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Project Summary

A Feasibility Study for the Coprocessing of Fossil Fuels With Biomass by the Hydrocarb Process

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A new process concept for the production of carbon and methanol from fossil fuels is described and assessed. The Hydrocarb Process consists of the hydrogasification of carbonaceous material to produce methane, which is subsequently thermally decomposed to carbon black and hydrogen, part of which is recycled to the hydrogasifier. With an oxygen-containing feedstock, the carbon monoxide (CO) is converted with hydrogen to methanol in an intermediate step. Background process chemistry data are available for each step of the process. A process simulation model has been developed to perform complete mass and energy balances based on approaching thermodynamic equilibrium compositions. Preliminary process design and analysis indicates economic potential. By coprocessing fossil fuels with biomass to produce hydrogen-rich fuels, it is shown that the carbon dioxide (CO_2) emissions can be substantially reduced compared to direct combustion of fossil fuel. Additional experimental data on the kinetics of hydrogasification of wood and methane decomposition are required before a process demonstration unit can be constructed.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project tht is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A feasibility study was undertaken at Brookhaven National Laboratory (BNL) to determine the potential of coprocessing biomass with fossil fuel to produce a clean carbon fuel and coproduct methanol by the Hydrocarb Process. The process may be useful for mitigating the global warming problem by reducing CO_2 emissions. The Hydrocarb Process consists of three basic process steps: (1) the exothermic hydrogasification of a carbonaceous feedstock to a methane-rich process gas stream, (2) the endothermic thermal decomposition of methane to carbon and hydrogen, part of which is recycled to step (1), and (3) the conversion of CO and hydrogen to methanol. Any carbonaceous material can be used as feedstock. The coproducts are clean particulate carbon black, liquid methanol, and gaseous hydrogen or methane. There are distinctive benefits of clean carbon and methanol as environmentally acceptable utility and transportation fuels. Carbon can be used separately or combined in slurry form with methanol which significantly improves the volumetric energy density of methanol while methanol improves the ignition characteristics of the carbon in the slurry.

Basic Hydrocarb Process

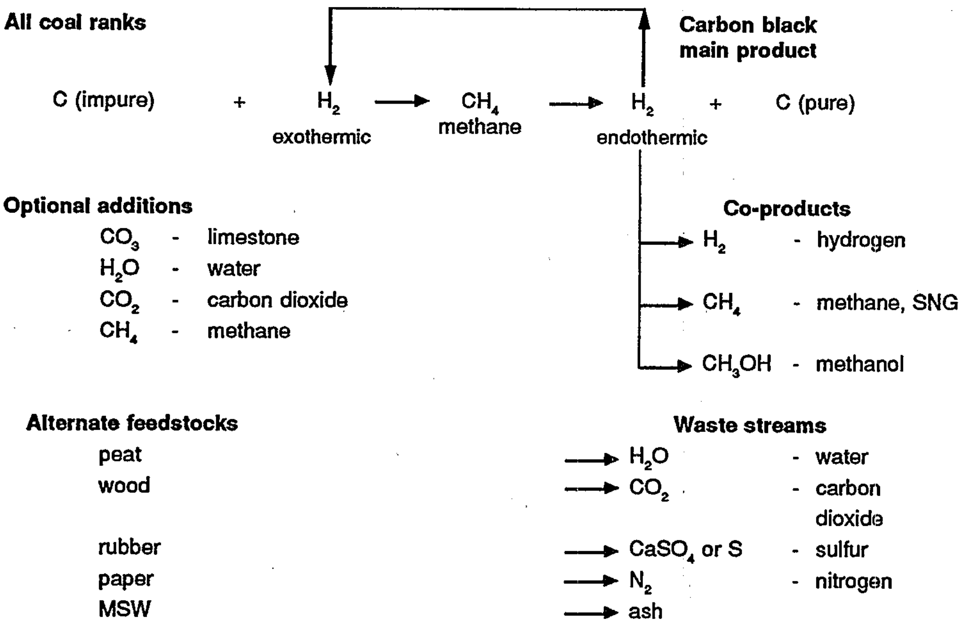
The basic Hydrocarb Process can be operated with any carbonaceous feedstock or with combinations of feedstocks. Furthermore other coproducts can be formed. Feedstock which contains some oxygen material, which includes coal and wood, when hydropyrolyzed forms some amounts of CO. The CO then can be catalytically combined with hydrogen to form methanol. Table 1, a generalized schematic of the Hydrocarb Process, indicates possible alternate feedstocks and coproducts. Figure 1 shows one version of several flowsheets in which methanol is produced between the methane pyrolyzer and the hydrogasifier without an alumina heat transport system between the reactors. A further step in the Hyrdrocarb Process converts the methanol to gasoline by the MTG (methanol to gasoline) process. Alternate reactors, including moving and fluidized beds can be used.

