**RATES OF REACTION AND PROCESS DESIGN DATA
FOR THE HYDROCARB PROCESS**

by

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ABSTRACT

In support of studies for developing the coprocessing of fossil fuels with biomass by the Hydrocarb Process, experimental and process design data are reported. The experimental work includes the hydropryolysis 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 including biomass with natural gas and biomass with coal were evaluated. Additional feedstocks including green waste, sewage sludge and digester gas were also evaluated for a pilot plant unit.

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METRIC CONVERSION FACTORS

Readers more familiar with the metric system may use the following factors to convert the non-metric units used in this report:

Nonmetric	Times	Yields Metric
atm	101.3	kPa
bar	100	kPa
Btu/ft ³	37,233	J/m ³
Btu/gal.	278.5	J/liter
Btu/lb	2324	J/kg
ft	0.3048	m
ft ³	0.02832	m ³
gal.	3.785	liter
lb	0.4536	kg
ton	907.2	kg
Btu/lb mol	0.555	cal/gm ¹ mol
kcal	103	cal
Btu	1.06	kJ
psi	6.89	kPa

ABBREVIATIONS

HPR – Hydropyrolysis reactor
HGR – Hydrogasifier reactor; HPR and HGR are equivalent
MPR – Methane pyrolysis reactor
BTX – Benzene, toluene and xylene
HCSP – Hydrocarb process simulation program
FHP – Flash hydropyrolysis
MTG – Methanol to gasoline process
MSW – Municipal solid waste
PDU – Process demonstration unit
GW – Green Waste

Part O

SUMMARY

A feasibility study for the coprocessing of fossil fuels with biomass by the Hydrocarb process was performed for the U.S. Environmental Protection Agency and a report (EPA 600/7-91-007) was issued dated November 1991, entitled "A Feasibility Study for the Coprocessing of Fossil Fuels with Biomass by the Hydrocarb Process." The results of this 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 CO₂ problem, coprocessing fossil fuels with biomass, sequestering all or part of the carbon and mainly utilizing the methanol 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 Brookhaven 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, and Part III gives the results of an analysis of the Hydrocarb process with alternative and multiple feedstocks. The following is a summary of all three parts.

The hydrolysis and hydrolysis of biomass was investigated in the tubular reactor and the experimental runs with poplar wood sawdust were performed using the tubular

reactor having dimensions 25.4 mm inside diameter and 2.44 m long heated to temperatures of 800°C and pressures between 30 and 50 atm. 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 pressurized thermogravimetric analysis (PTGA). Under conditions of rapid heat-up at higher temperatures and higher hydrogen pressure, gasification and hydrogasification of biomass is especially effective in producing carbon monoxide 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 increase 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.

The reaction rate of methane decomposition using a tubular reactor having a 25.4 mm inside diameter with an 2.44 m long heated zone using the same tubular reactor facility was investigated in the temperature range of 700 to 900°C with pressures ranging from 28.2 to 56.1 atm. The rate is represented by a conventional model, $\frac{-dC_{CH_4}}{dt} = k C_{CH_4}$, where C is the molar concentration and k is the rate constant. When initial H_2 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 submicron carbon particles found adhering to the inside of the reactor tend to catalyze the methane decomposition. The rate constant has been found to be approximately constant at 900°C in the pressure range investigated. The rate of methane decomposition increases with methane partial pressure to the first-order. The conclusion is reached 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.

The designed 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 (sub-bituminous) coal Kentucky (bituminous) coal, North Dakota (lignite) coal and Wyodak (sub-bituminous) coal. A Process Simulation Computer Model was used to design the process, and obtain complete energy and mass balances. Boundary conditions of pressure, temperature and mass balances for the cyclical process were determined. 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 maximum allowable feed ratios of sludge to biomass or sludge to coal were determined. The effect of pressure and temperature for the biomass and sludge feedstock cases were also developed.

Part I

HYDROPYROLYSIS OF BIOMASS

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Hydropyrolysis of Biomass

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ABSTRACT

The pyrolysis and hydropyrolysis of biomass was investigated. Experimental runs using the biomass (Poplar wood sawdust) were performed using a tubular reactor of dimensions 25.4 mm inside diameter and 2.44 m long heated at a temperature of 800 C and pressures between 30 and 50 atm. At low heat-up rate the reaction proceeds in two steps. First pyrolysis takes place at temperatures of 300 to 400 C and subsequent hydropyrolysis takes place at 700 C and above. This was confirmed by pressurized thermogravimetric analysis (PTGA). Under conditions of rapid heat-up at higher temperatures and higher hydrogen pressure gasification and hydrogasification of biomass is especially effective in producing carbon monoxide and methane. An overall conversion of 88 to 90 wt% of biomass was obtained. This value is in agreement with the previous work of flash pyrolysis and hydropyrolysis of biomass for rapid heat-up and short residence time. Initial rates of biomass conversion indicate that the rate increases significantly with increase in hydrogen pressure. At 800 C and 52.4 atm the initial rate of biomass conversion to gases is 0.92 l/min.

INTRODUCTION

The Hydrocarb Process involves two main reactions; (1)hydrogasification of the carbonaceous feedstock to produce methane-rich gas, and (2)the thermal decomposition of methane to produce hydrogen-rich gas, which is recycled to the hydrogasification section, and finally produces clean carbon black as product.⁽¹⁻¹⁾ A third step combines the CO formed from the hydrogasification section with hydrogen and produces methanol as co-product. The hydrogasification step is important in this process because the composition and the rate of formation of the methane-rich gas can determine the performance of the methane decomposition and methanol reactors as well as the overall performance of the cyclical Hydrocarb Process.

This work was performed in order to investigate both the rate and degree of conversion for the pyrolysis and hydrolysis of biomass using a tubular reactor at a temperature of 800 C and at pressures of 30 to 50 atm in a hydrogen atmosphere. Data at higher loading densities of biomass compared to previous experiments were also investigated. Previous experiments were performed under flash hydrolysis conditions in dilute phase at low CH_4 , CO, and CO_2 in the gaseous phase.^(1-2,1-3)

EXPERIMENTAL DESCRIPTION

BIOMASS PREPARATION

The biomass, essentially Poplar wood sawdust, is ground and sieved to less than 150 micron diameter. This particle size was chosen in order that the external heat and gaseous hydrogen in the reactor could penetrate through the biomass particles easily and the biomass could be smoothly fed into the tubular reactor from the feeder attached to the top of the reactor. The ground biomass is first dried in an oven, in which the temperature is kept constant at about 100 C until the moisture content of the biomass is reduced to less than 3 wt% so that the effect of water on the rate of the hydropyrolysis reaction is minimized. The dried biomass component was analyzed by standard analytical procedure and the elemental analysis is shown in Table I-1.

TABLE I-1. BIOMASS (POPLAR SAWDUST) COMPOSITION

Component	Weight Percentage
C	51.32
H	6.16
N	1.18
S	0.13
O	34.57
Ash	6.64
	<hr/> 100 wt% (total)

A very fine silica flour (Cab-O-Sil) was mixed with the ground biomass to prevent agglomeration and allow smooth flow of the sawdust from the feeder into the reactor. This process also prevented plugging inside the reactor. The weight content of silica flour was fixed at about 20 wt% as determined from past experience.^(1-2,1-3)

EXPERIMENTAL PROCEDURE

Figure I-1 shows the schematic flow sheet of the experimental equipment which consists of a biomass feeder, a tubular reactor, a carbon trap, and a gas-chromatograph. Experiments were performed under two different modes; (1) In the first mode of operation, the biomass was

loaded into the reactor on top of a 50.8 mm height of packing consisting of 3.18 mm alumina balls which rests on a perforated disk made of stainless steel positioned at the bottom of the reactor. After a helium purge, hydrogen was introduced into the system up to 52.4 atm and heated up from room temperature 800 C by the external electrical clamshell heaters. The pressure in the reactor was monitored by a pressure gauge and the concentrations of the effluent carbon containing gases, CH_4 , C_2H_4 , C_2H_6 , CO , and CO_2 , were analyzed with the thermal conductivity detector in the on-line gas-chromatograph; (2) In the second mode of operation, the reactor temperature was raised to 800 C and the reactor was pressurized with hydrogen over the range 32.0 to 52.4 atm, and the biomass was fed into the reactor at a rate between 10 and 20 grams/min. The pressure in the reactor was monitored and the effluent gases were analyzed in the same manner as mentioned method.

The reactor was a 25.4 mm diameter Inconel 617 tube with 6.35mm wall thickness. The total tube height was 3.35 m of which 2.44 m is heated externally with electrical clamshell heaters. As described earlier, it had a disk of stainless steel positioned 0.61 m up from the bottom of the heated zone to act as a hold-up platform for the biomass, and 3.18 mm alumina balls about 50.8 mm in height is also set on the disk to assist in holding the biomass sawdust. The sawdust bed height ranges from 1.52 to 1.83 m in the heated zone.

EXPERIMENTAL RESULT AND DISCUSSION

Data Table I-1 and Figure I-2 show the results of the experimental Run No. 1154 for the conditions of biomass and hydrogen preloaded into the reactor, system purge and heated up from room temperature to 800 C at an initial pressure of 52.4 atm. The temperature and the concentrations of the gases generated are plotted as a function of the run time and are shown in Figure I-2. At first, CO and CO₂ gases are generated before CH₄ is formed. The volume of CO₂ generated is much larger than CO at the beginning of the run. These gases begin to form around 470 C. CH₄ also begins to generate slowly around 470 C and it rapidly increases above 700 C. This phenomena appears to indicate that pyrolysis of biomass starts around 470 C and hydropyrolysis starts about 700 C.

A pressure calibration run is shown in Figure I-3 which indicates the pressure change in the reactor with the temperature for the above mentioned conditions. The dotted line in the figure indicates the calibration line with hydrogen pressure as the reactor is heated up in the same manner as in the run when the biomass was present. This is compared with the pressure change for the Run No. 1154 when the biomass was present as shown by the solid line. At approximately 300 C, the pressure increases sharply compared with the calibration line. The difference between solid line and dotted line indicates that a reaction has occurred in the biomass itself or between the heated biomass and the gaseous hydrogen. As indicated by the composition of the gases generated, CO, CO₂, CH₄, and others, as shown in Figure I-2, the pyrolysis of the biomass begins around 300 C. Above 400 C, there appears to be almost no change in pressure shown in Figure I-3. However taking into account the data shown in Figure I-2, certainly some gases are generated in that temperature range. A zero pressure change in this region would mean that there is a balance between the gases generated and the hydrogen consumed by hydropyrolysis. Taking this effect into account, pyrolysis and hydropyrolysis of the biomass can be totally represented by following two steps;

First Step ; Pyrolysis of
 Biomass $\xrightarrow{\text{heat}}$ CO + CO₂ + H₂O
 at temperatures of 300 – 400 C

Second Step ; Hydropyrolysis of

$$\begin{array}{ccc} \text{Biomass} + \text{H}_2 & \xrightarrow{\hspace{1cm}} & \text{CH}_4 \\ \text{C} + \text{H}_2 & \xrightarrow{\hspace{1cm}} & \text{CH}_4 + \text{other} \\ \text{(remaining char or carbon)} & & \text{hydrocarbons} \end{array}$$
 at temperature above 700 C

In the first step, at the lower temperatures of 300 through 400 C pyrolysis of the biomass occurs in the early stage of the reaction to produce mainly CO and CO₂. In the subsequent step, at higher temperatures above 700 C and at elevated hydrogen pressure, CH₄ and some higher hydrocarbons are generated by hydropyrolysis.

In connection with this work R. Khan⁽¹⁻⁴⁾ performed two pressurized thermogravimetric analyses (PTGA) for us on Poplar and Fir wood. The PTGA data are shown in Figures I-4 and I-5 at 28.2 atm in helium (solid line) and hydrogen (dotted line) atmospheres. The hydrogen line for weight loss in Figure I-4 for Poplar wood shows 3 steps. The first weight loss of about 10 wt% takes place at the temperature of 150 to 300 C, which is probably due to water vaporization from the biomass. A large second weight loss of about 55 wt% starts at approximately 300 C and continues to about 450 C. Up to 450 C, both the helium and hydrogen curves are very similar. Thus in the low temperature regime, the pyrolysis reaction in the biomass occurs independent of the atmosphere present. On the other hand, beyond this temperature region, the hydrogen atmosphere data line decreases more than the helium data line which stops losing weight at about 600 C. The third weight loss of 10 to 15 wt% is probably due to the reaction of hydrogen with the remaining carbon to produce CH₄ and other hydrocarbons. Similar results are shown in Figure I-5 for Fir wood. These PTGA results are in accord with our tubular reactor experimental results.

