50
-19-81
EW

72

②

sh. 89

DOE/CS/40202-T5
(M82001173)

CONVERSION OF CELLULOSIC WASTES TO LIQUID FUELS

MASTER

By
James L. Kuester

September 1981

Work Performed Under Contract No. AS02-76CS40202

College of Engineering and Applied Sciences
Arizona State University
Tempe, Arizona

U.S. Department of Energy

Solar Energy

DISCLAIMER

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A04
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts, (ERA); Government Reports Announcements* and Index (*GRA* and I); *Scientific and Technical Abstract Reports (STAR);* and publication, NTIS-PR-360 available from (NTIS) at the above address.

DOE/CS/40202-T5
(COO-2982-74)
(DE82001173)
Distribution Category UC-61a

CONVERSION OF CELLULOSIC WASTES TO LIQUID FUELS

by

James L. Kuester
Principal Investigator

Interim Report to the
Alternate Materials Utilization Branch
Industrial Programs Division
Office of Conservation and Renewable Energy
U. S. Department of Energy
Contract No. DE-AC02-76CS40202

September 1981

College of Engineering and Applied Sciences
Arizona State University
Tempe, Arizona 85287

TABLE OF CONTENTS

SUMMARY

The previous history, current status and future plans for a project to convert waste cellulosic (biomass) materials to quality liquid hydrocarbon fuels is described. This report will update two previous Interim Reports (COO-2982-38, March 1979 and COO-2982-57, September 1980).

The process utilizes an indirect liquefaction approach (gasification followed by liquefaction) to produce a quality liquid hydrocarbon product similar to diesel fuel. A variety of feedstocks can be processed with product quality essentially independent of feedstock type. Previous contract periods have concentrated on assessment of alternative feedstocks in the gasification step and detailed factor studies for the gasification and liquefaction stages operated separately. The current contract period (June 1, 1980 to May 31, 1981) had the prime objective of operating the entire system in an integrated, continuous mode and directly measuring and assessing product yields. Secondary objectives were additional factor studies (gasification fluidizing gas type, solid type, operating conditions; liquefaction catalyst improvements, operating conditions), and evaluation of additional alternative feedstocks.

A series of integrated, continuous runs were performed at the start of the contract period with almond prunings and guayule bagasse feedstocks

and utilizing a cobalt-alumina catalyst in the liquefaction reactor. The runs were operationally successful and a high quality product was produced similar to No. 2 diesel fuel. However a direct yield measurement was not possible because of an inconsistent scale of the gasification system (larger) and the liquefaction system. Thus some pyrolysis gas was vented. A larger (6" x 6') fluidized bed liquefaction reactor was then designed, fabricated and installed in the system. A short series of runs were performed at the end of the contract period with this system on cobalt and iron catalysts with the objective of direct measurement of product yields incorporating recycle of liquefaction reactor off gas (heavy in normal paraffins) back to the gasification system. Again, the system was operationally reliable but liquefaction catalyst activity problems were encountered. These are being analyzed and addressed in the new contract period (starting June 1, 1981).

The major factor studies reported were pyrolysis gas composition vs. temperature for almond prunings feedstock, steam fluidization of the pyrolyzer, use of dolomite as the gasification heat transfer media and alternative liquefaction reactor catalyst studies. As expected, H_2 composition increases with temperature while olefin, paraffin and CO_2 composition declined. CO appears to peak at about 1500°F. Addition of steam results in a water gas shift reaction effect with the magnitude of the effect significantly increased by the use of dolomite as the heat transfer media (vs. sand). A study of alternative iron and cobalt based liquefaction catalysts was started during the contract period with the effort continuing into the renewal period on an escalated scale.

A number of new feedstocks were assessed during the contract period. Olefin composition in the pyrolysis gas ranged from 5-15 mole % while the H_2/CO mole ratio varied from 0.2 to 1.6. An unusual amount of methane (36 mole %) was achieved with cornstarch feedstock. A run with Portugese Oak Cork feedstock was performed to compare with the 39 mole % olefin composition achieved with guayule cork feedstock in a previous contract period. Again, a high olefin content was produced. A study was inaugurated to relate feedstock characterization analysis to reaction system performance.

Continuing research will be grouped into the categories of factor studies (with particular emphasis on catalyst development), alternative feedstock evaluation, staged reaction system development, alternative products and gasification system regenerator analysis. Some new equipment will be purchased (catalyst preparation, testing and characterization; feedstock analysis, liquid feed system, regenerator controls, solids feeder, etc.) to implement the tasks.

A comprehensive economic assessment of the project with regard to commercialization potential was performed by Energetics, Inc. It was concluded that the process was attractive compared with other alternatives to produce liquid fuels from biomass. The major unknown was the demonstration of yields of 40 + gals/ton in the laboratory unit.

INTRODUCTION

Biomass Conversion Options. The various options available for processing a biomass feedstock base are indicated in Figure 1. The various approaches have been discussed in several recent references (1-4). In general, the mechanisms for the biological options are feedstock dependent, sensitive to poisons and process condition fluctuations and require lengthy processing times. The thermochemical routes require higher temperature and more sophisticated processing equipment but have the capability to handle multiple feedstocks at low processing times. For a liquid fuel product using renewable feedstocks, fermentation is the only state of the art technology available today. However this is restricted to fermentable feedstocks and, thus, if a hydrolysis step is required for a biomass base, commercial scale technology has not been demonstrated. Also the product (alcohol) is not necessarily compatible with the existing distribution system and engine designs.

Indirect liquefaction via thermochemical conversion appears to be the primary route for converting renewable biomass to a high quality transportation fuel equivalent to that derived from petroleum (and thus without alterations to the distribution system and engine design). Direct liquefaction, a noble goal, is hampered by the oxygen content of the biomass. Thus, for a liquid hydrocarbon fuel product, the oxygen has to be removed in the pyrolysis step (probably using reducing agents at

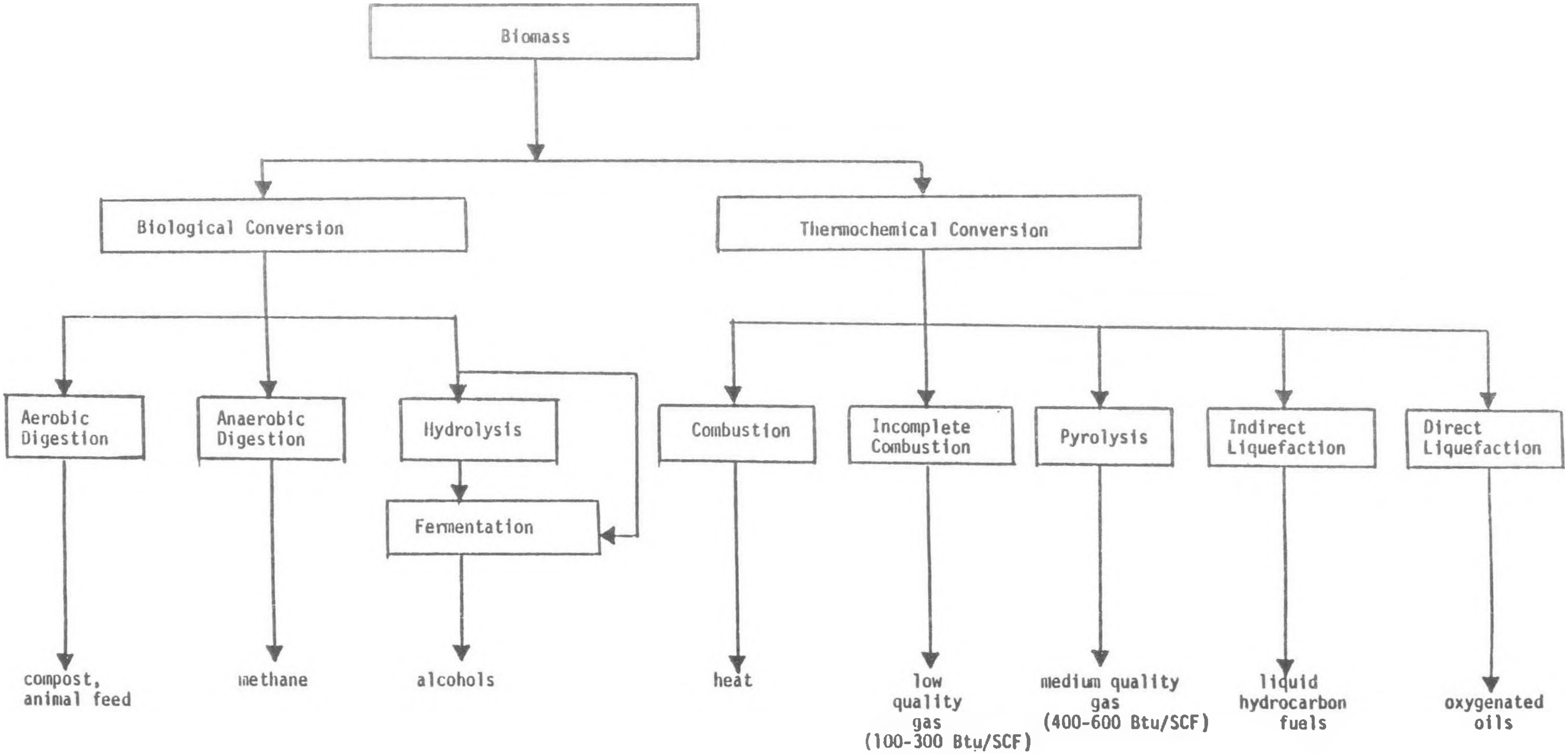


Figure 1.

Biomass Conversion Option Diagram

severe reaction conditions) or oxygenated oils from the pyrolysis step will be subject to a considerable amount of refining to produce a marketable product.