Analysis of Proposed Biomass/ Fossil Fuel Hydrocarb Coprocess

The Hydrocarb processing of fossil fuel alone, sequestering the carbon and using only the hydrogen generated, can extract 56% of the energy from natural gas, 25 to 37% from crude oil, and 19% from coal. With this energy penalty, a hydrogen economy can be based on utilizing fossil fuel with no generation or emission of CO_2.

Coprocessing fossil fuel with biomass, employing the Hydrocarb system to produce carbon and methanol while sequestering the carbon and only using methanol

Table 1. Clean Coal Technology: Production of a Clean Carbon Fuel and Coproducts



Notes: 1) Three methods of heat transfer - gas, solid, or steam
2) Three reactor types - fluidized bed, moving bed, entrained bed

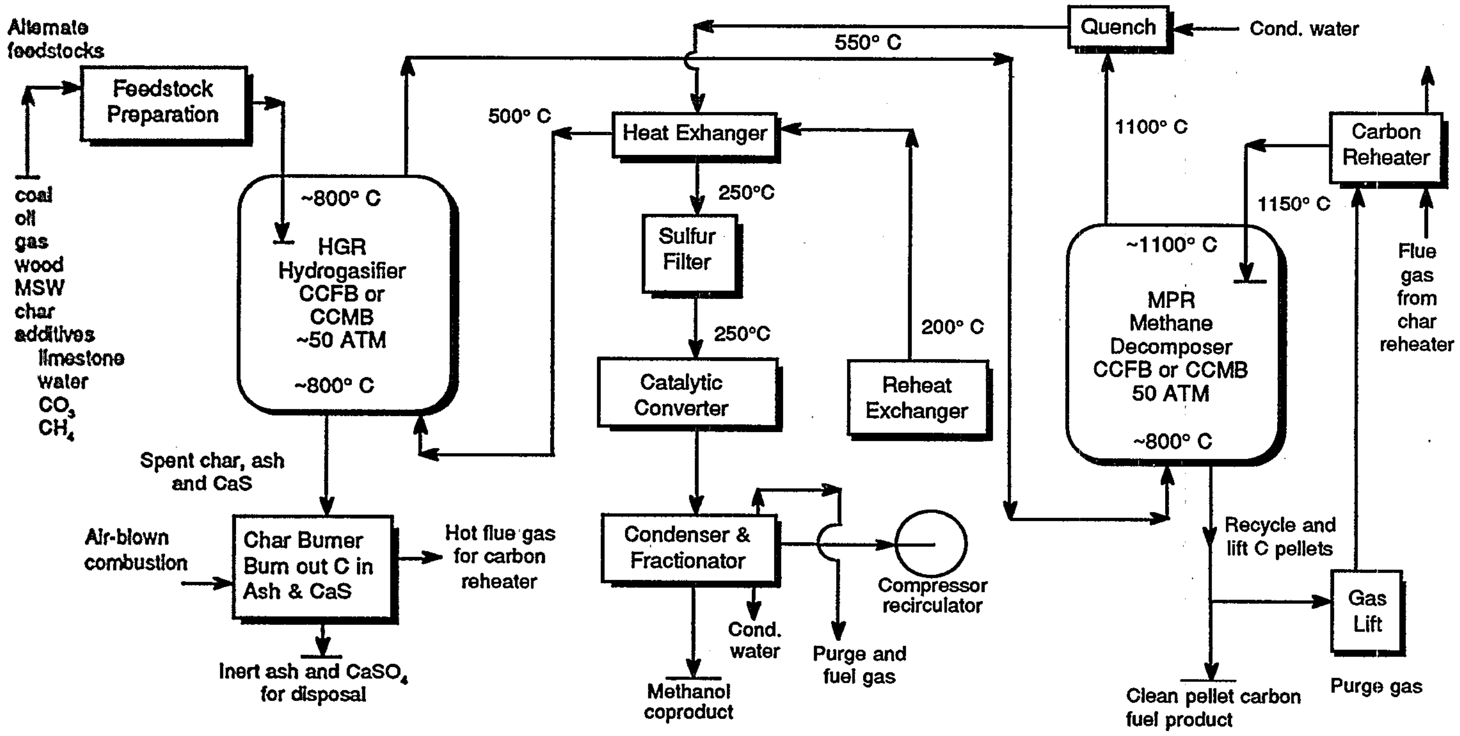


Figure 1. Carbex version of the Hydrocarb Process: Clean carbon and coproduct fuels from carbonaceous feedstocks

as fuel, not only can reduce CO_2 emissions to zero, but also can actually show a removal of CO_2 from the atmosphere. Table 2 gives the stoichiometry of the photosynthesis process for producing biomass (wood) and the coprocessing of biomass with natural gas, oil, and coal. For various methods of methanol synthesis, including conventional and Hydrocarb, Table 3 summarizes the carbon and energy utilization efficiencies, and the CO_2 generated when using only the methanol and when using both the methanol and carbon.