Data Tables I-2 and I-3 show the results of measurements that were obtained for conditions when the biomass is gradually fed into the reactor by the feeder. The reactor was heated up to 800 C before the start of the experimental run, and the system is filled with hydrogen to pressures of 32.0 and 52.4 atm respectively. Data Table I-3 showing the results of Run No. 1152 gives the measurements obtained at 800 C and 52.4 atm initial pressure of hydrogen, whereas Data Table I-2 of Run No. 1144 was obtained at 800 C and an initial pressure of 32.0 atm. Table I-2 shows the initial conditions of the experiments for the two runs referred to in Data Tables I-2 and I-3, respectively.

TABLE I-2. INITIAL CONDITION FOR THE EXPERIMENTAL RUNS

Exp. No.	Temperature C	Initial Pressure atm	Biomass* Feed Rate grams/min.	Biomass* Quantity grams
Data Table I-2 Run No. 1144	800	32.0	16.9	184
Data Table I-3 Run No. 1152	800	52.4	10.1	152

*The biomass used in both runs includes 20 wt% Silica

The biomass feeding times are 11 min. for Data Table I-2 and 12 min. for Data Table I-3. The total conversion of biomass to generated gases in these two runs are 88.5 wt% and 89.6 wt% respectively, based on the remaining char in the reactor at the end of the runs. These results confirm the earlier dilute phase, short residence time flash hydrolysis^(1-2,1-3) where over 90 % conversions were obtained at 800 to 1000 C and 35.0 atm pressure.

The change in the number of moles of gas in the reactor during the run has been calculated from the pressure change and is graphically given in Figure I-6 and I-8. The calculated data include the net molar change of both the generated gases, CO, CO₂, and CH₄ and the hydrogen gas consumed. These calculated data do not accurately indicate the change of the total moles in the gas phase, because water (H₂O) formed in the gases was not measured. However the

data gives some indication of the rate of the reaction. The slope of the change in numbers of moles in the reactor shown in Figure I-6, increases with time more slowly than that shown in Figure I-8. The reaction appears to continue for 30 min. of residence time, which is almost 20 min. after all of the biomass was fed into the reactor. On the other hand, under the condition of 52.4 atm of initial hydrogen atmosphere in Figure I-8, it appears to stop at around 15 min, only 3 min. after completion of feeding the biomass. These results indicate that the hydrogasification is favored by higher hydrogen pressure.

Table I-3 below shows the initial rate of molar change. These data were calculated by taking into account the initial molar change data in each run and dividing by the feed rate of the biomass.

**TABLE I-3. INITIAL RATE OF MOLAR CHANGE
IN THE HYDROLYSIS OF WOOD**

Exp. No.	Molar Change Rate mol/min ram-biomass
Data Table I-2 800 C 32.0 atm	0.012
Data Table I-3 800 C 52.4 atm	0.036

The initial rate of molar numbers change of Data Table I-3 is 3 times as large as that of Data Table I-2, even though the biomass used was smaller than in Data Table I-2. This result also implies that the total pressure of gaseous hydrogen strongly affects the rate of the reaction of biomass.

The gaseous concentrations shown in Data Table I-3 are also higher than those of Data Table I-2; CH₄ concentrations in Data Table I-3 are in the range between 25 and 30 vol%, whereas those in Data Table I-2 are 16 to 20 vol%. As indicated previously, the amount of biomass fed into the reactor in Data Table I-3 is smaller than in Data Table I-2. These results indicate that the higher pressure is more effective in promoting gasification and hydrogasification of biomass.

In both Data Tables I-2 and I-3, the average ratio of the gases generated, CO, CO₂, and CH₄, are approximately 3 : 1 : 3. Taking this ratio, and unreacted carbon of 10 to 15 wt%, into account and performing C, H and O mass balances, the following stoichiometric overall equation for hydropyrolysis of biomass at 800 C is derived.

This equation indicates that hydrogen is generated from the biomass. However, hydrogen is necessary to enhance the formation of CH₄. Taking the sum of the molar number, 0.82 mol/mol-biomass, of gas generated in this equation and the initial rate of molar change cited earlier into account, the initial rate of biomass conversion to gases is determined in Table I-4.

TABLE I-4. INITIAL RATE OF THE BIOMASS CONVERSION

Exp. No.	Initial Rate of Biomass to Gas (1 / min.)
Data Table I-2 800 C 32.0 atm	0.31
Data Table I-3 800 C 52.4 atm	0.92

According to the result of the initial rate from Data Table I-3 at 800 C and 52.4 atm, approximately 92 wt% of the biomass appears to be converted to gases in one minute. For the conditions of Data Table I-2 at 800 C and 32.0 atm, a 31 % per min. conversion rate is obtained. The fact that an increase in pressure by a factor of 2 results in an increase in rate by a factor of 3, indicates the very strong effect of pressure on the rate.

It should be noted that a number of additional runs were made during the course of this work, but the data could not be accurately presented because of operational leaks of gases from the system during the runs.

CONCLUSION

The following conclusions are derived from this work.

- (1) Biomass hydrolysis conversion of 88 through 90 wt% can be obtained at temperature up to 800 C and initial hydrogen pressure of 32.0 and 52.4 atm respectively.
- (2) The initial rate of biomass conversion of 0.31 l/min. is obtained at an initial pressure of 32.0 atm and 800 C, and a higher value of 0.92 l/min. is obtained at the higher pressure of 52.4 atm and 800 C. Hydrogen pressure has a significant enhancing effect on the rate of conversion of biomass to gases.
- (3) Higher temperatures, above 700 C, and rapid heat-up rate enhance the conversion of biomass to CH_4 and CO.
- (4) At low heat-up rate the reaction appears to proceed in two steps: pyrolysis at 300 to 400 C followed by hydrolysis at temperatures up to 700 C or higher.

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- 1-4 R. Khan, Private Communication (August 19, 1991)

TABLE I-5. EXPERIMENTAL DATA FOR THE HYDROGASIFICATION

Hydropyrolysis of biomass Run No. 1154						
November 26, 1991 14: 30 - 17: 00						
Preloaded biomass is heated up in the closed system						
Wood 130 gram preloaded including SiO ₂ 26 grams						
Alumina balls 50 grams						
Hydrogen feed rate 0 m ³ /min.						
Temperature - 800 degree centigrade						
Pressure 52.4- atm						
Time min.	Press atm	Reactor Temperature C	Concentrations of Generated gases			Vol%
			CO	CO ₂	CH ₄	C ₂ H ₆
0	52.4	35				
1	52.4	46				
6	52.4	118				
11	53.0	212				
16	53.5	305				
20	54.4	375				
21	55.7	383				
24	55.6	432				
26	55.6	452				
31	55.6	504				
33			5.2	8.9	0.4	
38	55.7	575				
41	55.7	595	9.7	21.3	0.9	
46	55.7	628	11.0	23.3	1.5	
51	55.7	652				
54			11.6	23.0	3.5	0.4
56	55.6	681				
61	55.7	718				
66	55.7	729				
71	55.6	750	7.8	21.7	12.1	1.8
76	55.6	768	7.0	24.3	18.8	2.8
81	55.6	783				
86	55.6	800				
91	55.6	813				
96	55.6	813				
101	55.6	814				
106	55.6	814	5.6	29.4	25.7	3.4
111	55.6	814				
123	55.4	813				
135	55.3	813				
Residue in the reactor and char trap						
63 grams including 26 grams Silica						
Some water (about 5 cc) remained in the char trap and inside reactor.						

TABLE I-6. EXPERIMENTAL DATA FOR THE HYDROGASIFICATION IN THE RAPID HEATING UP OF THE BIOMASS.

AT 800 C AND AT 32.0 atm OF INITIAL HYDROGEN PRESSURE

Hydrocarb Process Test for Biomass

Run Number 1144

October 21, 1991

Wood 184.8grm

Wood content 80 % SiO2 content 20 %

147.8 grms 36.96 grms

800 C 32.0 atm Biomass Feed Rate 16.9 grms/min.

Residue 54 grms including SiO2 Biomass Conversion 88.5 wt%

Generated Gases				Molar		Total
time	CO	CO2	CH4	Press	Num. Change	Molar Num.
	Volt	Volt	Volt	psig	dn/dt	
				atm	mol/min	mol
0	0	0	0	455 r 31.95	0.0000	0.0000
1				462.5 ave 32.46	0.2448	0.2448
2	19.7	7.1	20.1	470 r 32.97	0.2448	0.4896
3				478 r 33.52	0.2611	0.7507
4				476.5 ave 33.41	-0.0490	0.7017
5	16.4	8.9	16.8	475 r 33.31	-0.0490	0.6528
6				478.5 ave 33.55	0.1142	0.7670
7				482 r 33.79	0.1142	0.8813
8				486 r 34.06	0.1306	1.0118
9				486 r 34.06	0.0000	1.0118
10				488 ave 34.2	0.0653	1.0771
11	16	6	16	490 r 34.33	0.0653	1.1424
12				491 ave 34.4	0.0326	1.1750
13				492 r 34.47	0.0326	1.2077
14				497.5 ave 34.84	0.1795	1.3872
15	16.2	4.4	17.5	503 r 35.22	0.1795	1.5667
16				506 ave 35.42	0.0979	1.6646
17				509 ave 35.63	0.0979	1.7625
18	18.5	7.2	18.8	512 r 35.83	0.0979	1.8604
19				514 ave 35.97	0.0653	1.9257
20				516 r 36.1	0.0653	1.9910
21				519 ave 36.31	0.0979	2.0889
22				522 r 36.51	0.0979	2.1868
23				526 ave 36.78	0.1306	2.3174
24				530 r 37.05	0.1306	2.4480
25				532 ave 37.19	0.0653	2.5132
26				534 r 37.33	0.0653	2.5785
27				536 ave 37.46	0.0653	2.6438
28				538 ave 37.6	0.0653	2.7091
29	24	7.7	26.8	540 r 37.73	0.0653	2.7744
30				541 ave 37.8	0.0326	2.8070
31				542 r 37.87	0.0326	2.8396
32				542 ave 37.87	0.0000	2.8396
33				542 r 37.87	-0.0000	2.8396
34				540 ave 37.73	-0.0653	2.7744
35	16.4	5.1	18.6	538 r 37.6	-0.0653	2.7091
36				536.5 ave 37.5	-0.0490	2.6601
37				535 ave 37.39	-0.0490	2.6112
38				533.5 ave 37.29	-0.0490	2.5622
39				532 r 37.19	-0.0490	2.5132
40				531.4 ave 37.15	-0.0196	2.4937
41				530.8 ave 37.11	-0.0196	2.4741
42				530.2 ave 37.07	-0.0196	2.4545
43				529.6 ave 37.03	-0.0196	2.4349
44				529 r 36.99	-0.0196	2.4153
45				528.2 ave 36.93	-0.0261	2.3892
46				527.4 ave 36.88	-0.0261	2.3631
47				526.6 ave 36.82	-0.0261	2.3370
48				525.8 ave 36.77	-0.0261	2.3109
49				525 r 36.71	-0.0261	2.2848
50				522.8 ave 36.57	-0.0707	2.2140
51				520.7 ave 36.42	-0.0707	2.1433
52				518.5 ave 36.27	-0.0707	2.0726
53				516.3 ave 36.12	-0.0707	2.0019
54				514.2 ave 35.98	-0.0707	1.9312
55				512 r 35.83	-0.0707	1.8604
56				500.7 ave 35.06	-0.1699	1.4905
57				489.3 ave 34.29	-0.1699	1.1206
58				478 r 33.52	-0.1699	0.7507

TABLE I-7. EXPERIMENTAL DATA FOR THE HYDROGASIFICATION IN THE RAPID HEATING UP OF THE BIOMASS.

