



Project Summary

Rates of Reaction and Process Design Data for the Hydrocarb Process

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In support of studies for developing the coprocessing of fossil fuels with biomass (wood) by the Hydrocarb process, experimental and process design data are reported. The experimental work includes the hydrolysis of biomass and the thermal decomposition of methane in a tubular reactor. The rates of reaction and conversion were obtained at temperature and pressure conditions pertaining to a Hydrocarb process design. A Process Simulation Computer Model was used to design the process and obtain complete energy and mass balances. Multiple feedstocks were also evaluated, including biomass with natural gas, biomass with coal, and sewage sludge (SL) and digester gas (DG) as additional feedstocks.

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 that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A feasibility study for the coprocessing of fossil fuels with biomass by the Hydrocarb process was performed for the U.S. EPA (the related report is dated November 1991). Results of the study indicated technical and economic feasibility compared to conventional processes for converting carbonaceous feedstocks such as coal, natural gas, and biomass to clean carbon and methanol fuels. For purposes of mitigating the global greenhouse carbon dioxide (CO₂) problem, coprocessing fossil fuels with biomass, sequestering all or part of the carbon and using the metha-

nol mainly as a power or transportation fuel, presents the option of reducing and eliminating CO₂ emissions to the atmosphere while still employing the world's fossil fuel resources. The report recommended that additional confirmation be obtained of the kinetics of the major steps in the Hydrocarb process, which includes the hydrolysis of biomass and the thermal decomposition of the methane-rich process gas. To this end, an experimental study was undertaken using the Brookhaven National Laboratory's Tubular Reactor Facility.

In addition to the experimental work, it was recommended that further process design studies be performed employing the Process Simulation Computer Model developed by the Hydrocarb Corporation with alternative carbonaceous feedstocks. This report describes the experimental and process design work.

The report is divided into three sections. Part I deals with the hydrolysis of biomass. Part II deals with the thermal decomposition of methane in a tubular reactor. Part III gives the results of an analysis of the Hydrocarb process with alternative and multiple feedstocks.

Part I. Hydrolysis of Biomass

The pyrolysis and hydrolysis of biomass in the form of poplar wood sawdust having particle size less than 150 mm in diameter was investigated in a 25 mm ID and 2.5 m long tubular reactor facility at Brookhaven National Laboratory. The tests were conducted at temperatures up to 800°C and pressures between 30 and 50 atm.* The experiments were performed in

* 1 atm = 101.3 kPa.



two different modes, depending on the heat-up rate. In the low heat-up rate mode, the biomass was first loaded in the reactor at room temperature. Hydrogen was then introduced into the system up to a desired initial pressure level. The reactor was slowly heated up at a rate of less than 10°C/min. The change in the pressure in the reactor and the composition of the effluent gas were monitored with time. In the higher heat-up rate mode, the reactor was heated up and pressurized with hydrogen up to the desired reaction conditions before introducing the biomass. The variations of pressure and gas composition versus time were then recorded and analyzed. From these data, rates of reaction and degree of conversion were determined. A typical run shown in Figure 1 indicates the calculated number of moles of gas generated as a function of time.

At low heat-up rate, the reaction proceeds in two steps. First pyrolysis takes place at temperatures of 300 to 400°C and then hydrolysis takes place at 700°C and above. This is also confirmed by experiments using pressurized thermogravimetric analysis. Under conditions of rapid heat up at higher temperatures and higher hydrogen pressure, gasification and hydrogasification of biomass is especially effective in producing CO and methane. An overall conversion of 88 to 90 wt% of biomass was obtained. This is in agreement with previous work on flash pyrolysis and hydrolysis of biomass under rapid heat up and short reaction residence time conditions. Initial rates of biomass conversion indicate that the rate increases significantly with in-

crease in hydrogen pressure. At 800°C and 51.3 atm the initial rate of biomass conversion to gases is found to be 92% per min.

Part II. Thermal Decomposition of Methane

The reaction rate of methane decomposition using the same reactor facility was investigated in the temperature range of 700 to 900°C at pressures ranging from 28 to 56 atm. In these experiments, methane was fed into the reactor continuously. Gas from upstream and downstream of the reactor was analyzed on-line to calculate the reaction rate. The variations in methane concentration vs. residence time under different operating conditions are shown in Figure 2. It can be seen from the experimental data that the gas residence time of about 2 min. is required for the reaction to reach near equilibrium composition at 50 atm and 900°C. The rate is represented by a conventional model,

$$-\frac{dCH_4}{dt} = kC_{CH_4}$$

where C is the molar concentration and k is the rate constant.

When the initial hydrogen concentration is zero, the activation energy for methane decomposition is 31.3 kcal/mol,* as determined by an Arrhenius Plot. This value is lower than for previously published results for methane decomposition and appears to indicate that the high-surface-area sub-micron carbon particles found adhering to the inside of the reactor tend to catalyze the methane decomposition reaction. The

* 1 kcal = 4.183 kJ.