Conventional steam reforming and air oxidation processes generate more than 50% greater amounts of $CO_2/10^6$ Btu of methanol energy than if the fossil fuel were burned directly. Using Hydrocarb with bituminous coal alone reduces CO_2 emissions by about 60%; however, the energy utilization efficiency is reduced by 38% because the carbon is not used. The coprocessing of biomass with natural gas and oil can actually remove as much as 78 lb of $CO_2/10^6$ Btu from the atmosphere while generating 166 and 115% more energy, respectively, than the energy content of gas and oil. These results occur because solar energy utilized in growing biomass is assumed to be free. Coprocessing with coal shows a zero emission of CO_2 and a 50% utilization of the energy in coal. Utilizing both the methanol and carbon more than doubles the utilization of coal and reduces the CO_2 generation by 50% compared to conventional production of methanol from coal.

Table 2. *Reduction of Atmospheric CO_2 by Photosynthesis and Thermochemistry*

I. **Photosynthesis** - Driven by solar energy - biomass formation

$$CO_2 + 0.72\ H_2O = CH_{1.44}O_{0.66} + 1.03\ O_2$$

hemi-cellulose
biomass

II. **Thermochemical Cracking** - Thermal energy driven - high efficiency Hydrocarb Process

1. Biomass alone

$$CH_{1.44}O_{0.66} = C + 0.66\ H_2O + 0.06\ H_2$$

Sequester C in the earth
O emission/MMBtu of H_2 energy
Fraction of biomass energy used = 6%

2. Biomass + natural gas

$$CH_{1.44}O_{0.66} + 0.34\ CH_4 = 0.64 + 0.66\ CH_3OH$$

Sequester C - utilize methanol for energy
CO_2 removed from atmosphere = 78 lb CO_2 /MMBtu
Energy Enhancement of Natural Gas = 163%

3. Biomass + oil

$$CH_{1.44}O_{0.68} + 0.7\ CH_{1.7} = C + 0.66\ CH_3OH$$

Sequester C - utilize methanol for energy
CO_2 removed from atmosphere = 78 lb CO_2/MMBtu
Energy enhancement of oil = 115%

4. Biomass + bituminous coal

$$0.32\ CH_{1.44}O_{0.66} + CH_{0.8}O_{0.1} = C + 0.32\ CH_3OH$$

Sequester C - utilize methanol for energy
CO_2 balance - O emission of CO_2
Fraction of coal energy used = 50%

Background Process Data Supporting the Hydrocarb Process

There is an abundance of coal hydrogasification data. Work at BNL on flash hydropyrolysis indicates that 90% conversion of carbon in lignite to methane can be obtained at 2500 psi* and 900° C at residence times of 5-10 sec. The Rheinbraun Co. in West Germany operated a 240 ton/day (T/D) brown coal fluidized bed hydrogasifier, and obtained over 80% carbon conversion of which 90% was converted to methane, the remainder being CO and CO_2

At BNL, experiments on the hydrogasification of wood in and entrained flow tubular dilute phase reactor indicated that over 90% of the carbon in the wood can be converted to methane and CO at residence times of up to 2 sec, temperatures of 800 - 1000° C, pressures of 200 - 500 psi, and concentrations of less than 10%. The reactivity of wood towards hydrogasification is greater than that of coal. However additional data are needed to obtain higher concentrations of methane much closer to equilibrium values, necessary for the Hydrocarb Process to work efficiently.

Methane decomposition has been practiced for a long time by industry in making thermal black from natural gas by pyrolysis. Literature data also indicate that the reaction is catalyzed by substrates of iron oxide, aluminum oxide, and (to some extent) by carbon itself. A process called Hypro was actually operated by an oil company to produce hydrogen for a refinery from methane by thermal decomposition. Additional work is required to determine the kinetics of methane cracking at elevated pressures.

Methanol formation is basically conventional by the well-known low pressure ICI copper catalysts. The main difference is that Hydrocarb operates on the synthesis gas stream once through, without recycling.