AT 800 C AND AT 52.4 atm OF INITIAL HYDROGEN PRESSURE

Hydrocarb Process Test for Biomass

Run number 1152

November 18, 1991

Wood 152 grms

Wood content 80 % and SiO2 20 %

121.6 grms

30.4 grms

800 C 52.4 atm

Wood Feed Rate

10.1 grms/min.

Residue

43grms including SiO2

Biomass Conversion 89.6wt%

Generated Gases				Molar		Total	
time	CO	CO2	CH4	Press	Press	Num.Change	Molar Num.
	Vol%	Vol%	Vol%	psig	atm	dn/dt	
						mol/min	mol
0	0	0	0	755	52.36	0.0000	0.0000
1				769	53.31	0.4570	0.4570
2				776	53.79	0.2285	0.6855
3				779	53.99	0.0979	0.7834
4				780	54.06	0.0326	0.8160
5				783	54.27	0.0979	0.9139
6				784	54.33	0.0326	0.9466
7				786	54.47	0.0653	1.0119
8				788	54.61	0.0653	1.0771
9				791.5	54.84	0.1142	1.1914
10				795	55.08	0.1142	1.3056
11				800	55.42	0.1432	1.4688
12				804	55.69	0.1306	1.5994
13				807	55.90	0.0979	1.6973
14				809	56.03	0.0653	1.7626
15				811	56.17	0.0653	1.8279
16				812	56.24	0.0326	1.8605
17				811.5	56.20	-0.0163	1.8442
18				811	56.17	-0.0163	1.8279
19				810.5	56.14	-0.0163	1.8116
20				810	56.10	-0.0163	1.7952
21				809.5	56.07	-0.0163	1.7789
22				809	56.03	-0.0163	1.7626
23				808.5	56.00	-0.0163	1.7463
24	33.4	14.7	29.5	808	55.97	-0.0163	1.7300
25				807.5	55.93	-0.0163	1.7136
26				807	55.90	-0.0163	1.6973
27				806.5	55.86	-0.0163	1.6810
28				806	55.83	-0.0163	1.6647
29				806	55.83	0.0000	1.6647
30				806	55.83	0.0000	1.6647
31				806	55.83	0.0000	1.6647
32				806	55.83	0.0000	1.6647
33				806.5	55.86	0.0163	1.6810
34	26	8.4	24.9	807	55.90	0.0163	1.6973
35				806.75	55.88	-0.0082	1.6892
36				806.5	55.86	-0.0082	1.6810
37				806.25	55.85	-0.0082	1.6728
38	25.7	8.1	28.6	806	55.83	-0.0082	1.6647
39				805.33	55.78	-0.0218	1.6429
40				804.67	55.74	-0.0218	1.6212
41				804	55.69	-0.0218	1.5994
42				804.25	55.71	0.0082	1.6076
43				804.5	55.73	0.0082	1.6157
44				804.75	55.74	0.0082	1.6239
45				805	55.76	0.0082	1.6320
46				805	55.76	0.0000	1.6320
47				805	55.76	0.0000	1.6320
48				805	55.76	0.0000	1.6320
49				804.67	55.74	-0.0109	1.6212
50				804.33	55.72	-0.0109	1.6103
51				804	55.69	-0.0109	1.5994
52				804.5	55.73	0.0163	1.6157
53				805	55.76	0.0163	1.6320
54				804.8	55.75	-0.0065	1.6255
55				804.6	55.73	-0.0065	1.6190
56				804.4	55.72	-0.0065	1.6125
57				804.2	55.71	-0.0065	1.6059
58				804	55.69	-0.0065	1.5994

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FIGURE I-1. Schematic Flow Sheet of Tubular Reactor Equipment.

Hydropyrolysis of Biomass

FIGURE I-2. Reactor Temperature, Generated Gases, vs. Lapse of Time at 52.4 atm, 100% hydrogen of the beginning pressure

FIGURE I-3. Pressure Change in Reactor vs. Reactor Temperature.

FIGURE I-4. Weight Losing Curve of Biomass (Poplar Wood) with Temperature using PTGA (Pressurized Thermogravimetric Analyzer) at Heat-up Rate of 50 C/min. and 28.2 atm.

FIGURE I-5. Weight Losing Curve of Biomass (Fir Wood) with Temperature using PTGA (Pressurized Thermogravimetric Analyzer) at Heat-up Rate of 50 C/min. and 28.2 atm.

Hydropyrolysis of Biomass

Figure I-6. The Change in Number of Moles in the Reactor with Time at 800 C and 32.0 atm of Initial Hydrogen Pressure.

Run No. 1144 - Data Table I-2

Figure I-7. The Rate of Molar Change with Time at 800 C and 32.0 atm of Initial Hydrogen Pressure.

Run No. 1144 - Data Table I-2

Hydropylorysis of Biomass

Figure I-8. 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 - Data Table I-7

Figure I-9. The Rate of Molar Change with Time at 800 C and 52.4 atm of Initial Hydrogen Pressure.

Run No. 1152 - Data Table I-7

Part II

THE THERMAL DECOMPOSITION OF METHANE IN A TUBULAR REACTOR

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The Thermal Decomposition of Methane in a Pressurized Tubular Reactor

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ABSTRACT

The reaction rate of methane decomposition using a tubular reactor having a 25.4 mm inside diameter with a 2.44 m long heated zone was investigated in the temperature range of 700 to 900 C with pressures ranging from 28.2 to 56.1 atm. Representing the rate by a conventional model, $-dC_{CH_4}/dt = k_1 C_{CH_4} - k_2 C_{H_2}^2$, the rate constant k_1 for methane decomposition was determined. The activation energy, 31.3 kcal/mol, calculated by an Arrhenius Plot was lower than for previously published results for methane decomposition. This result indicates that submicron particles found in the reactor adhere to the inside of the reactor and these submicron high surface area carbon particles tend to catalyze the methane decomposition. The rate constant has been found to be approximately constant at 900 C with pressure range cited above. The rate of methane decomposition is first-order with respect to methane partial pressure. The rate of the methane decomposition is favored by higher temperatures and pressures while the thermochemical equilibrium of methane decomposition is favored by lower pressures.

INTRODUCTION

The Hydrocarb Process^(II-1) consists of the two main reactions; (1) hydrogasification of the carboneous feedstock to produce a methane-rich gas and (2) the thermal decomposition of methane to produce carbon black and a hydrogen-rich gas. The section on methane decomposition is especially important in order to maintain high efficiency in the process. A key element in the process is that the hydrogen-rich gas produced in the methane decomposition reactor is recycled to the hydrogasification reactor as the reactant gas. Furthermore, the product carbon black is produced in the methane decomposition section.

This work was performed in order to investigate the phenomena of methane decomposition and to obtain data on the kinetics of the reaction for the purpose of designing the methane decomposition reactor.

CHEMICAL EQUILIBRIUM

Since the methane decomposition is endothermic, the methane concentration decreases with increasing temperature. Due to the increase of volume during methane decomposition, the decomposition of methane is favored by decreasing pressure.

Figure II-1 shows the equilibrium data of the methane at temperature from 600 to 1200 C and at pressures of 25, 30, 40, and 50 atm. These data are calculated from the following Gibbs Free Energy and equilibrium constant.

$$R T \ln K_x = -dG \quad (2)$$

$$K_x = X_{\text{H}_2}^2 / X_{\text{CH}_4} \quad (3)$$

where X is the mol fraction of each gaseous component, and

$$K_p = (P_{\text{H}_2})^2 / P_{\text{CH}_4} \quad (4)$$

where p is the partial pressure of each component

EXPERIMENTAL DESCRIPTION

Figure II-2 shows the schematic flow sheet of the experimental equipment which mainly consists of a tubular reactor, a carbon trap, a gas-chromatograph and gas meter. Methane enters the system through a remotely controlled regulator located next to the methane cylinders which keeps the pressure approximately constant at selected pressure of 28.2, 41.8 or 56.1 atm in the system. Methane then flows through a preheater and enters the reactor which consists of a 25.4 mm inside diameter by 6.35 mm wall Inconel 617 tube. The total length of the reactor tube is 3.35 m of which the first 2.44 m is externally heated and selectively maintained at constant experimental temperatures of 700, 800 and 900 C by clamshell electric heaters. Methane is decomposed into carbon and hydrogen in the heated reactor and the effluent gas flows through the carbon trap connected at the bottom of the reactor, where the carbon generated by the reaction is separated. Gas is sampled before and after the reactor and analyzed by an on-line gas-chromatograph which measures the concentrations of CH_4 , CO, and CO_2 in the gas by a thermal conductivity detector. The flow rate of exit gas is controlled in the range between 10 and 150 liters/min. by a flow valve located after the reactor. The exit gas flows through the gas meter where the flow rate is measured and the gas is finally vented to the atmosphere.

EXPERIMENTAL RESULT AND DISCUSSION

Table II-1 shows the results of the data for the experimental runs to measure the conversion of methane into hydrogen and carbon at 700, 800, and 900 C and at 56.1, 41.8 and 28.2 atm. Figure II-3 shows the relationship between the methane concentrations in exit gas and residence time in the reactor under these conditions. The residence time of the methane gas in the reactor is given by the inlet gas velocity. The concentration of the methane decreases with increasing temperature and residence time. At both 700 and 800 C and at 56.1 atm the concentration of methane decreases less with residence time than that at 900 C and 56.1 atm. Under the latter conditions, the concentration of methane decreases dramatically with residence time and appears to be approaching equilibrium conditions. The concentration of methane at a residence time of 103 seconds was 48.1 vol%, and in this case the equilibrium concentration of the methane is 39.6 vol%.

The equilibrium data at the lower temperatures of 700 and 800 C and at 56.1 atm are 54.3 and 69.3 vol% respectively and higher than that at 900 C. Taking these conditions into account and considering the curves of methane decomposition in Figure II-3, the rate of methane decomposition in the lower temperature range seems to be much smaller than that at the higher temperature of 900 C.

Generally the equation for the rate of decomposition of methane is derived as follows:

where k_1 is the rate constant of methane decomposition, and k_2 is the rate constant of methane formation.

The rate equation for this reversible reaction can be written as follows:

$$\begin{aligned} -r_{\text{CH}_4} &= -dC_{\text{CH}_4} / dt = k_1 C_{\text{CH}_4} - k_2 C_{\text{H}_2}^2 \\ &= k_1 C_{\text{CH}_4} \left(1 - 1 / K_e \times C_{\text{H}_2}^2 / C_{\text{CH}_4} \right) \end{aligned} \quad (6)$$

where C_{CH_4} , C_{H_2} are the molar concentrations of CH_4 and H_2 respectively.

The above differential equation for methane decomposition in the tubular reactor is solved for the condition of $C_{H_2O} = 0$ (initial concentration of hydrogen is 0), for inlet methane concentration C_{CH_4O} , exit methane concentration C_{CH_4} and equilibrium concentration of methane C_{CH_4E} . Figure II-4 shows a model of the tubular reactor and the derivation of the following rate equation.

$$k_1 \times t = \frac{C_{CH_4O} - C_{CH_4E}}{C_{CH_4O} + C_{CH_4E}} \ln \frac{C_{CH_4O}^2 - C_{CH_4} \times C_{CH_4E}}{C_{CH_4O} \times (C_{CH_4} - C_{CH_4E})} \quad (7)$$

where t is the residence time

Table II-2 shows the calculated data of inlet, outlet and equilibrium concentrations of methane, inlet flow rate, and $k_1 \times t$ values. Figure II-5 shows the relationship between $k_1 \times t$ value versus residence time at 700, 800, and 900 C and at 56.1 atm. Each slope in the Figure 5 indicates a rate constant k_1 of the methane decomposition at each temperature. Table II-3 represents the k_1 value at these conditions.