Three indirect liquefaction routes for biomass have been reported: (1) ASU (5-16), (2) Naval Weapons Center (NWC) at China Lake (17), and (3) Mobil (18). The primary process steps are indicated in Figure 2. All three options incorporate a gasification step to produce a synthesis gas. ASU uses a fluidized bed with circulating solid heat transfer system. NWC recommended an externally heated tubular reactor. The Mobil technology does not address the gasification step, i.e., it is assumed that appropriate technology is available. For the NWC tubular reactor, the main problem would appear to be scaleup. Thus the problem of distribution of a solid feed to a large array of parallel tubes required for a wall heat transfer system would appear to be insurmountable. Circulating solid fluidized bed systems, on the other hand, have been utilized on a commercial scale in the catalytic cracking step in petroleum refineries for forty years and are currently undergoing large scale demonstration on municipal refuse in Japan (1,19). Although the feedstock is different for the ASU project, the function and operation of the reactor system is quite similar.

The ASU system converts the unseparated synthesis gas to a diesel type fuel in a catalytic second stage. A high octane gasoline requires a

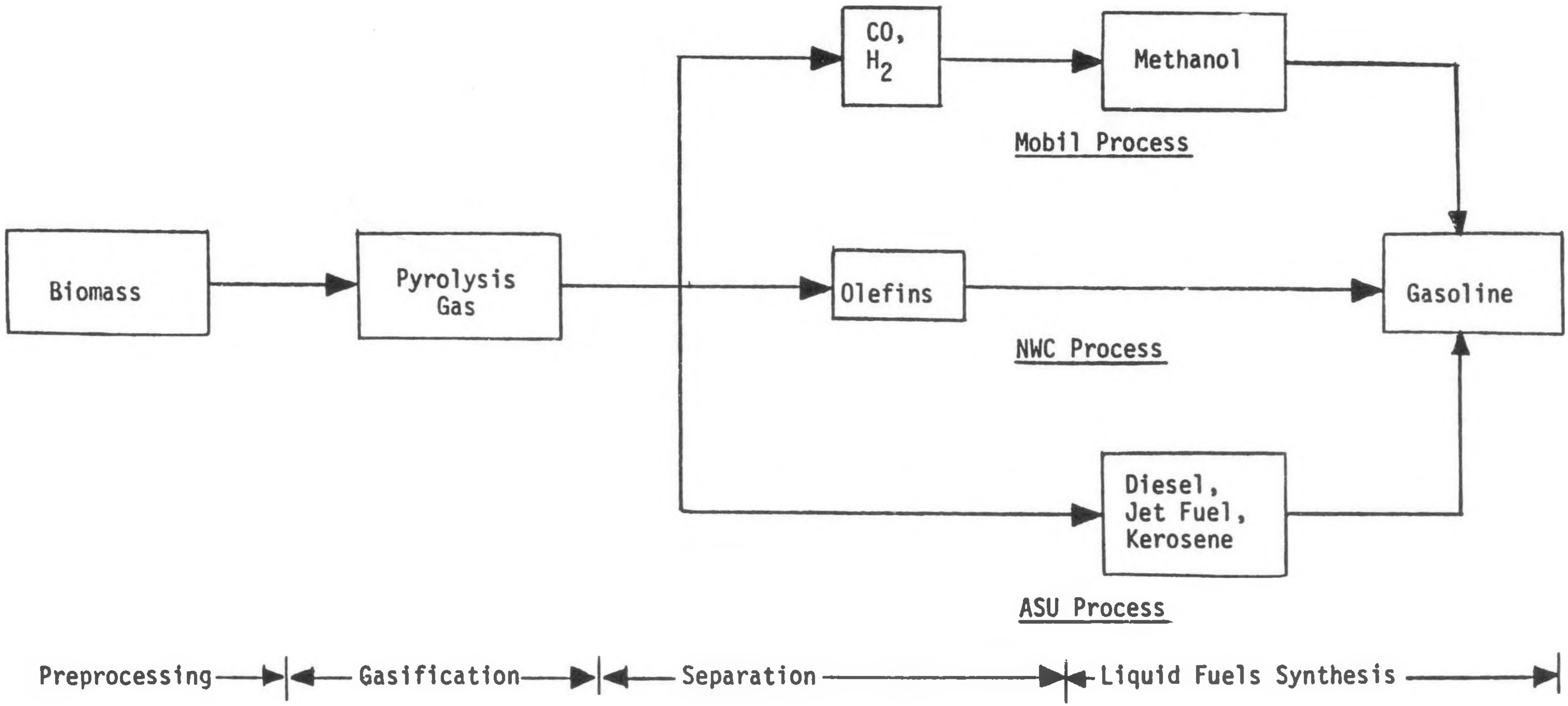


Figure 2.

Indirect Liquefaction Approaches for Conversion of Biomass to Hydrocarbon Liquid Fuels reforming step (or an alternative catalyst in the second stage reactor). The NWC project suggested that olefins be isolated in a series of high pressure separation steps and then fed into a thermal polymerization reactor to produce a high octane gasoline. The Mobil approach suggests that the synthesis gas be converted to methanol via existing technology which in turn is then converted to high octane gasoline using a Mobil developed zeolite catalyst.

The primary virtue of the ASU approach would appear to be the capability to produce a diesel type fuel free of oxygenated compounds in a relatively simple two stage process. Intermediate gas separation and/or production of a methanol intermediate is not required. A diesel product compatible with existing distribution systems and engine design would appear to be the most desirable product from a biomass base, i.e., most trucks, farm machinery and industrial processing equipment run on diesel fuel and thus the diesel product is compatible with local market conditions.

ASU Process Research Work. The proposed process has been under development since 1975. Funding has been provided by ERDA/DOE, U. S. Navy, USDA, Arizona Solar Energy Commission, and Arizona State University. The general conversion scheme is shown in Figure 3. The process is capable of accepting a wide variety of feedstocks. Potential products include medium quality gas, normal propanol, paraffinic fuel and/or

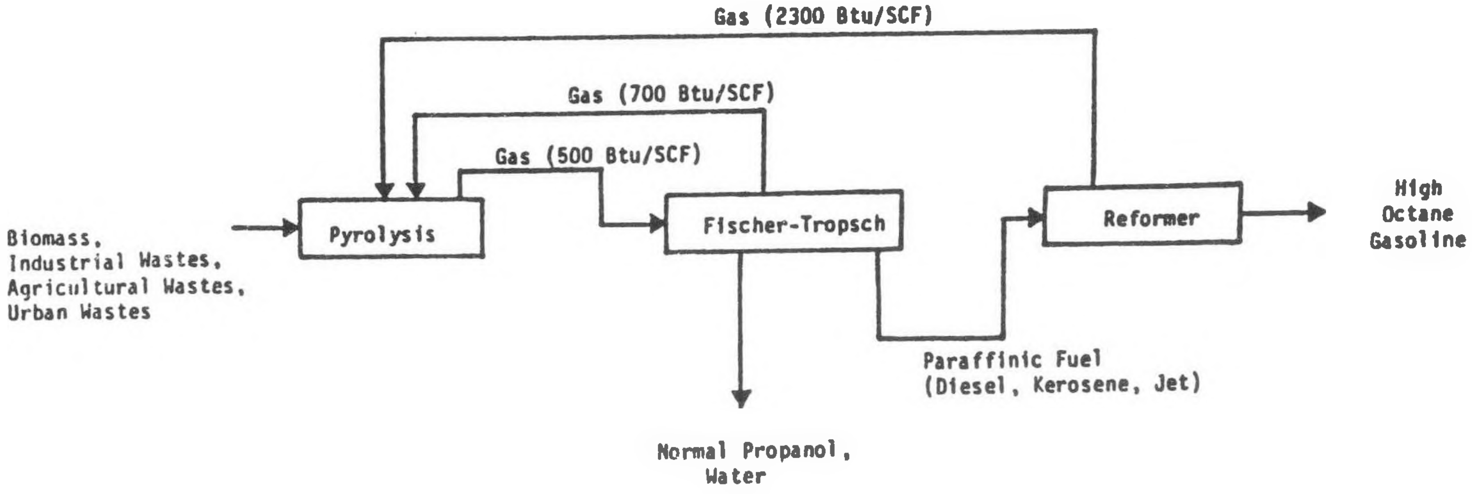


Figure 3.

Basic Chemical Conversion Scheme

high octane gasoline. Conceivably, the process could be optimized for different products at different locations depending on local marketing conditions and needs. To date most industrial interest has been in diesel type fuels for transportation vehicles (trucks, farm machinery, etc.).

A flow diagram of the continuous laboratory unit is shown in Figure 4. Capacity is about 10 lbs/hr of feedstock. The pyrolyzer can be fluidized with recycle pyrolysis gas, steam or recycle liquefaction system off gas or some combination thereof. Tars are removed in a wet scrubber. Unseparated pyrolysis gases are utilized as feed to a modified Fischer-Tropsch reactor. The liquid condensate from the reactor consists of a normal propanol-water phase and a paraffinic hydrocarbon phase. The reactor can be operated to optimize for either product. If a high octane gasoline is desired, the paraffinic fuel is passed through a conventional catalytic reformer. The normal propanol could be used as a fuel extender if blended with the hydrocarbon fuel products. Off gases from the downstream reactors are of high quality because of the accumulation of low molecular weight paraffins.