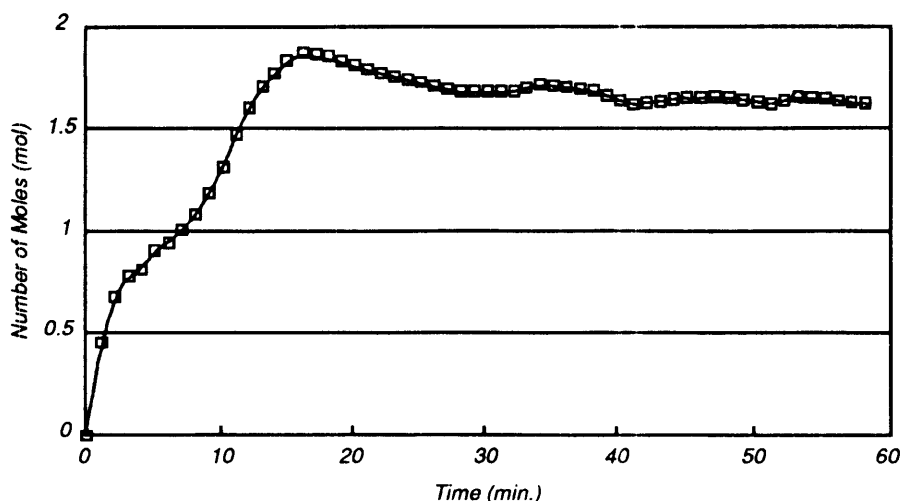


Figure 1. Hydrolysis of poplar sawdust biomass. The change in number of moles in the reactor with time at 800 °C and 52.4 atm of initial hydrogen pressure. Run No. 1152.

rate constant has been found to be approximately constant at 900°C in the pressure range investigated, 28 to 56 atm. The rate of methane decomposition increases with methane partial pressure to the first order. It is concluded that the rate of methane decomposition is favored by higher temperatures and pressures, while the thermochemical equilibrium of methane decomposition is favored by lower pressures. By extrapolating to higher temperatures, the residence time to reach near equilibrium at 50 atm would be 41 sec. at 1000°C and 12 sec. at 1140°C.

Part III. Design Analysis of the Hydrocarb Process with Alternate and Multiple Feedstocks

The design performance of the Hydrocarb process with alternative and multiple feedstocks was investigated. The alternative feedstocks studied for the Hydrocarb process included biomass (wood), Alaska Beluga coal, Kentucky (bituminous) coal, North Dakota (lignite) coal, and Wyodak (subbituminous) coal. A thermodynamic-equilibrium-limited Process Simulation Computer Model was used to design the process and obtain complete energy and mass balances. Boundary conditions of pressure, temperature, and mass balance for the cyclical process were determined. Two cycles were investigated depending on whether process gas from the HPR goes directly to the MPR (cycle 1) or whether the HPR gas first goes to the methanol synthesis reactor and condenser and then to the HPR (cycle 2). Cycle 1 produces a higher ratio of methanol to carbon and is preferred. The study also included using sludge and digester gas from sewage plants as additional feedstocks. It was found that these feedstocks have to be coprocessed with either biomass or coal to obtain a workable mass balance. The effect of pressure and temperature for both biomass and sludge feedstock was also investigated. Carbon conversion efficiency ranges from 70 to 80% and thermal efficiency between 60 and 80%. Increasing the HPR and MPR temperature improves methanol production and thermal efficiency. The methanol to carbon production rate decreases with decreasing system pressure.

From this study it is concluded that a most favorable operating conditions for coprocessing biomass and methane is 50 atm system pressure, and 900°C for the HPR and 1000°C for the MPR. Figure 3 is a complete flowsheet showing the rates and compositions of each stream to and

from the major pieces of equipment in the Hydrocarb process for coprocessing biomass (wood) and methane (natural gas). This process design and the experimental rate data are being applied to the design of reactors for an integrated 22.7 kg/h Hydrocarb pilot plant.