TABLE II-3. RATE CONSTANTS AT 56.1 ATM

Temperature	k_1 value
700 C	5.758E-4 1/sec
800 C	1.753E-3 1/sec
900 C	9.306E-3 1/sec

In Figure II-6, the rate constants, k_1 , for methane decomposition are plotted versus reciprocal temperature. From this Arrhenius plot an activation energy for methane decomposition and the rate constant k_1 are calculated as follows;

$$E = 31.3 \text{ kcal/mol}$$

$$k_1 = 5.4 \times 10^3 \exp(-E/RT) \quad 1/\text{sec} \quad (8)$$

The activation energy appears to indicate a diffusion controlled process which usually has values up to about 30 kcal/mol as opposed to a chemical reaction controlled process which has much higher activation energies ranging above 50 kcal/mol. From the limited methane

decomposition data in the literatures,^(II-2,3,4,5, and 6) the homogeneous activation energy for methane decomposition is determined to be 65 kcal/mol. The data gathered in these experiments appear to be influenced by a heterogeneous effect of surfaces. During our experiments some of the carbon formed from methane decomposition adhered to the walls of the Inconel high alloy steel of the tubular reactor. In fact, at the end of several extended runs, it was found that the carbon plugged the tube to the extent that it restricted the gas flow. Thus, the fine sub-micron carbon particles could tend to catalyze the thermal decomposition of the methane. References 7 and 8 clearly indicate that different materials increase the rate of the methane decomposition in the order of iron oxide, alumina, graphite, and quartz. In the tubular reactor the small submicron particle size of the carbon presents a very large surface area on which methane can decompose and thus a lower activation energy for decomposition results.

The influence of the total pressure in this system on the rate constant of the methane decomposition was investigated because the Hydrocarb Process is being operated under pressure and it is important to determine the influence of the total pressure on the reaction rate. Figure II-7 shows the relationship between the $k_1 \times t$ value and residence time at 28.2, 41.8, and 56.1 atm at 900 C. The slopes in Figure II-7 represent the rate constants k_1 at their respective conditions. These values are calculated and listed in Table II-4.

TABLE II-4. RATE CONSTANTS AT 900 C

Pressure	k ₁ value	
28.2 atm	1.066E-2	1/sec
41.8 atm	1.380E-2	1/sec
56.1 atm	9.036E-3	1/sec

average rate constant 1.126E-2 1/sec

Although there is not enough data to establish a relationship with pressure, the rate constant appears to be really independent of pressure. The variation in the rate constant with pressure is probably within the deviation in the experimental measurements for this type of equipment.

Some other studies to obtain the rate data of carbon formation from methane on silicate substrate indicate that the rate increased in first-order with pressure up to 15 atm.^(II-2) The rate equation (6) modelled in this paper indicates that since the methane molar concentration is first-order in pressure, the result that the rate constant is constant and independent of pressure is in accord with other published results; and the rate of the methane decomposition indeed increases with partial methane pressure approximately in first-order. The thermochemical equilibrium for methane decomposition is favored by lower pressures, but as our results indicate, the rate is favored by higher pressure.

CONCLUSION

The influence of the temperature and total pressure on the rate of the methane decomposition has been determined by using a tubular reactor assembly. The following results and conclusions were obtained.

(1) A model for methane decomposition was developed, which resulted in the following rate equation;

$$\begin{aligned} -r_{\text{CH}_4} &= -dC_{\text{CH}_4} / dt = k_1 C_{\text{CH}_4} - k_2 C_{\text{H}_2}^2 \\ &= k_1 C_{\text{CH}_4} \left(1 - 1 / k_e \times C_{\text{H}_2}^2 / C_{\text{CH}_4} \right) \end{aligned}$$

k_1 value was calculated as follows;

$$k_1 \times t = \frac{C_{\text{CH}_4\text{O}} - C_{\text{CH}_4\text{E}}}{C_{\text{CH}_4\text{O}} + C_{\text{CH}_4\text{E}}} \ln \frac{C_{\text{CH}_4\text{O}}^2 - C_{\text{CH}_4} \times C_{\text{CH}_4\text{E}}}{C_{\text{CH}_4\text{O}} \times (C_{\text{CH}_4} - C_{\text{CH}_4\text{E}})}$$

An Arrhenius Plot of the k_1 values resulted in the following rate constant equation.

$$k_1 = 5.4 \times 10^3 \exp (-31.3 \text{ kcal/RT }) \quad 1/\text{sec}$$

The activation energy appears to indicate a diffusion controlled process most likely influenced by the high surface area of the submicron carbon particles deposited in the reaction zone.

(2) Although a definitive influence of the total pressure on the rate constant of the methane decomposition could not be clearly determined, at 900 C, within experimental error, the rate constant appears to be constant and independent of pressure in the range of 28.1 to 56.1 atm. Taking into account the rate equation modelled in this paper, the rate of decomposition is influenced by the methane partial pressure to the first-order. Taking into account these results together with literature data, the conclusion is reached that although the thermochemical equilibrium decomposition of methane is favored by lower pressure, the rate of methane decomposition is favored by higher pressure.

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Figure II-1. Schematic Flow Sheet of Tubular Reactor for Methane Decomposition.

TABLE II-1. EXPERIMENTAL DATA OF METHANE DECOMPOSITION

Run Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature centigrade	900	900	900	900	800	800	800	700	700	700	900	900	900	900	900	900
Pressure atm	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	28.2	28.2	28.2	41.8	41.8	41.8
Methane concentration in inlet gas vol%	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Exit gas flow rate at standard condition liters / min. (25°C, 1 atm)	54.34	30.24	21.89	13.85	50.57	20.6	14.89	56.63	26.96	15.06	65.58	16.53	17.25	149.0	86.99	27.24
Residence time sec. based on inlet gas flow rate	21.8	42.3	60.5	103.0	23.7	58.9	83.6	22.8	48.3	86.8	8.94	16.8	37.0	5.54	10.3	35.7
Methane concentration in exit gas vol%	78.6	65.4	59.7	48.1	92.6	89.8	85.7	97.4	95.7	95.0	81.2	72.7	66.4	90.8	75.5	61.8
Methane conversion %	10.7	17.3	20.2	26.0	3.7	5.1	7.2	1.3	4.3	2.5	9.4	13.7	16.8	4.6	12.3	19.1

TABLE II-2. CALCULATED DATA OF METHANE DECOMPOSITION

Run Number	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Temperature Centigrade	900	900	900	900	800	800	800	700	700	700	900	900	900	900	900	900
Pressure atm	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	56.1	28.2	28.2	28.2	41.8	41.8	41.8
Methane concentration in inlet gas vol%	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Inlet gas flow rate liters / min. at environmental condition	3.40	1.75	1.23	0.72	3.12	1.26	0.89	3.25	1.53	0.85	8.29	4.40	2.00	13.4	7.19	2.07
Residence time sec. based on inlet gas flow rate ^{a1}	21.8	42.3	60.5	103.0	23.7	58.9	83.6	22.8	48.3	86.8	8.94	16.8	37.0	5.54	10.3	35.7
Inlet methane conc. C _{CH₄} mol/liter	0.583	0.583	0.583	0.583	0.637	0.637	0.637	0.703	0.703	0.703	0.293	0.293	0.293	0.434	0.434	0.434
Exit methane conc. C _{CH₄} mol/liter	0.458	0.381	0.348	0.280	0.590	0.572	0.546	0.684	0.672	0.668	0.238	0.213	0.195	0.394	0.328	0.268
Equilibrium conc. C _{CH₄} mol/liter	0.231	0.231	0.231	0.231	0.346	0.346	0.346	0.487	0.487	0.487	0.083	0.083	0.083	0.150	0.150	0.150
k ₁ x t ^{a2} (-)	0.246	0.457	0.578	0.976	0.073	0.109	0.158	0.026	0.044	0.052	0.210	0.325	0.423	0.097	0.288	0.516

a1: Reactor Volume 1.236 liters

a2: $k_1 \times t = \frac{C_{CH_4O} - C_{CH_4E}}{C_{CH_4O} + C_{CH_4E}} \ln \frac{C_{CH_4O} - C_{CH_4} \times C_{CH_4E}}{C_{CH_4O} (C_{CH_4} - C_{CH_4E})}$

Equilibrium Data of Methane

Figure II-2. Equilibrium Data of Methane.

Methane Concentrations with Time

Figure II-3. Methane Concentration vs. Residence Time.

Tubular Reactor Model

Mass Balance of A component

$$F_a = F_a + dF_a + (-r_A) \times dV$$

$$-dF_a = (-r_A) \times dV$$

$$F_a = F_{ao} \times (1 - X_A)$$

$$dV/F_{ao} = dX_A/(-r_A)$$

$$F_{ao} = Q_o \times C_{ao}$$

$$dV/Q_o = C_{ao} \times dX_A/(-r_A)$$

$$dV/Q_o = dt$$

$$C_a = C_{ao} \times (1 - X_A)$$

$$-dC_a/dt = -r_A$$

F_a : molar velocity (mol/sec)

Q : volume velocity (liters/sec)

C_a : concentration of A component (mol/liter)

X_A : degree of conversion of A component (-)

Subscript o : initial condition

Reaction Rate Model

$$-r_{\text{CH}_4} = -dC_{\text{CH}_4}/dt = k_1 \times C_{\text{CH}_4} - k_2 \times C_{\text{H}_2}^2$$

initial condition

$$\text{at } t = 0 \quad C_{\text{H}_2} = 0$$

$$\text{at equilibrium} \quad -dC_{\text{CH}_4}/dt = 0$$

solution of differential equation

$$k_1 \times t = \frac{C_{\text{CH}_4 0} - C_{\text{CH}_4 E}}{C_{\text{CH}_4 0} + C_{\text{CH}_4 E}} \ln \frac{C_{\text{CH}_4 0}^2 - C_{\text{CH}_4} \times C_{\text{CH}_4 E}}{C_{\text{CH}_4 0} \times (C_{\text{CH}_4} - C_{\text{CH}_4 E})}$$

k_1 : methane consumption rate constant (1/sec)

k_2 : methane production rate constant (liter/sec/mol)

t : residence time (sec)

$C_{\text{CH}_4 0}$: methane initial concentration (mol/liter)

C_{CH_4} : methane concentration of outlet (mol/liter)

$C_{\text{CH}_4 E}$: methane equilibrium concentration (mol/liter)

Figure II-4. Tubular Reactor Model and Derivation of Rate Equation.

Figure II-5. $k_1 \times T$ vs. Residence Time at 700 to 900°C and 56.1 atm.

Arrhenius Plot

Figure II-6. Rate Constant of Methane Decomposition vs. Recipical Temperature.

Figure II-7. $k_1 \times t$ vs. Residence Time at 900°C and 28.2 to 56.1 atm.

Part III

**DESIGN ANALYSIS OF THE HYDROCARB PROCESS
WITH ALTERNATIVE AND MULTIPLE FEEDSTOCKS**

by

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Design Analysis of the Hydrocarb Process With Alternative and Multiple Feedstocks

by

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ABSTRACT

The designed 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 (sub-bituminous) coal, Kentucky (Bituminous) coal, North Dakota (lignite) coal and Wyodak (sub-bituminous) coal. A Process Simulation Computer Model was used to design the process, and obtain complete energy and mass balances. Boundary conditions of pressure, temperature and mass balances for the cyclical process were determined. 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 maximum allowable feed ratios of sludge to biomass or sludge to coal were determined. The effect of pressure and temperature for the biomass and sludge feedstock cases were also developed.

INTRODUCTION

In our previous report,^(III-1) an analysis was performed for the Hydrocarb Process to produce methanol and carbon black from biomass (wood) with methane (natural gas) as co-feedstock. The effects of different types of reactors, different process configurations (flowsheet arrangements), as well as operating conditions on process efficiency and product distribution were studied by using the Hydrocarb Process Simulation Program (HCSP) based on the thermodynamic equilibrium in the ternary system C-H-O. The following conclusions were reached in the previous study:

(1) In order to process wood feedstock, methane should be added into the system as required by the stoichiometry. The minimum required methane depends upon the cycle (process configuration) and reactor type used.

(2) A fluidized bed reactor can simplify the procedure for mixing and separation of different kinds of solids, and, therefore, is recommended for use in the Hydrocarb Process.

(3) Cycle 1 is defined as the process configuration in which the hydropyrolyzer (HPR) output is led to the methane pyrolyzer (MPR), and then to the methanol Synthesis reactor (MSR). Cycle 1 usually provides a higher methanol yield than Cycle 2 in which the configuration is HPR to MSR to MPR. Also Cycle 2 requires two heat exchangers whereas Cycle 1 needs only one.