Progress in the laboratory scale system for previous ERDA/DOE contract periods (through May, 1979) have been reported in two previous Interim Reports (6,12), project Progress Reports (16) and various publications and presentations (5-11,13-15). The project history is depicted in

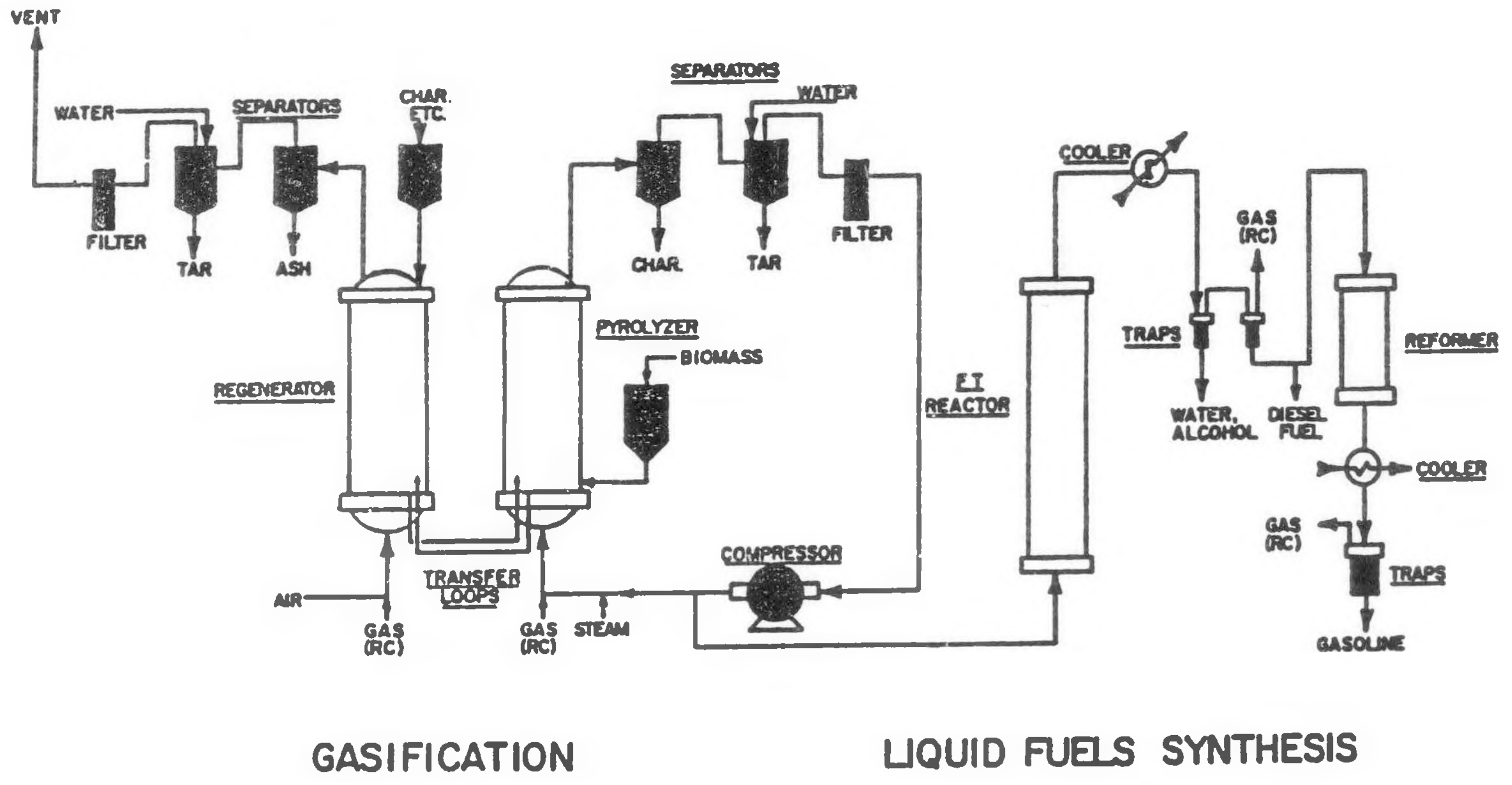


Figure 4

Conversion System Schematic

Figure 5. In general, the initial effort in the project was to develop a suitable liquefaction catalyst to convert synthesis gas representative of that obtainable from cellulosic material into gasoline suitable for use in existing internal combustion engines. A series of catalyst screening runs were performed utilizing fixed and fluidized bed reactor operating modes with a synthetic pyrolysis gas feed consisting of ethylene, hydrogen, carbon monoxide, methane and carbon dioxide from pure gas cylinders. A cobalt-alumina blended catalyst operating in a fluidized bed mode (to control the reaction temperature) was deemed to be an attractive system. A factor study (temperature, pressure, residence time, feed composition) to optimize reactor performance followed (maximize product yields subject to quality constraints). General conclusions were as follows:

(1) Two condensed phases are produced -- a paraffinic organic phase in the C_5-C_{17} range, and a water-alcohol phase with normal propanol the dominant alcohol constituent.

(2) Product composition is relatively insensitive to changes in process conditions with liquefaction reactor temperature having the largest effect.

(3) Maximum liquid hydrocarbon phase yields are produced at the following reaction conditions:

reactor temperature = 250-300°C
reactor pressure = 100-150 psig
reactor residence time = <15 seconds

GASIFICATION SYSTEM

1. 4" reactor
   - a. base point
   - b. factor studies
   - c. alternative feedstocks
   - d. integrated runs
2. 10" reactor
   - a. construction
   - b. base point
   - c. factor studies
   - d. alternative feedstocks
   - e. integrated runs

LIQUEFACTION SYSTEM

1. Fischer-Tropsch
   - a. catalyst screening/improvements
   - b. base point (2")
   - c. factor studies (2")
   - d. integrated runs (2")
   - e. construction (6", recycle)
   - f. integrated runs (6", recycle)
2. Reformer
   - a. base point
   - b. factor studies
   - c. alternative catalyst
   - d. hydrogenation, isomerization

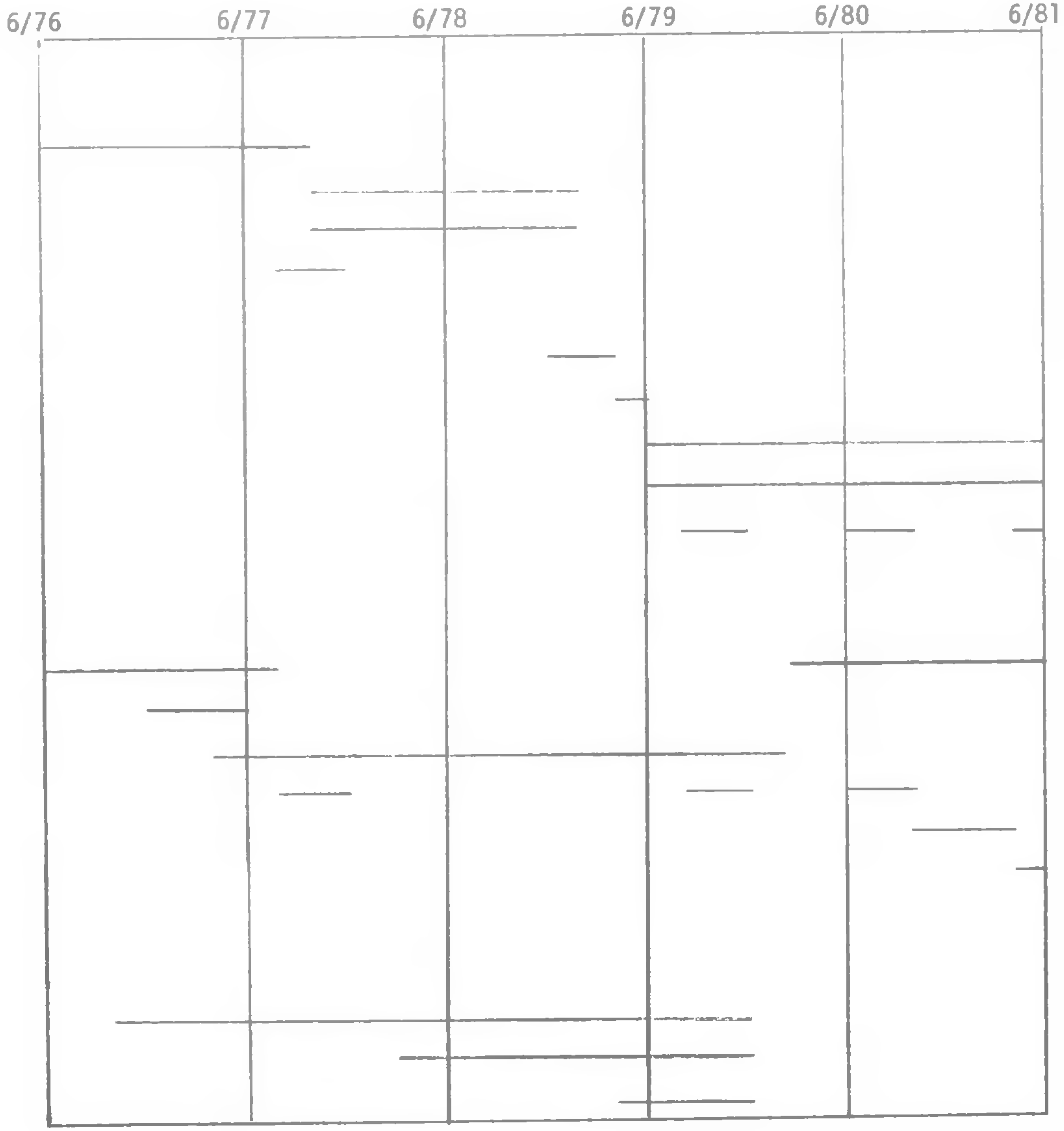


Figure 5.

Project History

H_2/CO mole ratio in feed gas = 1-1.5

C_2H_4 content in feed gas = 20 mole% +

(4) Hydrogen and ethylene in the feed gas are depleted in the liquefaction reactor for realistic pyrolysis gas compositions; about 20 mole% of the carbon monoxide is depleted.