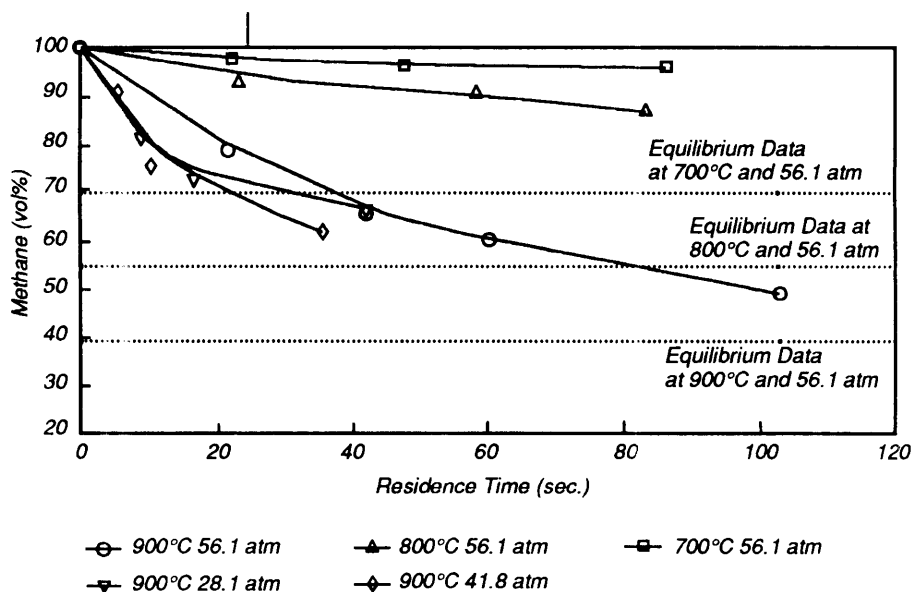


Figure 2. Methane concentrations vs. residence time.

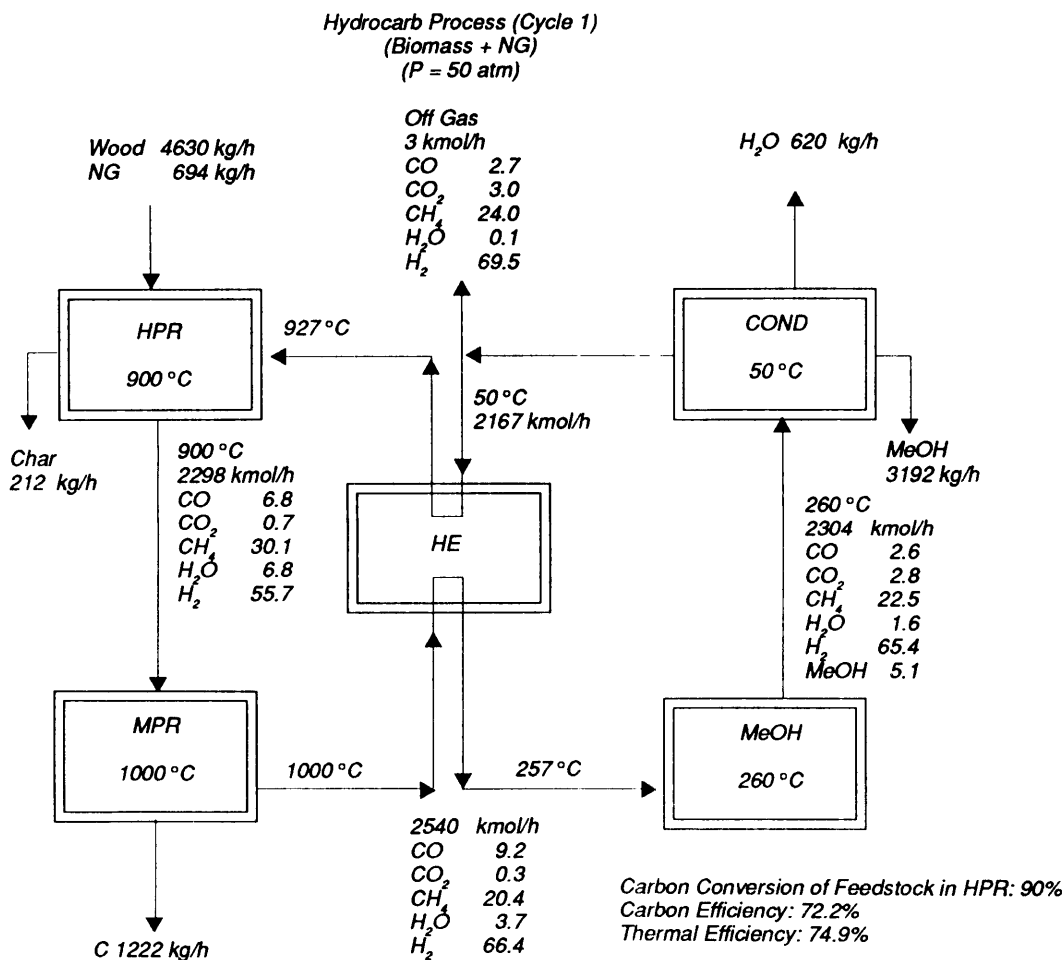


Figure 3. Data summary with wood and CH₄ as feedstocks.

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Robert H. Borgwardt is the EPA Project Officer (see below).

The complete report, entitled "Rates of Reaction and Process Design Data for the Hydrocarb Process," (Order No. PB93-155976; Cost: \$27.00; subject to change) will be available only from

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