(4) The reaction temperature in the HPR may be controlled by adjusting the temperature of the process gas into the reactor.

Although the previous report has gained some insight into the main features of the Hydrocarb Process, particularly for the case where wood is used as a feedstock, more work was needed to explore the feasibility of using alternative feedstocks and multiple feedstocks.

Furthermore, Steinberg^(III-2,III-3) indicated that the use of biomass through photosynthesis in combination with Hydrocarb Process can offer a solution to the global greenhouse problem, utilizing biomass as a co-feedstock with fossil fuel to produce methanol while

sequestering the carbon can significantly reduce and even eliminate CO₂ greenhouse gas emissions to the atmosphere.

A pilot plant project, treating 22.7 kg/hr of sludge and municipal solid waste (MSW) together with methane to produce methanol and carbon black, has been proposed and is being conducted in California.⁽⁴⁾ Our preliminary calculation showed that the sludge can not be utilized alone to make up heat balance in the HPR due to its very low heating value. Thus, multiple feedstocks have to be considered. This requires an investigation of multi-feedstock utilization in the Hydrocarb Process.

According to a proposal^(III-4) by Acurex Corporation to the South Coast Air Quality Management District (SCAQMD), a typical water quality control plant, where a Hydrocarb may be built, treats about 113,562 m³ per day of wastewater. It provides 28 tons/day of dried sludge (90% solids content) and, at the same time, produces 13.3 tons/day of digester gas. The latter contains 61.2 mol% CH₄ and 37.5 mol% CO₂. The question consequently raised here is whether this digester gas can be fed into the process instead of pure pipeline methane.

To meet the above challenge, our program has been extended to treat the case where we can co-feed as many different feedstocks as we wish including digester gas.

In the present study, the following topics are investigated:

(1) Feasibility of using alternative feedstocks:

Kentucky Coal, Alaska Beluga Coal, North Dakota Coal, and Wyodak Coal have been chosen for this study, because they range over a wide variety of ranks and from different locations;

(2) Co-feeding Biomass with Kentucky Coal;

(3) Utilization of sludge and digester gas;

(4) Effects of heat sources for operating the MPR on the process efficiency; and

(5) Pressure and temperature effects on process efficiency.

BASIC DATA AND DEFINITION

Table III-1 lists the basic data of different feedstocks used in this analysis. It should be noted that the heating value here is provided in both English and Metric Units on a dry basis, while the heat of formation is expressed on a moisture and ash free basis.

For each set of feedstocks, both Cycle 1 and Cycle 2 were calculated and compared to each other. Brief flowsheets of Cycle 1 and Cycle 2 are illustrated in Figure III-1. Our previous report^(III-1) gives a detailed description of these cycles. In Cycle 1, the process gas at 1000 C from the MPR is cooled down by a gas heat exchanger to around the reaction temperature of the methanol convertor, and this recovered energy is used in the heat exchanger to heat the process gas from the condensers at 50 C up to about the HPR's temperature. When an energy balance is performed, the temperature of process gas into the HPR, T_7 , is so determined that the reaction heat generated in the HPR is just balanced by the enthalpy difference of inlet and outlet streams. The temperature of process gas into the MSR, T_5 , is then calculated by the heat balance around the gas heat exchanger. In Cycle 2, two gas exchangers are used as shown in Figure III-1. One exchanger is to cool the gas stream from the temperature of the HPR to the temperature of the MSR by heating up the gas stream coming from the condensers. Before entering the MPR, the process gas is further heated in the second gas heat exchanger by the hot gas stream from the MPR. In this case, the calculation is made to first determine T_7 by balancing the heat load of the HPR to be zero. Then, T_6 and T_8 , the temperatures of gas leaving the two heat exchangers can be calculated respectively from the heat balances of the two heat exchangers.

All calculations were made based on the use of fluidized beds for the HPR and the MPR.

The heat source for the MPR could be any of the following fuels: (1) the residual char discharged from the HPR, (2) purge gas discharged from the recycle stream after the condensers, and (3) additional natural gas or solid fuel including any type of coal and biomass. In this study, two cases were investigated: one for burning char, off gas and biomass or digester gas

or fossil fuel; and another for burning off gas and natural gas only without using solid fuel in the combustor.

The carbon conversion of any solid feedstock in the HPR was assumed to be 90%. This may lead to a conservative estimate for wood conversion because of its higher reactivity in the hydrogasifier.

Except for those runs made for investigating the effects of operating conditions, the system pressure was chosen to be 50 atm and the temperatures for the HPR and MPR were 900 and 1000 C respectively. The choice of temperature of 900 C for operation of the HPR is to ensure the effectiveness of sulfur removal with the use of limestone and dolomite. The MPR temperature was chosen by consideration of the state of the art for limitation of the materials of construction. The temperature of the methanol convertor is assumed to be 260 C and the condenser is operated at 50 C. Preliminary calculation showed that these conditions resulted in a satisfactorily high process efficiency (70-80%).

All calculations were made on a capacity basis of 100 tons per calendar day of the major solid feedstock. The actual feed rate into the HPR is equal to the above capacity divided by the operating factor which is assumed to be 90%. Therefore, for a 100 tons per calendar day plant of an as-received coal, for instance, the feed rate of this feedstock into the HPR is $100/0.9 = 111.1$ tons/day or 4629.6 kg/h if no drying is needed before feeding into the HPR.

When a single solid feedstock was tested, the strategy of calculation is shown in Figure III-2. First of all, an as-received (AR) undried feedstock is tried to see whether a material and energy balance can be achieved. If the answer is positive, then feeding additional water into the HPR may be tried until a maximum allowable value of additional water is found. If the balance can not be made for the AR feedstock, two approaches may be tried depending on whether the material balance or the energy balance is in question. If the material balance fails, co-feeding some methane into the HPR may be the way to make up the balance. A minimum CH_4 requirement is then calculated. However, CH_4 has little effect on the heat load of the

HPR. Thus, if the HPR is endothermic in spite of adjusting the temperature of the inlet gas, drying the feedstock may be necessary and the calculation then is aimed at obtaining the maximum allowable moisture of feedstock. In some cases, both adding methane and drying feedstock may be needed to obtain a workable cycle.

When multiple feedstocks are investigated, and sludge is used as one of the feedstocks, the digester gas is always assumed as a co-feedstock. Considering its availability in the Riverside Water Quality Sewage Plant in California, the weight ratio of digester gas to sludge was set as 0.5. The calculations were aimed at obtaining a maximum allowable sludge feed rate.

In the calculation, limestone feed rate is determined by assuming a molar ratio of Ca to S of 2. The composition of CaCO_3 in limestone is assumed to be 70%, and the rest being ash.

RESULTS AND DISCUSSION

SINGLE SOLID FEEDSTOCK

Alaska Beluga (Sub-Bituminous) Coal:

Table III-2 shows that, for Cycle 1, as-received (AR) Beluga coal has to be dried from 21.76% of moisture to 11% before it can be fed into the HPR in order to obtain material and energy balances. If the coal is directly used without drying, there would be a minimum requirement for methane co-feedstock at a ratio of 5 wt.% to the as-received Beluga coal. Since the water may react with carbon to form CO, the use of the as-received Beluga coal greatly increases the methanol production and improves the methanol ratio in the product streams. The latter case also showed about a 2% higher thermal efficiency compared to the drying case. It is also found in most of the calculations that, if the residual char discharged from the HPR is used together with other heat sources for the MPR, it reduces the consumption of other fuels for combustion and provides an increase of about 5% in thermal efficiency. A comparison of the results of Cycle 1 with Cycle 2 for Beluga coal shows that Cycle 2 can directly use as-received Beluga coal without the need to dry the coal. Furthermore, additional water is allowable for feeding into the HPR with as-received coal. The gas circulation for Cycle 2 is relatively less than that for Cycle 1. However, Cycle 2 usually produces more carbon and less methanol in comparison with Cycle 1, and its thermal efficiency is lower.

Kentucky (Bituminous) Coal:

It was found from Table III-2 that, when as-received Kentucky coal is used alone as a single solid feedstock, the material and energy balances can be established for both Cycle 1 and Cycle 2. For Cycle 1, an additional amount of water can be co-fed into the HPR at a maxi-

mum allowable content of 29 wt.% of the as-received Kentucky coal according to the material and energy balance. For Cycle 2, the allowable additional water is as high as 67 wt.% of the coal. The addition of the water for Cycle 1 improves the thermal efficiency (the ratio of the total heating value of carbon and methanol to the total heating value of feedstocks and methane), however, its effect in Cycle 2 is the reverse. The gas circulation rate appears higher than when Beluga coal is used. The thermal efficiency for Cycle 2 is better than for Cycle 1 if as-received Kentucky coal is used alone.

North Dakota (Lignite) Coal:

Table III-2 shows that neither Cycle 1 and Cycle 2 can use North Dakota lignite alone without drying. For Cycle 1, in addition to drying the coal from 30.1 wt% moisture to 5 wt%, a minimum methane feed rate of 2 wt.% of the coal has to be co-fed into the HPR; for Cycle 2, the coal is required to be dried down to only 15 %. Cycle 2 gives a 5 % lower thermal efficiency than Cycle 1.

Wyodak (Sub-Bituminous) Coal:

The results in Table III-2 indicate that Wyodak coal also needs drying when it is fed alone into the HPR for Cycle 1. The maximum allowable moisture in this case is 13 wt.%. For Cycle 2, however, as-received Wyodak coal can be used. The results also show that the maximum additional water rate is 7 wt.% of the coal for Cycle 2. Residual char burning may raise the thermal efficiency by an additional 4-5%, which is essentially similar to the results obtained for other feedstocks.

Biomass (Wood):

The calculated results for wood feedstock, as listed in Table III-2, show the necessity of co-feeding methane for both Cycles when as-received wood is directly fed into the HPR.

The required minimum methane feed rate is 15 wt.% of the as-received wood for Cycle 1; while Cycle 2 needs a methane rate of only 6 wt.%. It can be seen that, in general, the product ratio (methanol/pure carbon) for wood as feedstock is relatively higher, and more methanol and less carbon black are produced in comparison with other feedstocks. It also shows that Cycle 1 has a higher thermal efficiency than Cycle 2.

The computer printout for Cycle 1 under 100 tons per calendar day of wood and 15 tons per calendar day of methane feed rate conditions is shown in Appendix III-1. Figure III-3 summarizes the flow rates, compositions and temperatures of the major streams in the system. After purging a small amount of off-gas (3 kgmol/hr) for use with other fuels (char, biomass and methane) to heat up the MPR, the temperature of the remaining process gas of 2170 kgmol/hr from the condenser is raised up to 927 C by the gas heat exchanger to meet the requirement of a neutral energy balance around the HPR. In the gas heat exchanger, the heat is provided by recovering the energy from the process gas at 1000 C leaving the MPR. The calculated temperature of the hot gas stream leaving the heat exchanger is 257 C which then enters the methanol converter. The residual char of 212 kg/hr is discharged from the HPR and is then burned in the combustor together with the 3 kmol/hr of off-gas and 1546 kg/hr of wood to provide the heat required by the endothermic reactions in the MPR. Thus, the total wood consumption for producing 3192 kg/hr of methanol and 1222 kg/hr of carbon black is 6176 kg/hr, of which about one fourth is used for combustion. The use of wood as fuel is desirable because it is produced by photosynthesis and its net CO₂ emission is zero.

MULTIPLE-FEEDSTOCKS WITH SEWAGE SLUDGE AND DIGESTER GAS

Since sludge has quite a low heating value, in order to maintain a desired temperature in the HPR, the utilization of sludge has to be accompanied by biomass and/or other fossil fuel. In this study, wood, Kentucky coal and Wyodak coal are used as co-feedstock with sludge respectively to calculate the possible maximum capacity of sludge. The feed rate of digester

gas is always kept at 50 wt.% of the sludge rate, according to the gas availability in a water quality control plant. The calculated results are summarized in Table III-3.