(5) Limited feed gas composition conditions (H_2 + CO, C_2H_4 only, H_2 + C_2H_4) decrease the liquid hydrocarbon yield substantially and affect the product composition.

(6) The paraffinic liquid hydrocarbon product utilizing the cobalt-alumina catalyst has a low octane number (~ 50) but favorable cetane number (50-70). Thus the product is a candidate for a diesel, jet or kerosene type fuel but not a high octane gasoline fuel.

To achieve the goal of producing a high octane gasoline, the paraffinic liquid hydrocarbon material was fed to a conventional fixed bed catalytic reformer containing a platinum based catalyst. The desired effect of increasing the octane number was achieved with optimum operating conditions as follows:

reactor temperature = 490°C

reactor pressure = 400 psig

reactor residence time = 11 seconds

In general, the conditions that increased octane number tended to decrease reformer gasoline yields. For an octane rating of > 80, approximately a 20% volumetric yield loss was encountered. The off gas however consisted of C_1-C_4 paraffins with a heating value of ~ 2300 Btu/SCF thus indicating substantial hydrocracking reaction occurrence. Recycle of the off gas would enhance the overall process yields. Also further optimization of the reforming step should decrease the one-pass yield losses closer to the ~ 10% loss experiencedin a petroleum refinery. Work on the reforming step was halted at this point based on the advanced stage of the research and also the strong industrial interest in a diesel fuel type product rather than a high octane gasoline.

Development of the gasification step was performed in parallel with the liquefaction system studies. The initial effort was dedicated to establishing the operational reliability of the system. The possibility for premature shutdown of the gasification system is much greater than that for the liquefaction system because of the solids handling steps involved (solids feeding, hot solids transfer, tar removal). A number of modifications/improvements were accomplished for this system to improve the monitoring, control, reliability and reproducibility. Factor studies were conducted for alternative feedstock assessment, temperature effects, recycle gas type (steam, recycle pyrolysis gas) and fluidized solid type (sand, catalysts). Results are summarized as follows:

(1) A wide variety of feedstocks can be processed through the gasification system to a gas with a heating value of about 500 Btu/SCF.

(2) Some feedstocks are more attractive than others with regard to producing a high olefin content in the pyrolysis gas.

(3) The H_2/CO ratio can be manipulated over a wide range in the gasification system with steam addition. Most materials appear to exhibit an auto-catalytic effect with respect to the water-gas shift reaction (probably catalyzed by the ash components of the feedstock). A commercial water gas shift catalytic step will also shift the H_2/CO ratio.

(4) H_2S content (beyond the gasification system wet scrubber) is negligible for the feedstocks surveyed.

(5) The water gas shift reaction appears to be enhanced with an increase in pyrolysis temperature over the range of 1300-1700°F.

The operating conditions considered to be optimal for the gasification system at this point were as follows:

reactor temperature = ~ 1400°F
reactor pressure = atmospheric
residence time = < 5 seconds
fluidizing gas = steam

The outstanding remaining task for the project at the laboratory scale was to demonstrate that economically attractive product yields could be achieved (~ 40 gals diesel fuel/ton of dry, ash free feedstock) with continuous operation of the system from solids feeding to liquid product collection and utilizing commercially viable feedstocks.

CURRENT STATUS

The Work Statement for the contract period from June 1, 1980 to May 31, 1981 is contained in Appendix 1. The major equipment modifications during this period are summarized in Appendix 2. The Work Statement will be addressed by the stated major categories: (1) integrated runs, (2) factor studies, and (3) alternative feedstocks. In general, integrated run performance was always the top priority with sufficient staffing available to address this objective on a weekly basis (barring equipment modification interruptions). Factor studies and alternative feedstock assessment were addressed as secondary objectives.

Integrated Runs. Prior to this contract period, most experimental work involved separate operation of the gasification and liquefaction steps. Thus several assumptions were incorporated to project the process material balance. Continuous operation from solids feeding to liquid product collection with direct measurement of yields thus was deemed to be the prime objective of this contract period. Realistic feedstocks (near term commercial potential) and feasible catalysts (reasonable cost) were to be utilized.

The initial integrated runs were performed with the existing 2" x 6' fluidized bed liquefaction reactor with resistance wire heaters and containing a cobalt oxide-alumina catalyst. Almond prunings (from cultivated California orchards) and guayule bagasse (from native bushes in Mexico) were tested as feedstocks. Results are given in Tables 1-3 and Figure 6. As indicated (Table 2), the pyrolysis gas is of high fuel value for both feedstocks (approximately 500 Btu/SCF) but with some variation in gas composition. The water-alcohol phase from the liquefaction reactor contains about 9 wt % normal propanol for each feedstock. Chromatograms of the liquid hydrocarbon phase (Figure 6) reveals that the product from both feedstocks are very similar and in the C_7 - C_{17} range. A comparison with commercial No. 2 diesel fuel indicates that the major difference is the presence of C_7 - C_9 compounds for the experimental material. External consultation (see COO-2982-59) indicates that the experimental material should be directly usable as a transportation fuel without distillation.

A properties comparison table of the experimental liquid hydrocarbon product with commercial materials is given in Table 4. As indicated, the closest match (without distillation) is to JP-4 jet fuel. It should be emphasized that no oxygenated compounds are detected in the liquid hydrocarbon product, i.e., the oxygen in the feedstocks goes primarily to CO, CO_2, normal propanol and water.

Direct yield measurements (volume product/wt. feedstock) were not possible for the initial integrated runs due to inconsistent scale of the gasification system (larger) and the liquefaction system. Thus some generated pyrolysis gas was vented. A larger liquefaction reactor

Table 1.

Operating Conditions - Integrated Runs

	Pyrolysis Reactor		Liquid Fuels Reactor	
	Almond Prunings	Guayule Bagasse	Almond Prunings	Guayule Bagasse
Temperature, degrees F	1420	1520	(500)	
Pressure, psig	0.4	0.8	(110)	
Heat transfer media/catalyst	(sand)		(cobalt-alumina)	
Residence time, sec.	(4)		(20)	
Fluidizing gas	(pyrolysis gas)		(pyrolysis gas)	

Table 2.

Pyrolysis Reactor Gas Composition - Integrated Runs

(mole%[1])

Feedstock:	Almond Prunings	Guayule Bagasse
H_2	25.70	25.02
O_2	0.16	0.07
CO	42.68	39.61
CO_2	5.97	6.11
H_2S	0.00	0.00
CH_4	14.88	15.36
C_2H_2	0.17	0.21
C_2H_4	5.68	7.14
C_2H_6	1.05	0.63
C_3 olefins	0.21	0.00
C_3H_8	0.00	0.13
C_4 olefins	0.08	0.06
C_4H_{10}	0.01	0.00
C_5H_{12}	0.00	0.00
C_5 + olefins	3.41	5.64
total unsaturated	9.55	13.05
H_2/CO ratio	0.60	0.63

---

[1] water, nitrogen free basis

Table 3.

Liquid Fuels Reactor Water Phase Composition
Integrated Runs (wt%)

Feedstock:	Almond Prunings	Guayule Bagasse
H_2O	89.51	89.03
ethanol	0.88	0.96
2-propanol	0.77	0.25
1-propanol	8.57	9.54
2-butanol	0.12	0.10
1-butanol	0.14	0.12

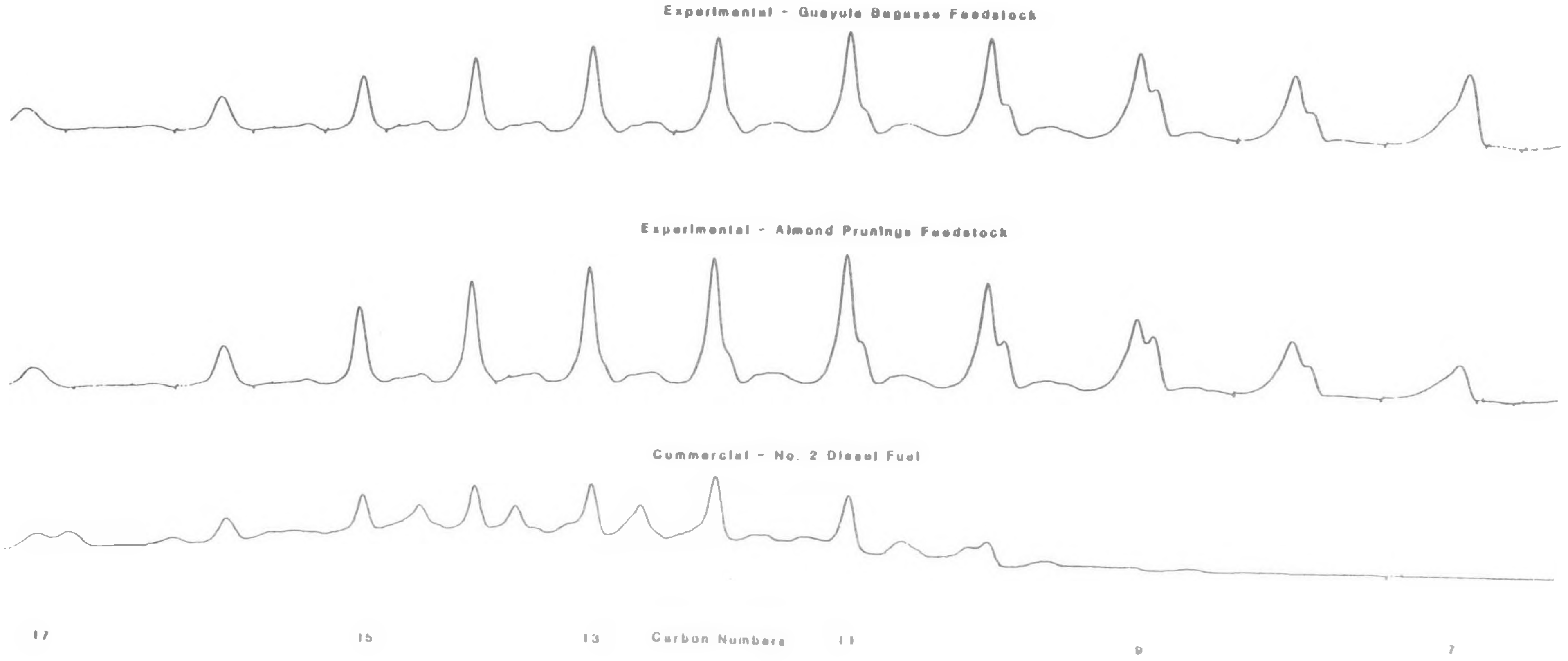


Figure 6.

