum CO_2 emission on combustion of the original feedstock. Table 3 gives the stoichiometry and energetics of the products formed from the HYDROCARB Process with various fossil fuel feedstocks. The main fuel co-products formed are carbon, hydrogen, methane and methanol. The emission on combustion of these fuel products are given in terms of C/H ratio as (CO_2/H_2O in the combustion products), lb/CO_2 emitted per 10^6 Btu produced and the fraction of energy available as fuel from the original feedstock assuming the carbon is not used. Thus, one goes from zero lb CO_2/MMBtu for H_2 from bituminous coal and 19% availability to 40 lb CO_2/MMBtu and 24% availability to 120 lb CO_2/MMBtu at 29% availability for methane fuel from coal. This compares to 110 lb CO_2/MMBtu emitted by combustion of the natural gas which is about half that of coal at 210 lb CO_2 emitted/MMBtu. Emission from oil at 160 lb CO_2/MMBtu which is halfway between coal and gas.

It is also interesting to note in Table 3 that synthetic fuels defined conventionally to produce hydrocarbons, SNG and liquids (kerosene and gasoline) from coal would generate and emit a total of at least 50% more CO_2 per unit of energy at 310 to 330 lb CO_2/MMBtu compared to burning coal directly at 210 lb CO_2/MMBtu. By using wood as a feedstock, carbon can be sequestered in the earth from atmospheric CO_2 fixed photosynthetically by growing trees and converting the biomass to carbon by applying the the HYDROCARB Process. This is the only method that can commercially reduce the CO_2 concentration directly from the atmosphere.

Process Development and Preliminary Economic Development

There is much background technology available in the United States, United Kingdom, and Germany on the hydrogenation of coal and carbonaceous material. Also, there is industrial information on batch decomposition of methane to the carbon black market in the United States. Development work can then proceed on maximizing hydrogen production from carbonaceous and fossil fuels, coal, oil, gas and wood. A preliminary cost estimate for production of hydrogen from coal in a world-size plant processing 25,000 T/D of bituminous coal indicates a plant capital investment of $610 million and hydrogen will have a selling price of $10 to $12/MMBtu with no credit for the carbon and depending on method of financing (private vs public) (ref. 3). If the carbon is used as fuel, the CO_2 emission increases, and the cost of hydrogen and carbon, when completely used, is reduced to between $2.00 and $2.50/MMBtu which competes with current prices of oil ($12 to $15/Bbl) (ref. 3). Smaller capacity plants will give higher costs. For example, a 7,500 T/D coal plant would have a plant investment of $230 million, and hydrogen will have a selling price of $18/MMBtu (private financing with no credit for the carbon) (ref. 4). Studies on capital investment in non-fossil (nuclear and solar) plants for hydrogen production indicate similar or higher cost for generating hydrogen (ref. 5). The HYDROCARB technology thus provides the coal industry with an option for dealing with the greenhouse problem and a response to the non-fossil energy critics.

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TABLE 1

HYDROCARB (CARBEX) PROCESS FOR PRODUCTION OF ASH-FREE AND SULFUR-FREE CLEAN CARBON FUEL (CARBOLINE) AND FUEL GAS FROM COAL

Two Basic Steps:

I. <u>Hydrogasification</u> of Coal with Hydrogen to Methane.

Bituminous Coal + Hydrogen ⟶ Methane + Water + Hydrogen + Ash

$$CH_{0.8}O_{0.08}S_{0.016}N_{0.015} + 2H_2 \longrightarrow CH_4 + 0.08\,H_2O + 0.32\,H_2 + 0.008\,N_2$$

$$+ \text{Ash} + \text{Limestone } (CaCO_3) \qquad\qquad \text{Ash} + 0.016\,CaS$$

Reaction is ∿-18 Kcal/mol <u>Exothermic</u>.

II. <u>Thermal Decomposition of Methane</u>.

Methane ⟶ Carbon Black + Hydrogen.

$$CH_4 \longrightarrow C + 2\,H_2$$

Reaction is +18 Kcal/mol <u>Endothermic.</u>

Hydrogen is recycled. Excess hydrogen is a by-product and is used as fuel, and carbon black is used neat slurried with water methanol or oil to produce CARBOLINE CWM fuel product.