Sludge with Wood:

When sludge is treated together with wood, methane must be used as a co-feedstock at a rate of 15 wt% of wood. It was found that, for Cycle 1, both wood and sludge have to be dried before being used. The sludge was assumed to be dried to contain 5 wt% moisture, and its feed ratio is dependent upon the moisture content of the dried wood. Figure III-4 plots the product ratio of methanol to carbon and the thermal efficiency as functions of sludge feed rate. It shows that both methanol production and thermal efficiency increase with the ratio of sludge feed rate to the wood feed rate. There is a maximum allowable sludge feed ratio in order to maintain a desired reaction temperature in the HPR. When wood is dried to 5 wt% moisture and fed with 15 wt% of methane, the allowable maximum feed ratio of sludge to wood is 70 wt%. If wood is further dried to 1 wt% moisture, the feed ratio of sludge increases to 80 wt%. For Cycle 2, as-received wood and as-received sludge can be used with a maximum sludge feed rate of 50 wt%. If a dried wood of 5 wt% moisture is used, the sludge feed ratio reaches 90 wt%. However, comparing the two cycles, Cycle 2 has a lower thermal efficiency, and it produces more carbon and less methanol, though its gas circulation requirement is slightly smaller. It is interesting to note in Appendix III-2, that with feeding digester gas into the HPR, the CO_2 component reacts in the HPR to form CO and CH_4 , thus increasing the CO mole fraction in the process gas from 2.4% to 6.2%. These constituents are then converted to methanol and carbon black in the following steps. This ability for the HYDROCARB Process to convert CO_2 in the clean fuels should be significant for greenhouse gas mitigation. Figure III-5 summarizes the calculation results for this case.

Sludge with Kentucky Coal:

When Kentucky coal is used as co-feedstock with sludge, it was found that a methane cofeedstock is unnecessary. The coal and sludge can be used without drying. In Table III-3, the allowable maximum feed ratio of sludge to the as-received coal is 4:1 for Cycle 1 and 1.7 for Cycle 2. It shows that Cycle 1 has a much higher treatment ability for sludge.

Sludge with Wyodak Coal:

Wyodak coal can also be used as a co-feedstock with sludge. The results in Table III-3 show that as-received Wyodak coal can not make up the heat balance in the HPR and it has to be dried down to 5 wt% moisture. However, as-received sludge can be used in both cycles. For Cycle 1, the maximum allowable co-feeding rate of sludge is 120 wt%. In Cycle 2, only 90 wt% sludge can be fed together with Wyodak coal of 5 wt% moisture content.

PRESSURE AND TEMPERATURE EFFECTS

The effects of pressure and temperature on process efficiency and product distribution were investigated for the Alaska Beluga coal. Table III-4 summarizes the calculated results. The following trends can be found from the Table:

- (i) The minimum required methane feed per unit of biomass increases with a decrease in system pressure.
- (ii) The maximum allowable moisture in the coal decreases with a decrease in system pressure.
- (iii) The product distribution of methanol vs. carbon decreases with a decrease in system pressure.
- (iv) Higher temperatures in the HPR and MPR promote higher methanol production and higher thermal efficiency.

These trends, of course, are limited by the thermal and structural properties of the materials of construction used. Taking these factors into account leads to recommending the operating conditions of 50 atm and 900 C for the HPR and 1000 C for the MPR.

CONCLUSION

- (1) Cycle 1 usually provides a higher process efficiency and more methanol production than Cycle 2. Thus, Cycle 1 is recommended for most cases.
- (2) Burning residual char for heating up the MPR increases the thermal efficiency of the process by about 4 to 5% compared to that of the process without burning residual char.
- (3) Beluga coal can be fed with natural gas without drying. However it has to be dried when used alone, and the maximum allowable moisture content is 11 wt%.
- (4) Kentucky coal (8.6 % moisture) can be processed without drying, in which case additional water may be co-fed to improve thermal efficiency and methanol and carbon product distribution.
- (5) North Dakota coal and Wyodak coal, which have over 26% moisture, have to be dried before being used as a single solid feedstock.
- (6) As-received (AR) biomass (wood) together with 15 wt% of methane produces a 2.6:1 weight ratio of product methanol to carbon black. The thermal efficiency is about 75%.
- (7) Sludge can be processed together with woody biomass or coal. The maximum feed ratio of sludge to wood is 0.7 if both sludge and wood are dried to 5 wt% moisture, and the feed ratios of methane and digester gas are 0.15 and 0.35, respectively. The thermal efficiency in this case is 76%. The methanol product ratio to carbon black is 2.19.
- (8) CO_2 in the digester gas can be converted to CO in the hydrogasifier (HPR), which is further converted to carbon and methanol in the methane pyrolyzer (MPR) and the methanol converter. The ability of converting CO_2 , which causes global greenhouse problems, to the useful clean fuels, methanol and carbon black, is an attractive feature of the Hydrocarb Process, especially if biomass is used as co-feedstock.
- (9) Reference^(III-5) discussed the feedstock's effects on the material balance of the Hydrocarb Process. This study showed that there is a need to systematically investigate the effects of feedstock composition based on both material and energy balances to determine the allowable operational zone in the thermodynamic equilibrium ternary system, C-H-O.

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TABLE III-I. BASIC DATA FOR THE FEEDSTOCKS USED IN THE STUDY

Feedstock	Biomass Wood	Kentucky Coal	N.Dakota Coal	Wyodak Coal	Beluga Coal	Sewage Sludge
<hr/>						
Composition (wt%)						
C	45.86	67.02	43.37	49.95	49.33	28.55
H	5.27	4.54	2.78	3.51	4.00	4.09
O	36.07	7.22	13.97	12.58	15.56	16.03
H ₂ O	11.67	8.60	30.10	26.40	21.78	9.82
Ash	0.66	8.34	8.30	6.03	8.67	36.53
S	0.04	2.85	0.81	0.60	0.12	1.36
N	0.43	1.43	0.67	0.93	0.54	3.62
Heating Value (Higher)						
(BTU/lb-MF)	-8800.0	-13650	-10254	-11730	-11082	-5510
(kcal/kg-MF)	-4888.9	-7583.3	-5696.7	-6516.7	-6156.7	-3061.1
Heat of Formation						
(kcal/kg-MAF)	-1214.4	183.0	-593.0	-461.7	-584.9	-1769.7
Heat Capacity (kcal/kgMF/C)	0.570	0.315	0.315	0.315	0.315	0.250

MAF -- Moisture Ash Free
MF -- Moisture Free

Coal Rank: Kentucky coal - bituminous
N. Dakota coal - lignite
Wyodak coal - sub-bituminous
Beluga coal - sub-bituminous

TABLE III-2 RESULTS WITH SINGLE SOLID FEEDSTOCK.
(p=50atm/MPR=900 C/MPR=1000 C)

CYC	Feedstocks t/d	Comb. t/d	Carb t/d	MeOH t/d	PR	Ceff %	Teff %	GCR kmol/h
1	11B100*	TG11	32.3	32.4	1.0	77.1	68.2	1897
1	11B100	CTG8	32.3	32.4	1.0	80.2	72.7	1897
1	AB100+G5	TG12	29.3	49.6	1.7	77.3	70.7	2007
1	AB100+G5	CTG9	29.3	49.6	1.7	80.2	74.8	2007
2	AB100	TG11	34.5	23.5	.68	74.9	62.9	1769
2	AB100	CTG8	34.5	23.5	.68	77.8	67.0	1769
2	AB100+H11	TG15	32.3	32.4	1.0	73.0	62.4	1941
2	AB100+H11	CTG12	32.3	32.4	1.0	75.7	66.2	1941
1	AK100	CTK2	50.7	16.8	.33	83.1	68.8	2477
1	AK100	TG5	50.7	16.8	.33	80.3	64.0	2477
1	AK100+H29	CTK22	38.9	56.9	1.5	74.0	72.8	2541
1	AK100+H29	TG15	38.9	56.9	1.5	76.8	68.5	2541
2	AK100	CT	52.1	7.7	.15	83.9	73.4	2145
2	AK100	TG1	52.1	7.7	.15	80.8	63.2	2145
2	AK100+H67	CTK37	38.8	57.3	1.5	65.7	64.7	2872
2	AK100+H67	TG23	38.8	57.3	1.5	71.4	61.3	2872
1	5N100+G2	CTN23	32.1	22.0	.68	73.9	72.1	1745
1	5N100+G2	TG9	32.1	22.0	.68	77.8	67.6	1745
2	15N100	CTN28	33.0	16.2	.49	70.3	67.8	1546
2	15N100	TG11	33.0	16.2	.49	75.6	63.6	1546
1	13Y100	CTY22	33.8	29.4	.87	73.8	72.8	1925
1	13Y100	TG11	33.8	29.4	.87	77.3	68.2	1925
2	AY100	CTY26	35.0	24.4	.70	70.2	67.3	1813
2	AY100	TG12	35.0	24.4	.70	74.6	63.2	1813
2	AY100+H7	CTY33	33.6	30.0	.89	67.5	66.8	1919
2	AY100+H7	TG15	33.6	30.0	.89	73.4	62.9	1919
1	AW100+G15	CTW33	26.4	69.0	2.6	72.2	74.9	2167
1	AW100+G15	TG14	26.4	69.0	2.6	77.7	71.6	2167
2	AW100+G6	CTW39	32.9	33.6	1.0	66.7	64.7	1997
2	AW100+G6	TG15	32.9	33.6	1.0	73.5	61.4	1997

A -- As Received

B -- Beluga Coal

C -- Char

G -- Natural Gas

H -- Water

K -- Kentucky Coal

N -- North Dakota Coal

T -- Purged Off Gas

W -- Wood

Y -- Wyodak Coal

* 11B100 means that 100 t/d Beluga coal is dried to 11% moisture.

CYC -- Cycle

Comb.-- MPR heat sources by combustion

C -- Carbon black product

MeOH -- Methanol product

PR -- Product Weight Ratio (MeOH/C)

Ceff -- Carbon efficiency

Teff -- Thermal efficiency

GCR -- Gas circulation rate

TABLE III-3 RESULTS OF HYDROCARB PROCESS WITH MULTIPLE FEEDSTOCKS.
(p=50atm / HPR=900 C / MPR=1000 C)

CYC	Feedstocks tons/day	Comb. t/d	C t/d	MeOH t/d	PR	Ceff %	Teff %	GCR kgmol/h
1	5W100+5S70+G15+D35*	TG20	46.6	102	2.2	78.9	72.9	3520
1	5W100+5S70+G15+D35	CTW49	46.6	102	2.2	73.7	76.0	3520
1	1W100+5S80+G15+D40	TG20	50.7	102	2.0	79.3	72.8	3697
1	1W100+5S80+G15+D40	CTW47	50.7	102	2.0	74.5	76.0	3697
2	AW100+AS50+G15+D25	TG10	51.2	47.3	.92	76.6	64.2	2936
2	AW100+AS50+G15+D25	CTW20	51.2	47.3	.92	75.3	67.3	2936
2	5W100+AS90+G15+D45	TG11	65.4	55.0	.84	77.4	65.0	3605
2	5W100+AS90+G15+D45	CTW21	65.4	55.0	.84	76.4	68.0	3605
1	AK100+AS400+D200	TG65	140	297	2.1	78.8	74.4	10488
1	AK100+AS400+D200	CTD149	140	297	2.1	80.8	77.4	10488
2	AK100+AS170+D85	TG15	107	60.3	.57	78.7	65.6	5154
2	AK100+AS170+D85	CTG21	107	60.3	.57	81.2	69.2	5154
1	5Y100+AS120+D60	TG26	63.7	103	1.6	78.5	72.9	4304
1	5Y100+AS120+D60	CTD58	63.7	103	1.6	80.8	76.4	4304
2	5Y100+AS90+D45	TG13	68.2	37.3	.55	78.1	65.9	3271
2	5Y100+AS90+D45	CTD23	68.2	37.3	.55	80.7	69.6	3271

A -- As Received
C -- Char
D -- Digester Gas
G -- Natural Gas
H -- Water
K -- Kentucky Coal
S -- Sludge
T -- Purged Off Gas
W -- Wood
Y -- Wyodak Coal

CYC -- Cycle
Comb.-- MPR heat sources by combustion
C -- Carbon black product
MeOH -- Methanol product
PR -- Product Ratio (MeOH/C)
Ceff -- Carbon efficiency
Teff -- Thermal efficiency
GCR -- Gas circulation rate

* 5W100+5S70+G15+D35 means that the feedstocks consist of 100 t/d wood which is dried to 5% moisture, 70 t/d sludge which is also dried to 5% moisture, 15 t/d methane and 35 t/d digester gas.