<u>Liquid Fuels Reactor Hydrocarbon Phase Composition-Integrated Runs</u>

Table 4.

Properties of Fischer-Tropsch Product and Commercial Fuel Oils

		Commercial Fuel Oils			Fischer-Tropsch Product	
		No. 2 Diesel	Kerosene	JP-4	Almond Pruning Feedstock	Guayule Bagasse Feedstock
Specific gravity		.8360	.8108	.7586	.7902	.7950
Gravity, API°		37.8	43/43.4*	55/52.8*	47.6	46.5
Boiling point range, °F						
evaporated at	10%	369	336/373*	147/209*	235	238
	50%	458	410/418*	302/311*	352	414
	90%	563	479/480*	438/419*	471	535
Calculated cetane index		45.9	47.8/50.6*	48.3/46.6*	45.3	55.7
Heating value, Btu/lb.		19383	21676	22440	19354	21043

*from "Petroleum Products Handbook," McGraw-Hill, 1960.

(6" diameter x 6') was then designed, fabricated and installed to be compatible with the scale of the pyrolysis system. This system was started up in the final few weeks of the contract period utilizing iron and cobalt based catalysts. Results are summarized in Table 5. In general, the runs were an operational success with the possible exception of a poor fluidization pattern in the new liquefaction reactor (as determined by temperature profile measurements) and/or poor liquefaction catalyst activity. A run as long as 28 hours in length (continuous from solids feeding to liquid product condensation with liquefaction off-gas recycle to the pyrolysis reactor) was performed with planned shutdown. The recycle gas effect was inconclusive due to the poor liquefaction reactor conversion (thus nondepletion of the reactive components CO, H_2 and olefins). An analysis and correction of the liquefaction system problems was in progress at the end of the contract period.

The yield potential of the system is indicated in Tables 6-7 as a function of limiting assumptions and pyrolysis gas H_2/CO mole ratio and olefin content. The two tables differ in the amount of olefin content (C_2H_4). The first assumption converts the synthesis gas reactive components (H_2, CO, C_2H_4) to an "average" liquid hydrocarbon product ($C_{10}H_{22}$) plus water. The second assumption excludes water formation. The third assumption assumes that CO_2 and CH_4 could also be converted to product. Optimum yields for each assumption are listed with corres-

Table 5.

Summary of Integrated Runs Performed with a 6" Diameter Fischer-Tropsch Reactor
Feedstock: Almond Prunings

Pyrolyzer

Operating Conditions:

Biomass Feedrate (lbs/hr):	9-12
Reactor Temperature (°F):	1140-1400
Reactor Pressure (psig):	0.8-1.0
Residence Time (sec):	4.5-5.2
Fluidizing Gas[1] (lbs/hr):	30-50S+5RPG
Heat Transfer Media:	60 mesh sand

Gas Composition Summary (mole%[2]):

H_2/CO Ratio:	0.6-1.1
Olefins	10-15%

Fischer-Tropsch

Operating Conditions:

Inlet Fluidizing Gas (lbs/hr):	6-8
Reactor Temperature (°F):	480-510
Reactor Pressure (psig):	100-130
Residence Time (sec):	40-55

Catalyst Type:

Hall Chemical 72-73% Co
Alumina, MgO, K_2O

United Catalyst G64-D,
Harshaw MgO Catalyst

G64-D, Zeolon 900-H

G64-D, Alumina

---

[1] S-steam, RPG-recycled pyrolysis gas

[2] water, N_2 free basis

Table 6.

Maximum Yields

	Reaction	H_2/CO	Yield
1.	H_2, CO, C_2H_4 → $C_{10}H_{22} + H_2O$	2.21	94 gals/ton
2.	H_2, CO, C_2H_4 → $C_{10}H_{22}$	1.12	124 gals/ton
3.	H_2, CO, C_2H_4, CO_2, CH_4 → $C_{10}H_{22}$	1.05	175 gals/ton

where C_2H_4 = 10 mole %
CH_4 = 12
CO_2 = balance
gasification yields = 95

Table 7.

Maximum Yields

Reaction	H_2/CO	Yield
1. H_2, CO, C_2H_4 → $C_{10}H_{22} + H_2O$	2.55	151 gals/ton
2. H_2, CO, C_2H_4 → $C_{10}H_{22}$	1.39	168 gals/ton
3. H_2, CO, C_2H_4, CO_2, CH_4 → $C_{10}H_{22}$	1.36	213 gals/ton

where C_2H_4 = 30 mole %

CH_4 = 12

CO_2 = balance

gasification yields = 95

ponding required value of the H_2/CO mole ratio. In each case, a ratio of > 1 is required. Also an increase in olefin content is a virtue. The interpretation of the calculations is to expect yields of 50-100 gals/ton with the current state-of-the-art of the process.

A summary of product yield improvement tools considered during the contract period are listed in Table 8. These will be discussed in the next section. In general, improvement in liquefaction catalyst performance coupled with recycle of liquefaction reactor off gas (heavy in C_1-C_6 paraffins) to pyrolysis is considered to be the most promising path for demonstration of yields in the 50/100 gals/ton range.

Factor Studies. The major factor studies addressed in the contract period were as follows: (1) pyrolysis temperature, (2) pyrolysis reactor steam fluidization, (3) dolomite usage in the pyrolysis reactor, and (4) liquefaction catalyst development.

The temperature-pyrolysis gas composition profiles for almond prunings feedstock is shown in Figure 7. As indicated, hydrogen increases with temperature over the range of 1250-1750°F while the saturated and unsaturated hydrocarbon composition and carbon dioxide decline. Carbon monoxide production appears to peak at about 1500°F.

Table 8.

Product Yield Improvements

1. Increase Gasification Yields: T, Θ, catalysts, feedstock type and geometry
2. Improve Synthesis Gas Composition
    a. Increase H_2/CO: $(CO + H_2O \rightarrow H_2 + CO_2)$ T, Θ, steam, catalysts, feedstock type and geometry
    b. Increase olefins: T, Θ, dilution, recycle, catalysts, feedstock type and geometry
3. Increase Liquefaction Yields: T, P, Θ, catalysts

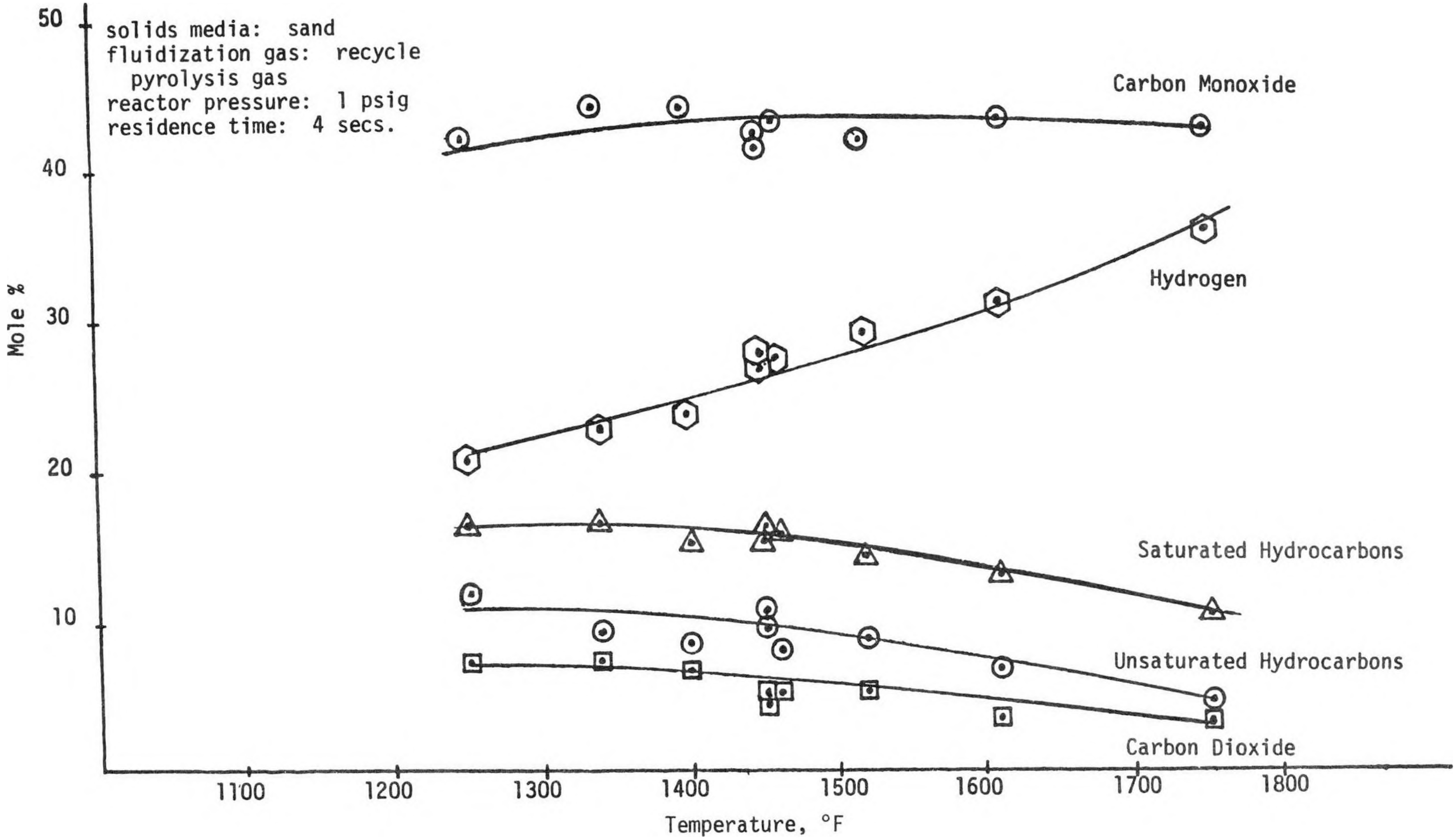


Figure 7.