Value of Carbon and Methanol as Fuel

Clean carbon and methanol can be used in heat engines (turbines and diesels) while coal because of its ash and sulfur content cannot be readily used because of corrosion and erosion of turbine blades and cylinder walls. Carbon with a density of 2 g/cm³ can be slurried with water, oil, and methanol to energy densify the liquid fuels. Experimental characteristics of a number of carbon slurries have been prepared and measured.

Process Design and Analysis

Extensive process design and analysis of the Hydrocarb Process has been made for several of its configurations. Mass and energy balances have been made based on approaching thermodynamic equilibrium among the five gaseous components CH_4, CO, CO_2, H_2 ,and H_2O. A Hydrocarb Pro-

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* Readers more familiar with the metric system may use the factors at the end of this summary to convert to that system.

Table 3. CO_2 Generated or Removed From the Atmosphere by Various Methanol Synthesis and Coprocessing Systems Using Fossil Fuel and Biomass Feedstocks

Feedstock	Methanol process	Carbon utilization methanol only based on fossil fuel feedstock only %	Energy utilization efficiency methanol only based on fossil fuel feedstock only %	CO_2 generated (+) CO_2 removed (-) lb CO_2/MMBtu of methanol generated energy	Energy utilization efficiency using both methanol and carbon based on fossil fuel feedstock only %	CO_2 generated(+) CO_2 removed (-) lb CO_2/MMBtu of both mehtanol and carbon generated energy
Conventional-Produces-CO_2						
natural gas	steam reforming	82	68	+170		
oil	partial oxidation	50	64	+280		
coal-bit.	steam-oxygen reforming	42	64	+330		
Hydrocarb-store carbon						
bit. coal (added H_2O)	Hydrocarb	27	40	+130	92	+250
lignite	Hydrocarb	18	30	+130	92	+270
Hydrocarb co-processing with biomass store carbon						
II biomass + natural gas	Photosynthesis + Hydrocarb	200	166	-78	280	+41
III biomass + Oil	Photosynthesis + Hydrocarb	85	115	-78	215	+76
IV biomass + bit. coal	Photosynthesis + Hydrocarb	30	50	0	130	+162

Note: 1) combustion of natural gas generates 110 lb CO_2/MMBtu, oil 160 lbs/MMBtu, bit. coal 215 lbs CO_2/MMBtu, Lignite 225 lbs CO_2/MMBTU
2) Assumes 90% conversion of feedstock to mehtanol in Hydrocarb Process.

cess Simulation model has been developed to obtain full mass, energy, and compositional data for each feedstock and process configuration.

Sulfur removal is a special problem. One approach is to feed dolomite or lime in conjunction with coal to the hydropyrolosis reactor. The bulk of the gasified sulfur is removed as CaS, which then must be properly disposed of with the ash. A zinc oxide guard filter is used to protect the catalytic converter from becoming poisoned by the sulfur. Reactor design can be of the moving bed or the fluidized bed type, with the former giving a higher thermal efficiency but more difficult operation.

Preliminary economic analysis indicates that for a 10,000 T/D fast rotational poplar tree crop supplying wood from an energy farm, at \$38/ton, to a Hydrocarb plant together with natural gas at \$2.50/1000 scf would require a capital investment of \$577 million and, taking credit for carbon at \$2.50/10^6 Btu, could yield a selling price for methanol of \$0.37/gal., which is economically competitive with conventional production of methanol from natural gas at \$0.45/gal.

Conclusions

It is concluded that the Hydrocarb coprocessing of fossil fuel with biomass is technically feasible. Methanol and carbon as clean fuel would be suitable for use in heat engines (turbines and diesels) at competitive prices with oil and gas. By sequestering the carbon and using only the hydrogen-rich methanol as fuel, the emission of CO_2 can be significantly reduced compared to the direct combustion of fossil fuel. Additional kinetic data for the hydrogasification of biomass under methane-rich conditions, as well as experimental data on the thermal decomposition of methane under pressure and temperature conditions designed for the Hydrocarb Process, are required before proceeding with a process demonstration unit.

Conversion Factors

Readers more familiar with the metric system may use the following factors to convert to that system.

Nonmetric	Multiplied by	Yields metric
atm	101.3	kPa
Btu	1.06	kJ
gal.	3.785	liter
psi	6.89	kPa
scf	0.028	sm^3
ton	907.2	kg

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The complete report, entitled "A Feasibility Study for the Coprocessing of Fossil Fuels with Biomass by the Hydrocarb Process," (Order No. DE91- 011971/AS; Cost: $26.00, subject to change) will be available only from:

National Technical Information Service
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