TABLE III-4 EFFECTS OF PRESSURE AND TEMPERATURE ON PROCESS EFFICIENCY
AND PRODUCT DISTRIBUTION.

(100 t/day of Beluga coal)

CYC	P atm	T(HPR/MPR) C	Moist %	CH ₄ /Coal	MeOH/C	Ceff %	Teff %
1	50	900/1000	21.78	.05	1.67	77.3	70.7
1	50	900/1000	11	0	1	77.1	68.2
1	50	800/900	21.78	.05	0.59	78.7	66.0
2	50	900/1000	21.78	0	0.67	74.9	62.8
2	50	800/900	21.78	0	0.09	77.5	61.2
1	35	800/900	21.78	.05	0.71	70.8	56.8
1	35	800/900	5	.05	0.29	76.8	60.1
1	35	800/900	5	.1	0.26	78.9	60.9
2	35	800/900	5	.05	0.04	78.9	61.2
2	35	800/900	21.78	.05	0.06	75.4	56.8
2	35	800/900	5	.1	0.04	80.2	72.3
1	30	800/900	5	.15	0.24	80.3	68.4
2	30	800/900	5	.1	0.03	80.2	71.4
2	30	800/900	5	.15	0.03	81.3	81.9
2	30	800/900	21.78	.15	0.05	78.2	71.0

CYCLE 1

CYCLE 2

Figure III-1. Brief illustration of Cycle 1 and Cycle 2.

Figure III-2. Strategy of computer calculation for a single solid feedstock.

HYDROCARB PROCESS (CYCLE 1)

(Biomass + NG)

(P = 50 atm)

Carbon Conversion of Feedstock in HPR: 90%
 Carbon Efficiency: 72.2%
 Thermal Efficiency: 74.9%

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

Figure III-4. Plot of Methanol Production and Thermal Efficiency vs. Sludge Feed Rate.

Figure III-5. Data summary with wood, sludge, CH₄, and digester gas as feedstocks.

Appendix III-1 Computer Printout with Wood and CH₄ as Feedstocks. (cont'd)

CONVERSION OF CARBON IN FEEDSTOCK FOR HPR (%): 90
CARBON EFFICIENCY (%): 72.16
THERMAL EFFICIENCY (%): 74.89

BALANCE CHECK:

C IN 202.3981	C OUT 202.3903
H IN 475.2008	H OUT 475.1611
O IN 134.358	O OUT 134.3459

UNIT 1# HYDROGASIFIER (HPR)

(I) OPERATING CONDITIONS, Pressure (atm): 50
Temperature (°C): 900

(II) INPUT:

(1) Feedstocks:

(i) Name: Wood

Rate (kg/h): 4629.63
Composition C% wt: 45.86
H% wt: 5.27
O% wt: 36.07
H₂O% wt: 11.67
Ash% wt: .66
S% wt: .04
Enthalpy (kcal/h): -6977758
Temperature (°C): 25

(2) CH₄ Feed Rate (kg/h): 694.4445
Enthalpy (kcal/h): -774179.9
Temperature (°C): 25

(3) Digester Gas Feed Rate (kg/h): 0
Enthalpy (kcal/h): 0
Temperature (°C): 25

(4) Additional Water Feed Rate (kg/h): 0
Enthalpy (kcal/h): 0
Temperature (°C): 100

(5) Limestone Feed Rate (kg/h): 16.508
Content: CaCO₃% wt: 70
Enthalpy (kcal/h): -33302.16
Temperature (°C): 25

(6) Gas Stream <F> Rate (kmol/h): 2166.787
Composition (vol%)
CO 2.717432
CO₂ 2.987879
CH₄ 23.91609
H₂O 8.341512E-02
H₂ 69.45669
CH₃OH .8384966
Enthalpy (kcal/h): -275321.9
at temp (°C): 926.5258

(III) OUTPUT:

Appendix III-1 Computer Printout with Wood and CH₄ as Feedstocks. (cont'd)

(1) Ash Discharge Rate (kg/h): 44.46702
 Enthalpy (kcal/h): -7573.43
 at temp (°C): 900

(2) Gas Stream <G> Flow Rate (kmol/h): 2297.939
 Composition (vol%)
 CO 6.810789
 CO₂ .6568884
 CH₄ 30.06123
 H₂O 6.788135
 H₂ 55.68296
 CH₃OH 0
 Enthalpy (kcal/h): -8119087
 at temp (°C): 900

(3) Residue Carbon Rate (kg/h): 212.3149
 Enthalpy (kcal/h): 66082.81
 Heating Value (kcal/h): -1662664

(IV) HEAT LOAD (kcal/h): -16.22302

(V) VALUE OF (H/O): 16.44135

(VI) BALANCE CHECK:

IN C: 862.399	OUT C: 862.3912
IN H: 5634.289	OUT H: 5634.249
IN O: 342.6967	OUT O: 342.6847

UNIT 2# METHANE PYROLYZER (MPR)

(I) OPERATING CONDITION, Pressure (atm): 50
 Temperature (°C): 1000

(II) INPUT:

(1) Gas Stream <G> Rate (kmol/h): 2297.939
 Composition (vol%)
 CO 6.810789
 CO₂ .6568884
 CH₄ 30.06123
 H₂O 6.788135
 H₂ 55.68296
 CH₃OH 0
 Enthalpy (kcal/h): -8119087
 at temp (°C): 900

(2) Alumina Rate (kg/h): 63042.24
 Temperature (°C): 1400

(III) OUTPUT

(1) Gas Stream <H> Rate (kmol/h): 2539.77
 Composition (vol%)
 CO 9.204524
 CO₂ .3098129
 CH₄ 20.4348
 H₂O 3.668596
 H₂ 66.38226
 CH₃OH 0

Appendix III-1 Computer Printout with Wood and CH₄ as Feedstocks. (cont'd)

Enthalpy (kcal/h): 116196.7
ta temp ('C): 1000

(2) Carbon Black <M> Discharge Rate (kg/h): 1222.042
(kmol/h): 101.7521
Enthalpy (kcal/h): 435849.1
at temp ('C): 1000

(3) Alumina Rate (kg/h): 63042.24
Temperature ('C): 1000

(IV) HEAT LOAD (kcal/h): .2649658

(V) VALUE OF (H/O): 16.44135

(VI) BALANCE CHECK:

IN C: 862.3912	OUT C: 862.3912
IN H: 5634.249	OUT H: 5634.249
IN O: 342.6847	OUT O: 342.6847

UNIT 3# METHANOL CONVERTER

(I) OPERATING CONDITION, Pressure (atm): 50
Temperature ('C): 260

(II) INPUT:

(1) Gas Stream <H> Rate (kmol/h): 2539.77
Composition (vol%)
CO 9.204524
CO₂ .3098129
CH₄ 20.4348
H₂O 3.668596
H₂ 66.38226
CH₃OH 0
Enthalpy (kcal/h): -1.710283E+07
at temp ('C): 256.5093

(III) OUTPUT:

(1) Gas Stream <S> Rate (kmol/h): 2304.104
Composition (vol%)
CO 2.559359
CO₂ 2.814074
CH₄ 22.52489
H₂O 1.57125
H₂ 65.41639
CH₃OH 5.114038
Enthalpy (kcal/h): -2.033917E+07
at temp ('C): 260

(IV) HEAT LOAD (kcal/h): -3236343

(V) VALUE OF (H/O): 16.4415

(VI) BALANCE CHECK:

IN C: 760.6392	OUT C: 760.6391
IN H: 5634.249	OUT H: 5634.248

Appendix III-1 Computer Printout with Wood and CH₄ as Feedstocks. (cont'd)

IN O: 342.6847

OUT O: 342.6846

UNIT 4# CONDENSER

(I) OPERATING CONDITION, Pressure (atm): 50

Temperature (°C): 50

(II) INPUT:

(1) Gas Stream <S> Rate (kmol/h): 2304.104
 Composition (vol%)
 CO 2.559359
 CO₂ 2.814074
 CH₄ 22.52489
 H₂O 1.57125
 H₂ 65.41639
 CH₃OH 5.114038
 Enthalpy (kcal/h): -2.033917E+07
 at temp (°C): 260

(III) OUTPUT:

(1) Gas Stream <U> Rate (kmol/h): 2170.074
 Composition (vol%)
 CO 2.717432
 CO₂ 2.987879
 CH₄ 23.91609
 H₂O 8.341512E-02
 H₂ 69.45669
 CH₃OH .8384966
 Enthalpy (kcal/h): -1.75192E+07
 at temp (°C): 50

(2) MeOH Rate (kmol/h): 99.63677
 (kg/h): 3192.362

(3) H₂O Rate (kmol/h): 34.39304
 (kg/h): 619.625

(IV) HEAT LOAD (kcal/h): -4668477

(V) VALUE OF (H/O): 24.76298

(VI) BALANCE CHECK:

IN C: 760.6391	OUT C: 760.6391
IN H: 5634.248	OUT H: 5634.249
IN O: 342.6846	OUT O: 342.6846

UNIT 5# GAS HEAT EXCHANGER

(I) OPERATING CONDITION, Pressure (atm): 50

(II) INSIDE

(1) Gas In <H> Rate (kmol/h): 2539.77
 Temp (°C): 1000
 Enthalpy (kcal/h): 116196.7

Appendix III-1 Computer Printout with Wood and CH₄ as Feedstocks. (cont'd)

(2) Gas Out <H> Rate (kmol/h): 2539.77
Temp ('C): 256.5093
Enthalpy (kcal/h): -1.710283E+07

(III) OUTSIDE

(1) Gas In <F> Rate (kmol/h): 2166.787
Temp ('C): 50
Enthalpy (kcal/h): -1.749266E+07

(2) Gas Out <F> Rate (kmol/h): 2166.787
Temp ('C): 926.5258
Enthalpy (kcal/h): -275321.9

(IV) HEAT LOAD (kcal/h): -1689.224

UNIT 6# COMBUSTOR

(I) INPUT:

(1) Residual Char (kg/h): 212.3149

(2) Off Gas (kmol/h): 3.287698

(3) Air (kmol/h): 16.00207

(4) Alumina (kg/h): 63042.24

(5) Wood (kg/h): 1545.508

(II) OUTPUT:

(1) Flue Gas (kmol/h): 19.28977 (approx.)

(2) Alumina (kg/h): 63042.24

(III) HEAT LOAD (kcal/h): -8671133

Appendix III-2 Computer Printout with Wood, Sludge, CH₄ and Digester Gas as Feedstocks.