Effect of Reactor Temperature on Pyrolysis Composition (Almond Prunings Feedstock)

The pyrolysis reactor is capable of being fluidized with recycle pyrolysis gas, steam, recycle liquefaction reactor off gas or some combination thereof. To maximize olefin production in the gasification step, it should be desirable to minimize the effective residence time in the pyrolysis reactor with respect to carbon monoxide, hydrogen and olefins, i.e., minimize the opportunity for gas phase reactions forming less desired synthesis gas components such as saturated paraffins. Also, previous results (6,12) have shown that, without hydrogen addition, most biomass feedstocks form a H_2/CO mole ratio of 0.5-0.8 in the synthesis gas as compared with a desired ratio of 1.0-1.5 for maximum liquid hydrocarbon fuel production. Finally, the nonreactive paraffinic hydrocarbons accumulate in the liquefaction reactor off gas. Thus the optimal pyrolysis reactor fluidization gas would appear to be a combination of steam (to produce hydrogen and deplete carbon monoxide via the water gas shift reaction, $CO + H_2O \rightarrow H_2 + CO_2$) and liquefaction reactor off gas (to supply higher molecular weight paraffinic hydrocarbons for cracking to olefins and hydrogen). The optimal combination was not established during the contract period due to liquefaction reactor problems (see previous section). However data was obtained utilizing various amounts of steam and recycle pyrolysis gas (Table 9). The objective here was to achieve 100% steam fluidization. The distribution system for pyrolysis system gas addition is as follows: (1) distributor plate, (2) solids transfer loop sparge, and (3) solids feeder sparge. Elimination of the recycle gas

Table 9

Steam Effects on Pyrolysis Gas Phase Composition

Feedstock: Guayule Bagasse

Operating Conditions[1]:	Run 1	Run 2	Run 3
Biomass Feedrate, lbs/hr:	8.0	8.0	8.0
Reactor Temperature, °F:	1100	1120	1100
Reactor Pressure, psig:	0.85	0.80	0.90
Residence Time, sec:	4.3	5.1	6.5
Fluidizing Gas, lbs/hr[2]:	48S+1.5RPG	40S+5RPG	20RPG
Heat Transfer Media	60 mesh sand		

Pyrolysis Composition (mole%[2]):	Run 1	Run 2	Run 3
H_2	27.37	27.30	19.73
O_2	0.34	0.30	0.29
CO	29.65	33.29	38.60
CO_2	8.62	9.12	7.10
CH_4	10.98	12.59	17.39
C_2H_2	0.05	0.03	0.03
C_2H_4	5.88	5.70	6.31
C_2H_6	1.42	1.57	0.96
C_3+ olefins	2.55	2.30	2.40
C_3H_8	0.15	0.14	0.27
C_4+olefins	1.63	1.60	1.45
C_4H_{10}	0.15	0.16	0.16
C_5+olefins[3]	11.23	5.91	5.31
Total Unsaturated (mole%):	21.34	15.54	15.47
H_2/CO Ratio (mole %)	0.92	0.82	0.51

---

[1] Run 1, steam fluidization + steam sparged loops + 1.5 RPG (recycle pyrolysis gas) feeder sparge
Run 2, steam fluidization + 3.5 lbs/hr RPG loop flows + 1.5 RPG feeder sparge
Run 3, RPG

[2] water, N_2 free basis

[3] C_5=, C_6+ backflush peak assumed to be predominately C_5 olefins

sparge to the feeder was not possible during the contract period because of steam condensation problems with cold biomass contact. The data in Table 9 does indicate an increase in H_2/CO ratio with increase in amount of steam addition. This effect would shift to a higher level for a higher reactor temperature (see Figure 7).

Most gasification runs to date have been performed using sand as the fluidized solid. A series of gasification runs were performed replacing sand with dolomite for almond prunings feedstock. Results are shown in Table 10 for sand (with and without steam usage) and dolomite (with and without steam usage). Clearly, steam addition increases the H_2/CO ratio for each solid and the use of dolomite shifts the effect to a much higher level. The effect is consistent with the presence of the water gas shift reaction. A series of runs for other feedstocks using dolomite + steam is planned for the new contract period. An escalation of the H_2/CO mole ratio is expected. The result could be quite significant for synthesis gas applications requiring a high H_2/CO ratio (such as some methanol synthesis processes). The virtue would be the possibility of elimination of a separate water gas shift catalytic reactor to achieve the desired ratio.

A study of alternative liquid catalyst candidates was started in the contract period. This included a detailed study of iron based catalysts as well as a reexamination of cobalt based catalysts. The

Table 10.

Effects of Dolomite as a Pyrolysis Catalyst

	Feedstock: Almond Prunings			
Operating Conditions:	No Steam	Partial Steam	No Steam	Partial Steam
Reactor Temperature, °F:	1340	1300	1390	1330
Reactor Pressure, psig:	0.8	0.8	0.9	0.9
Residence Time, sec.:	5.2	3.8	4.9	3.2
Fluidizing gas,[1] lbs/hr:	22RPG	44S+5RPG	29RPG	42S+5RPG
Heat Transfer Media/Catalyst:	sand	sand	dolomite	dolomite
Pyrolysis Gas Composition (mole%[2]):				
H_2	22.96	32.64	31.02	51.25
O_2	0.08	0.08	0.03	0.07
CO	44.87	33.52	36.82	16.43
CO_2	6.56	10.55	7.11	19.99
CH_4	14.89	7.38	16.65	9.25
C_2H_2	0.07	0.15	0.09	0.12
C_2H_4	6.11	6.28	5.15	0.60
C_2H_6	1.43	0.88	2.20	0.59
C_3+olefins	0.61	1.03	0.24	0.80
C_3H_8	0.03	0.04	0.04	0.04
C_4+olefins	0.18	0.36	0.08	0.25
C_4H_{10}	0.02	0.04	0.01	0.03
C_5+olefins	2.20	7.07	0.57	0.56
Total Unsaturated (mole%):	9.17	14.88	6.12	2.34
H_2/CO Ratio (mole%):	0.51	0.97	0.84	3.12
Gas Phase Yields (wt gas x 100/wt feedstock):	69	72	93	89

---

[1] S-steam, RPG-recycle pyrolysis gas

[2] water, N_2 free basis

[3] C_5=, C_6+ backflush peak assumed to be predominately C_5 olefins

strategy for the iron based catalyst study is indicated in Figure 8. A fixed bed small scale reactor and blended catalysts were utilized for the study. Catalyst candidates and constant reactor operating conditions are listed in Tables 11, 12. Results for the catalyst screening portion of the work (selection of best catalysts) are shown in Tables 13, 14. Based on the work to date, the most promising catalysts (highest organic yields with acceptable product constraints) are G64-D with Zeolon 900H and C73-1 with MgO. Note the lower optimal H_2/CO mole ratios (~ 0.8) for the iron based catalysts as compared with that for cobalt (1-1.5). Further work remaining on this study (Figure 8) at the end of the contract period was as follows:

(1) catalyst life (activity) study,
(2) alternate (mixed) feed gas composition,
(3) optimization with respect to temperature, pressure and residence time,
(4) experimental error assessment,
(5) ground and repelletizedcatalyst runs (more homogeneous), and
(6) mathematical model development.

Material balances were to be reported for selected runs as indicated.

The two most promising iron catalysts were assessed in single attempts at the end of the contract period in the larger scale liquefaction reactor using real pyrolysis gas (see Integrated Runs section). As mentioned, product yields were very poor (< 10 gals/ton) with an