<u>OVERALL COAL CRACKING REACTION</u>

$$CH_{0.8}O_{0.08}S_{0.016}N_{0.015} \longrightarrow C + 0.32\,H_2 + 0.08\,H_2O + 0.008\,N_2$$

$$+ \text{Ash} + CaCO_3 \qquad\qquad \text{Ash} + 0.016\,CaSO_4$$

(2.3)

Table 2

GENERATING ENERGY FROM FOSSIL FUEL WITHOUT CO_2 EMISSION

The Hydrogen Economy

Principle:
- Extract hydrogen from fossil fuels.
- Use hydrogen only as fuel.
- Return clean carbon to ground for possible future use as CO_2 environment permits.

Fossil fuel	Ht. of combustion HHV Kcal/mol	Overall cracking reaction	Atomic H fraction in fossil fuel %	Ht. of cracking Kcal/mol-C	Thermal efficiency net energy in hydrogen as % of HHV of fossil fuel
Nat. gas	-212	$CH_4 \longrightarrow C + 2H_2$	80	+18	64 - 8 = 56%
Petroleum					
alkanes	-165	$CH_2 \longrightarrow C + H_2$	67	+6	41 - 4 = 37%
aromatics	-142	$CH \longrightarrow C + 1/2H_2$	50	-3	24 + 1 = 25%
Coal	-116	$CH_{0.8}O_{0.08} \longrightarrow$ $0.96\ C + 0.04\ CO_2 + 0.4\ H_2$	43	0	24 ± 0 = 24%

Note: Ht. of Comb. of C = -94 Kcal/mol.
HHV of Comb. of H_2 = -68 Kcal/mol.

Note: Nuclear energy generates H_2 at 24% thermal eff.
32% (elec. eff.) x 80% (electrolysis eff.)

(2.4)

Table 3
REDUCING CO_2 EMISSIONS FOR MITIGATING THE CO_2 GREENHOUSE EFFECT THERMOCHEMISTRY OF FOSSIL FUEL CRACKING BY HYDROCARB SYSTEM WITHHOLDING CARBON

Fuel Type	Stoichiometry	HYDROCARB Derived Fuel Products	Emission of CO_2		
			Ratio Emitted C/H as CO_2/H_2O	lb CO_2 / MMBtu	Energy Avail. %
Coal	$CH_{0.8}O_{0.08}$	$= 1.00\ C + 0.32\ H_2 + 0.08\ H_2O$	0.00	0	19
		$= 0.96\ C + 0.40\ H_2 + 0.04\ CO_2$	0.05	40	24
		$= 0.84\ C + 0.16\ CH_4 + 0.08\ H_2O$	0.25	120	29
		$= 0.76\ C + 0.20\ CH_4 + 0.04\ CO_2$	0.30	140	37
		$= 0.92\ C + 0.08\ CH_3OH + 0.24\ H_2$	0.01	60	27
	Combustion	$= CO_2 + 0.4\ H_2O$	1.25	210	100
Lignite	$CH_{0.8}O_{0.22}$	$= 1.00\ C + 0.18\ H_2 + 0.22\ H_2O$	0.00	0	11
		$= 0.89\ C + 0.40\ H_2 + 0.11\ CO_2$	0.14	100	24
		$= 0.91C + 0.09\ CH_4 + 0.21H_2O$	0.25	120	17
		$= 0.69C + 0.20\ CH_4 + 0.11CO_2$	0.39	180	38
		$= 0.78\ C + 0.22\ CH_3OH$	0.25	130	35
	Combustion	$= CO_2 + 0.4\ H_2O$	1.25	220	100
Natural Gas	CH_4	$= C + 2\ H_2$	0.00	0	56
	Combustion	$= CO_2 + 2\ H_2O$	0.25	110	100
Oil	$CH_{1.7}$	$= C + 0.85\ H_2$	0.00	0	37
	Combustion	$= CO_2 + 0.85\ H_2O$	0.58	160	100
Synthetic Fuel	H_2 from Coal	$= H_2 + CO_2$	0.38	270	70
	SNG from Coal	$= CH_4 + CO_2$	0.79	330	70
	Synthetic Liq.	$= CH_2 + CO_2$	1.00	310	70
Wood	$CH_{1.44}O_{0.66}$	$= 1.00C + 0.66H_2O + 0.06H_2$	0.00	0	4
		$= 0.67C + 0.33CO_2 + 0.72H_2$	0.23	160	47
	Combustion	$= CO_2 + 0.72H_2O$	0.69	230	100

(2.4)

Fig. 1.

CLEAN COAL-DERIVED FUELS via THE HYDROCARB PROCESS