Remarks: 5W100+5S70+G15+D35

CPU Time (min): 5.88

FEEDSTOCKS:

No. 1 Name: Wood
PROCESS CAPACITY (AR tons/cd): 100
AR COMPOSITION (wt%):
 C: 45.86
 H: 5.27
 O: 36.07
 H2O: 11.67
 ASH: .66
 S: .04
 OTHER: .43
HEATING VALUE (kcal/kg-MF):-4888.9
HEAT OF FORMATION (kcal/kg-MAF):-1214.4
HEAT CAPACITY (kcal/'C*MAFkg): .57
MOISTURE AFTER DRYING (wt%): 5

No. 2 Name: Sludge (Riverside)
PROCESS CAPACITY (AR tons/cd): 70
AR COMPOSITION (wt%):
 C: 28.55
 H: 4.09
 O: 16.03
 H2O: 9.82
 ASH: 36.53
 S: 1.36
 OTHER: 3.62
HEATING VALUE (kcal/kg-MF): -3061.1
HEAT OF FORMATION (kcal/kg-MAF): -1769.7
HEAT CAPACITY (kcal/'C*MAFkg): .25
MOISTURE AFTER DRYING (wt%): 5

```
OTHER INPUT:  CH4 into HPR (tons/cd): 15
               (kg/kg-ARfeed#1): .15
               Digester Gas into HPR (tons/cd): 35
               (kg/kg-ARfeed#1): .35
               H2O in to HPR(tons/cd): 0
               (kg/kg-ARfeed#1): 0
               LIMESTONE (tons/cd): 8.843006
               FOR COMBUSTION (tons/cd):
               Wood: 48.97242
```

PRODUCT: CARBON BLACK (tons/cd): 46.57304
METHANOL (tons/cd): 101.964
GAS (tons/cd): 0

PRODUCT DISTRIBUTION (kg-MeOH/kg-C): 2.19

Appendix III-2 Computer Printout with Wood, Sludge, CH₄ and Digester Gas as Feedstocks.
(cont'd)

CARBON BLACK YIELD (kg/kg-ARfeed#1): .4657304
MEOH YIELD (kg/kg-ARfeed#1): 1.01964
WATER YIELD (kg/kg-ARfeed#1): .2113636
OFF GAS (kmol/kg-ARfeed#1): 3.458929E-03
(kg/kg-ARfeed#1): 2.555812E-02
(kmol/h): 16.01356
PURGE FRACTION (%): .452814
FRACTION OF BURNING OFF-GAS (%): 1.00
COMPOSITION (vol%):
CO 2.444442
CO2 2.597323
CH4 24.13597
H2O 8.682551E-02
H2 69.90885
CH3OH .8265951
TOTAL HEATING VALUE (kcal/h): -1637921

CONVERSION OF CARBON IN FEEDSTOCK FOR HPR (%): 90
CARBON EFFICIENCY (%): 73.68
THERMAL EFFICIENCY (%): 76.03

BALANCE CHECK:

C IN 331.6794	C OUT 331.6683
H IN 736.4289	H OUT 736.3698
O IN 203.0361	O OUT 203.0176

UNIT 1# HYDROGASIFIER (HPR)

(I) OPERATING CONDITIONS, Pressure (atm): 50
Temperature (°C): 900

(II) INPUT:

(1) Feedstocks:

(1) Name: Wood
Rate (kg/h): 4304.581
Composition C% wt: 49.32299
H% wt: 5.66795
O% wt: 38.79373
H2O% wt: 5
Ash% wt: .7098382
S% wt: 4.302049E-02
Enthalpy (kcal/h): -5257743
Temperature (°C): 150

(2) Name: Sludge (Riverside)
Rate (kg/h): 3076.316
Composition C% wt: 30.07596
H% wt: 4.308605
O% wt: 16.88678
H2O% wt: 5
Ash% wt: 38.48248
S% wt: 1.43269
Enthalpy (kcal/h): -3452120
Temperature (°C): 150

(2) CH₄ Feed Rate (kg/h): 694.4445
Enthalpy (kcal/h): -774179.9

Appendix III-2 Computer Printout with Wood, Sludge, CH₄ and Digester Gas as Feedstocks.
(cont'd)

Temperature (°C): 25

(3) Digester Gas Feed Rate (kg/h): 1620.37
 Enthalpy (kcal/h): -2845242
 Temperature (°C): 25

(4) Additional Water Feed Rate (kg/h): 0
 Enthalpy (kcal/h): 0
 Temperature (°C): 100

(5) Limestone Feed Rate (kg/h): 409.3984
 Content: CaCO₃ wt: 70
 Enthalpy (kcal/h): -825893.6
 Temperature (°C): 25

(6) Gas Stream <F> Rate (kmol/h): 3520.441
 Composition (vol%)
 CO 2.444442
 CO₂ 2.597323
 CH₄ 24.13597
 H₂O 8.682551E-02
 H₂ 69.90885
 CH₃OH .8265951
 Enthalpy (kcal/h): 1727492
 at temp (°C): 947.3911

(III) OUTPUT:

(1) Ash Discharge Rate (kg/h): 1559.402
 Enthalpy (kcal/h): -138272.5
 at temp (°C): 900

(2) Gas Stream <G> Flow Rate (kmol/h): 3704.471
 Composition (vol%)
 CO 6.23228
 CO₂ .5500355
 CH₄ 30.68466
 H₂O 6.275629
 H₂ 56.2574
 CH₃OH 0
 Enthalpy (kcal/h): -1.138444E+07
 at temp (°C): 900

(3) Residue Carbon Rate (kg/h): 304.838
 Enthalpy (kcal/h): 94880.56
 Heating Value (kcal/h): -2387225

(IV) HEAT LOAD (kcal/h): -147.7762

(V) VALUE OF (H/O): 18.21008

(VI) BALANCE CHECK:

IN C: 1387.964	OUT C: 1387.953
IN H: 9179.912	OUT H: 9179.854
IN O: 504.1222	OUT O: 504.1037

UNIT 2# METHANE PYROLYZER (MPR)

(I) OPERATING CONDITION, Pressure (atm): 50

Appendix III-2 Computer Printout with Wood, Sludge, CH₄ and Digester Gas as Feedstocks.
(cont'd)

Temperature (°C): 1000

(II) INPUT:

(1) Gas Stream <G> Rate (kmol/h): 3704.471
 Composition (vol%)
 CO 6.23228
 CO₂ .5500355
 CH₄ 30.68466
 H₂O 6.275629
 H₂ 56.2574
 CH₃OH 0
 Enthalpy (kcal/h): -1.138444E+07
 at temp (°C): 900

(2) Alumina Rate (kg/h): 100446.7
 Temperature (°C): 1400

(III) OUTPUT

(1) Gas Stream <H> Rate (kmol/h): 4091.234
 Composition (vol%)
 CO 8.414859
 CO₂ .2589349
 CH₄ 20.86308
 H₂O 3.388828
 H₂ 67.0743
 CH₃OH 0
 Enthalpy (kcal/h): 1662475
 at temp (°C): 1000

(2) Carbon Black <M> Discharge Rate (kg/h): 2156.159
 (kmol/h): 179.5303
 Enthalpy (kcal/h): 769007.8
 at temp (°C): 1000

(3) Alumina Rate (kg/h): 100446.7
 Temperature (°C): 1000

(IV) HEAT LOAD (kcal/h): 7.686876E-02

(V) VALUE OF (H/O): 18.21008

(VI) BALANCE CHECK:

IN C: 1387.953	OUT C: 1387.953
IN H: 9179.854	OUT H: 9179.854
IN O: 504.1037	OUT O: 504.1037

UNIT 3# METHANOL CONVERTER

(I) OPERATING CONDITION, Pressure (atm): 50
 Temperature (°C): 260

(II) INPUT:

(1) Gas Stream <H> Rate (kmol/h): 4091.234
 Composition (vol%)
 CO 8.414859
 CO₂ .2589349

Appendix III-2 Computer Printout with Wood, Sludge, CH₄ and Digester Gas as Feedstocks.
(cont'd)

CH ₄	.20.86308
H ₂ O	3.388828
H ₂	67.0743
CH ₃ OH	0
Enthalpy (kcal/h):-2.706722E+07	
at temp ('C): 228.2895	

(III) OUTPUT:

(1) Gas Stream <S>	Rate (kmol/h): 3738.103
	Composition (vol%)
	CO 2.312579
	CO ₂ 2.457213
	CH ₄ 22.83398
	H ₂ O 1.535146
	H ₂ 66.13769
	CH ₃ OH 4.723396
	Enthalpy (kcal/h):-3.094903E+07
	at temp ('C): 260

(IV) HEAT LOAD (kcal/h):-3881819

(V) VALUE OF (H/O): 18.21025

(VI) BALANCE CHECK:

IN C: 1208.423	OUT C: 1208.423
IN H: 9179.854	OUT H: 9179.854
IN O: 504.1037	OUT O: 504.1037

UNIT 4# CONDENSER

(I) OPERATING CONDITION, Pressure (atm): 50
Temperature ('C): 50

(II) INPUT:

(1) Gas Stream <S>	Rate (kmol/h): 3738.103
	Composition (vol%)
	CO 2.312579
	CO ₂ 2.457213
	CH ₄ 22.83398
	H ₂ O 1.535146
	H ₂ 66.13769
	CH ₃ OH 4.723396
	Enthalpy (kcal/h):-3.094903E+07
	at temp ('C): 260

(III) OUTPUT:

(1) Gas Stream <U>	Rate (kmol/h): 3536.455
	Composition (vol%)
	CO 2.444442
	CO ₂ 2.597323
	CH ₄ 24.13597
	H ₂ O 8.682551E-02
	H ₂ 69.90885
	CH ₃ OH .8265951

Appendix III-2 Computer Printout with Wood, Sludge, CH₄ and Digester Gas as Feedstocks.
(cont'd)

Enthalpy (kcal/h): -2.712234E+07
at temp ('C): 50

(2) MeOH Rate (kmol/h): 147.3333
(kg/h): 4720.558

(3) H₂O Rate (kmol/h): 54.3148
(kg/h): 978.5354

(IV) HEAT LOAD (kcal/h): -7473811

(V) VALUE OF (H/O): 28.04342

(VI) BALANCE CHECK:

IN C: 1208.423	OUT C: 1208.423
IN H: 9179.854	OUT H: 9179.854
IN O: 504.1037	OUT O: 504.1037

UNIT 5# GAS HEAT EXCHANGER

(I) OPERATING CONDITION, Pressure (atm): 50

(II) INSIDE

(1) Gas In <H> Rate (kmol/h): 4091.234
Temp ('C): 1000
Enthalpy (kcal/h): 1662475

(2) Gas Out <H> Rate (kmol/h): 4091.234
Temp ('C): 228.2895
Enthalpy (kcal/h): -2.706722E+07

(III) OUTSIDE

(1) Gas In <F> Rate (kmol/h): 3520.441
Temp ('C): 50
Enthalpy (kcal/h): -2.699952E+07

(2) Gas Out <F> Rate (kmol/h): 3520.441
Temp ('C): 947.3911
Enthalpy (kcal/h): 1727492

(IV) HEAT LOAD (kcal/h): -2674.644

UNIT 6# COMBUSTOR

(I) INPUT:

(1) Residual Char (kg/h): 304.838

(2) Off Gas (kmol/h): 16.01356

(3) Air (kmol/h): 78.41016

(4) Alumina (kg/h): 100446.7

(5) Wood (kg/h): 2267.242

(II) OUTPUT:

Appendix III-2 Computer Printout with Wood, Sludge, CH₄ and Digester Gas as Feedstocks.
(cont'd)

(1) Flue Gas (kmol/h): 94.42373 (approx.)

(2) Alumina (kg/h): 100446.7

(III) HEAT LOAD (kcal/h): -1.381593E+07

APPENDIX A

Quality Control Evaluation Report

The experimental measurements reported in this document were obtained with the use of the Brookhaven Tubular Reactor Facility. The design, construction operation and a description of the measurement equipment and instrumentation was initially reported in Brookhaven National Laboratory Report No. 50698, "Design, Construction, Operation and Initial Results of a Flash Hydropyrolysis Experimental Unit," by Peter Fallon and Meyer Steinberg (January 1977). The construction procedures and instrumentation used were in accordance with best practices available for this type of experiment. A Safety Analysis Report on the Brookhaven Hydropyrolysis Experimental Equipment was written in November 1991 to requalify and obtain approval from the Brookhaven National Laboratory Safety Committee for operation. Since initial construction and operation, the equipment has been requalified twice, the latest being November 1991, just before performing the experiments reported herein.

The facility contains the following measuring equipment: thermocouple temperature monitoring and control, pressure indicating and control, volumetric flow meter, and on-line gas chromatograph for determining the gaseous component concentration.

The temperature and pressure instrumentation were checked against secondary standards which were in turn calibrated against primary standards. The precision of temperature measurements was $\pm 5^{\circ}\text{C}$. The precision of pressure measurement was within ± 5 psi. The on-line gas chromatograph was calibrated before each run using standard gas calibrating gases obtained from vendors with certification. The gases monitored included H_4 , C_2H_6 , CO and CO_2 . The precision of the chromatograph calibration is estimated to be $\pm 5\%$ of the gas component concentration.

The feedstock composition of samples of biomass were analyzed in duplicate by Commercial Testing and Engineering Co., Lombard, Illinois, in accordance with well-established analytical procedures.

The mass balances after the flow runs with this tubular reactor facility could be made with an accuracy of within $\pm 5\%$.

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