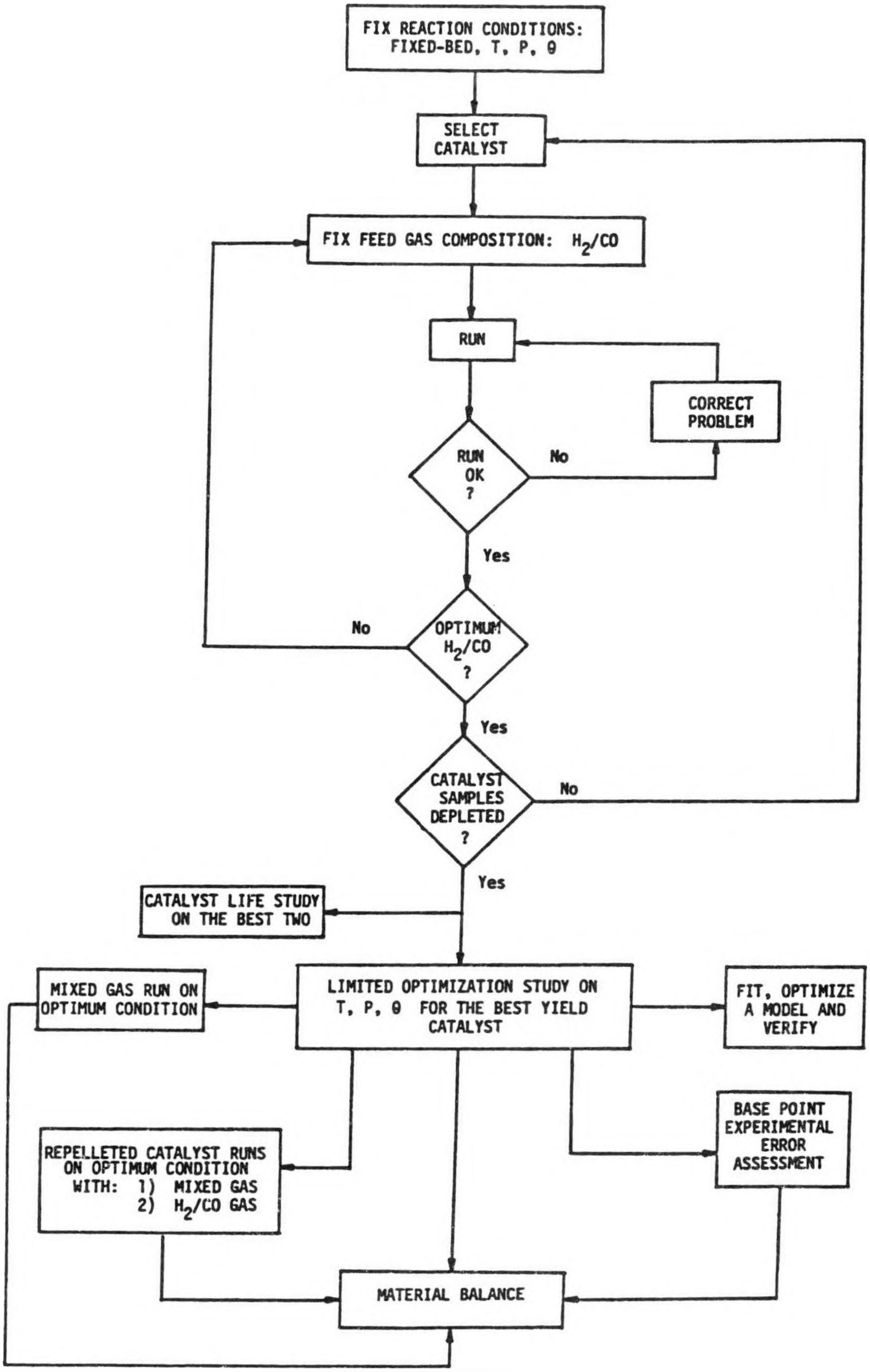


Figure 8.

Schematic Diagram for Study of Fischer-Tropsch Alternative Catalysts

Table 11.

Description of Catalysts

A. Iron Catalyst

1. C73-1 (United Catalyst)

content - triple promoted catalyst

Al_2O_3	2-3%
K_2O	0.5-0.8%
CaO	0.7-1.2%
$FeO+Fe_2O_3$	balance

2. G64-D (United Catalyst)

content - potassium promoted iron/chrome catalyst

Fe_2O_3	76%
K_2CO_3	20%
Cr_2O_3	4%

B. Support Catalyst

1. Al_2O_3 (99%)
2. MgO (98%)
3. Silica gel
4. SK500 - Linde type Y molecular sieve
5. Zeolon 900H - Norton synthetic mordenite
6. Reforming catalyst - Aeroform RHF-4A

Table 12.

Constant Reactor Operating Conditions

Temperature, °C	250
Pressure, psig	140
Volumetric feed rate, SCFH	2.5
Reactor volume, ft^3	0.0135
Residence time, sec	19.4

Table 13.

Operating Conditions and Product Analysis for Each Optimum H_2/CO Ratio Run in the C73-1 Catalyst Screening Study

Basic Catalyst		C73-1						
Mixed promoter, 3 x volume of C73-1		---	Al_2O_3	MgO	Silica Gel	SK-500	Zeolon 900H	Reforming Catalyst
Total weight of catalyst, g		720	400	400	300	350	400	350
Temperature, °C		250-327	250-280	250-260	250-371	---	250-266	250-332
Reactor character		Adiabatic fixed bed (initial temperature at 250°C)						
Pressure, psig		140						
Volumetric feedrate, SCFH		2.5						
Residence time, sec		19.44						
H_2/CO ratio		0.5	0.62	0.81	0.79	---	1.0	0.5
Mass feed rate, g/hr		56.8	52.9	47.9	48.6	---	44	56.8
Yield, $\frac{\text{g organic}}{\text{g feed-g catalyst}} \times 10^{6}$		76	57	115	144	---	68	65
Organic mass rate, g/hr		3.1	1.2	2.2	2.1	---	1.2	1.3
Grouped analysis, wt%	n-paraffins	25.6	57.0	53.5	39.1	---	47.0	58.6
	iso-paraffins	28.6	20.8	29.3	30.7		34.7	29.6
	olefins	40.4	13.0	18.8	23.4		1.3	3.5
	aromatics	---	1.3	1.7	1.9		9.8	5.1
	others	5.4	7.9	6.7	4.9		7.2	3.0
Aqueous mass rate, g/hr		4.9	6.2	5.2	3.6	---	2.3	5.2
Grouped analysis, wt%	water	95.0	98.1	96.2	96.9	---	99.8	99.8
	alcohols	5.0	1.9	3.8	3.1		0.2	0.2

Table 14.

Operating Conditions and Product Analysis for each Optimum H_2/CO Ratio Run in the G64-D Catalyst Screening Study

Basic Catalyst		G64-D						
Mixed promoter, same volume of G64-D		---	Al_2O_3	MgO	Silica Gel	SK-500	Zeolon 900H	Reforming Catalyst
Total weight of catalyst, g		400	340	340	270	300	340	300
Temperature, °C		250						
Reactor character		Isothermal fixed bed						
Pressure, psig		140						
Volumetric feed rate, SCFH		2.5						
Residence time, sec		19.44						
H_2/CO ratio		0.78	0.76	0.86	0.86	---	0.85	0.95
Mass feed rate, g/hr		48.6	49	47	47	---	46.9	44
Yield, $\frac{\text{g organic}}{\text{g feed-g catalyst}} \times 10^6$		92	159	175	164	---	174	101
Organic mass rate, g/hr		1.79	2.65	2.80	2.08		2.77	1.33
Grouped analysis, wt%	n-paraffins	21.1	52.2	31.2	23.4	---	44.2	70.0
	iso-paraffins	28.8	22.9	25.4	30.9		27.3	20.6
	olefins	38.0	12.4	28.7	37.7		17.0	0.6
	aromatics	6.1	5.4	8.2	5.6		7.5	5.9
	others	6.0	7.1	6.5	2.3		4.0	2.9
Aqueous mass rate, g/hr		2.97	3.96	6.53	5.44	---	4.55	3.96
Grouped analysis, wt%	water	95.2	97.2	95.8	95.7	---	97.6	99.8
	alcohols	4.8	2.6	4.2	4.3		2.4	0.2

analysis for cause in progress. It is expected however that iron based catalysts will be less receptive to olefins in the feed gas as compared with cobalt based catalysts. Optimization of the pyrolysis system performance for downstream iron catalyst usage is a distinct possibility and within the capabilities of the system.

A study of characterization and performance of alternative cobalt based catalysts was also started towards the end of the contract period. The purpose was to survey alternative (cheaper) vendors and achieve lower operating pressures (to minimize compression costs and for future staged reaction system development -- see CONTINUING RESEARCH). Characterization data to be accumulated included oxidation state analysis, surface area, pore volume, pore radius, elemental analysis, and surface and bulk chemistry analysis. Characterization analysis was performed on-site and via external laboratories. Data collection was in an early stage at the end of the contract period with an escalation planned for the new contract period. To aid this new phase of catalyst development work, on-site characterization capabilities will be increased in the new contract period. Also a bank of six small scale fluidized or fixed bed catalyst testing reactors will be fabricated and installed early in the new contract period with recycle capability.

<u>Alternative Feedstocks</u>. A large number of alternative feedstocks have

been under study on the project. A listing of materials presently on location is given in Table 15. The status of testing is as indicated. A listing of suppliers of feedstocks tested in the current contract period is given in Table 16. A large number of the materials in Table 15 have been processed through gasification and reported previously (6). Only a few materials (e.g., almond prunings, guayule bagasse, Eco-Fuel II) have been processed through liquefaction. With the possible exception of trace potential catalyst poisons, the synthesis gas composition data is considered an adequate predictor of liquefaction system performance however.

Pyrolysis reactor operating conditions and synthesis gas composition data for feedstocks tested in the current contract period are given in Table 17. As indicated previously, alternative feedstock testing was a secondary objective and thus was usually "piggybacked" on a run with the primary objective of an integrated performance and/or factor study. Thus the operating conditions listed in Table 17 vary somewhat, particularly with respect to temperature and fluidizing gas type. The total olefin content of the various feedstocks listed varied from 5-15 mole % while the H_2/CO mole ratio varied from 0.2 to 1.6. One unusual result was the very large amount of methane (36 mole%) produced for the cornstarch run (although perhaps influenced by the low reactor temperature -- see Figure 7). Gas phase yields for those runs where an accurate measurement was performed were approximately 80% (wt gas/wt feedstock).

Table 15

Feedstocks

Industrial Wastes

*sawdust
*fir bark
*hog fuel
cotton gin trash
*guayule bagasse
*guayule cork
*jojoba meal
euphorbia bagasse
**candelilla bagasse
lignin
kelp residue
*almond hulls
*almond shells
*paper chips
guayule resins
**sugarcane bagasse
**wheat straw
**almond prunings

Forest Residues

*creosote bush
*sugar sumac
*Arizona cypress
*pringle manzanita
*Wright silktassel
*pointleaf manzanita
*shrub live oak
*hairy mountain mahogany
*Utah juniper
*pinion pine
**greasewood
**mesquite

Urban Wastes

*Eco-Fuel II
sewage sludge

Energy Crops

*Russian thistle
**raw kelp
**euphorbia lathyris
**silver maple
**smooth sumac
common milkweed
**red tartarion honeysuckle
common elder
**giant ragweed
**field thistle
**cherry eleagnus
**pokeweed
*raw guayule
*water hyacinth
**tall boneset
**rosin weed
compass plant
**tall goldenrod
Canada wildrye
**sassafras
sweet sorgum
**coral berry
**wild bergamot
smiling sumac

Others

**corn starch
coal
*polyethylene
*polypropylene
*peat
**Portugese oak cork

Notes: *previous contract periods
**current contract period
(rest on hand but not yet evaluated)

Table 16.

Feedstock Suppliers

Corn Starch, Euphorbia Lathyris	Diamond Shamrock
Almond Prunings	Golden ByProducts, Inc. Turlock, California
Guayule Bagasse, Candelilla Bagasse	Centro de Investigacion en Quimica Aplicada Saltillo, Coahuila, Mexico
Portugese Oak Cork	Dependable Cork Morristown, N. J.
Raw Kelp	Kelco San Diego, California
Wheat Straw	Billings, Montana Source
Sugar Cane Bagasse	Combustion Equipment Associates Brockton, Massachusetts
Hog Fuel	Weyerhaeuser Corporation Tacoma, Washington
Sassafras, Tall Boneset, Silver Maple, Rosin Weed, Giant Ragweed, Tall Goldenrod, Smooth Sumac, Pokeweed, Coral Berry, Wild Bergamot, Red Tartarian Honeysuckle	USDA, Agricultural Research North Central Region Northern Regional Research Center

Table 17.

Pyrolysis Operating Conditions and Resulting Gasification Composition - Alternative Feedstock Study

Operating Conditions:	Hog Fuel	Candella Bagasse	Sugar-Cane Bagasse	Raw Kelp[3]	Wheat Straw[3]	Sassa-fras	Tall Boneset	Silver Maple	Rosin Weed
Reactor Temperature, °F:	1200	1420	1400	1500	1600	1190	1140	1080	940
Reactor Pressure, psig:	0.9	1.0	0.8	0.9	0.8	0.9	0.9	0.9	0.9
Residence Time, sec.:	4.8	3.2	4.8	3.7	4.7	4.0	4.7	5.0	5.2
Fluidizing Gas,[1] lbs/hr:	30S+5RPG	45S+5RPG	30S+5RPG	22RPG	22RPG	45S+5RPG	30S+5RPG	30S+5RPG	30S+5RPG
Heat Transfer Media:	sand	sand	sand	sand	sand	sand	sand	sand	sand
Pyrolysis Gas Composition (mole%[2])									
H_2	16.36	33.69	28.60	42.44	30.19	31.87	20.32	15.89	9.91
O_2	0.77	0.08	0.01	8.36	0.17	0.07	0.02	0.03	0.03
CO	36.25	36.17	36.74	27.36	48.27	36.00	35.15	44.64	52.32
CO_2	8.10	10.10	8.96	11.52	4.05	8.91	9.77	8.90	11.43
CH_4	23.14	8.80	13.54	7.97	14.55	7.30	16.06	14.54	18.45
C_2H_2	0.07	0.17	0.39	---	---	0.08	0.03	0.05	0.06
C_2H_4	4.73	7.86	7.29	1.43	2.57	6.84	8.22	4.39	1.07
C_2H_6	1.87	1.27	1.42	0.91	0.20	1.62	3.02	2.09	1.62
C_3+olefins	1.46	0.60	1.00	---	---	2.29	3.12	2.14	0.68
C_3H_8	0.06	0.00	0.05	---	---	0.16	0.20	0.23	1.19
C_4+olefins	2.35	0.00	0.31	---	---	0.91	1.46	0.10	0.27
C_4H_{10}	0.18	0.00	0.30	---	---	0.09	0.16	0.13	0.06
C_5+olefins[4]	4.64	1.24	1.39	---	---	3.86	2.46	5.97	2.90
Total Unsaturated (mole%):	13.26	9.82	10.37	---	---	14.00	15.30	13.55	4.99
H_2/CO Ratio (mole%)	0.45	0.93	0.77	1.55	0.63	0.89	0.58	0.36	0.19

---

[1] S-steam, RPG-recycle pyrolysis gas

[2] water, N_2 free basis

[3] Quantity on hand prohibited a complete analysis

[4] $C_5^{=}$, C_6^{+} backflush peak assumed to be predominately C_5 olefins

Table 17. (Continued)

Pyrolysis Operating Conditions and Resulting Gasification Composition - Alternative Feedstock Study

Operating Conditions:	Giant Ragweed	Tall Golden-rod	Smooth Sumac	Poke-Weed	Coral-Berry	Wild Berga-mot	Corn Starch	Red Tartarian Honeysuckle	
Reactor Temperature, °F:	1420	1260	1350	1260	1200	1220	970	1225	1400
Reactor Pressure, psig:	0.8	1.4	0.8	1.0	1.0	1.0	1.0	0.7	0.8
Residence Time, sec.:	4.1	4.25	4.9	5.0	5.3	5.2	5.0	5.2	3.4
Fluidizing Gas,[1] lbs/hr:	30S+5RPG	35S+5RPG	30S+5RPG	30S+5RPG	30S+5RPG	30S+5RPG	30S+5RPG	30S+5RPG	45S+5RPG
Heat Transfer Media:	sand	sand	sand	sand	sand	sand	sand	sand	sand
Pyrolysis Gas Composition (mole%[2]):									
H_2	37.14	37.02	34.98	37.52	28.37	36.85	10.41	25.32	44.08
O_2	0.04	0.02	0.01	0.02	0.01	0.01	0.12	0.01	0.06
CO	28.49	29.29	25.36	24.45	31.33	24.18	24.10	28.25	28.41
CO_2	11.07	7.81	11.44	14.93	11.65	11.50	18.51	26.06	9.26
CH_4	12.21	15.48	12.09	6.66	12.97	14.35	35.50	13.64	7.50
C_2H_2	0.17	0.02	0.18	0.13	0.07	0.15	0.00	0.11	0.18
C_2H_4	7.79	2.78	9.83	7.66	6.58	6.01	1.98	1.87	8.47
C_2H_6	1.06	1.35	1.50	1.56	1.66	2.35	1.12	0.89	0.81
C_3+olefins	0.76	1.87	1.35	1.75	1.43	1.39	1.33	0.14	0.74
C_3H_8	0.01	0.14	0.04	0.19	0.06	0.18	0.09	0.12	0.00
C_4+olefins	0.17	1.13	0.56	1.52	0.52	0.55	0.52	0.04	0.26
C_4H_{10}	0.01	0.11	0.04	1.00	0.06	0.05	0.08	0.01	0.02
C_5+olefins[3]	1.06	2.97	2.63	2.61	5.28	2.47	6.25	2.45	0.21
Total Unsaturated (mole%):	9.95	8.78	14.54	13.67	13.87	10.57	10.08	4.612	9.86
H_2/CO Ratio (mole%):	1.30	1.26	1.38	1.53	0.90	1.52	0.43	0.90	1.55

---

[1] S-steam, RPG-recycle pyrolysis gas

[2] water, N_2 free basis

[3] $C_5^=$, C_6^+ backflush peak assumed to be predominately C_5 olefins

The most spectacular feedstock with regard to olefin production reported previously (6) was guayule cork with a total olefin composition as high as 39 mole % in the pyrolysis gas. This material is a byproduct of an extraction facility in Saltillo, Mexico with the primary purpose of extracting natural rubber from raw guayule plants. Thus it was not known whether the high olefin content obtained from guayule cork was a function of possible residual latex content or rather a function of the cork composition itself. In an effort to isolate the cause for this result, a supply of commercial cork (Portugese Oak Cork) was purchased and processed through gasification. Results are compared with that of guayule cork in Table 18. Again, a large amount of olefins was obtained (26 mole%). This result indicated that the high performance of the guayule cork was a function of the cork composition and not a result of inefficient latex extraction.

The results from the alternative feedstocks studies and particularly the cork results, launched a study to relate feedstock composition to gasification system performance (partially funded by the USDA, Science and Education Administration, Grant No. 59-2043-0-2-094-0). As an initial attempt, crude protein, polyphenol, oil and polymeric hydrocarbon fraction data was determined on a number of feedstocks processed in the laboratory. Results are shown in Table 19. The bulk of the feedstock extractions were performed at the USDA Northern Regional Research Center (Peoria, Illinois). The procedures have been described in the literature (see, for example, reference 20). Additional feedstock

Table 18.

Comparison Data for Pyrolysis of Cork Type Feedstocks

Operating Conditions:	Feedstock: Guayule Cork			Portugese Oak Cork (Coml. Cork)
Reactor Temperature, °F:	1300	1200	1210	1080
Reactor Pressure, psig:	0.8	0.9	0.91	0.9
Residence Time, sec:	7.5	1.35	4.63	5.0
Fluidizing Gas[1], lbs/hr:	17RPG	95S+5RPG	22RPG	30S+5RPG
Heat Transfer:	sand	sand	sand	sand
Pyrolysis Gas Composition (mole%[2]):				
H_2	20.57	24.51	14.32	14.18
O_2	0.17	0.47	0.04	0.01
CO	22.14	10.87	22.23	33.07
CO_2	3.77	10.76	8.21	4.46
CH_4	26.03	10.95	27.75	19.68
C_2H_2	0.05	0.04	0.00	0.00
C_2H_4	14.80	16.67	11.03	11.74
C_2H_6	4.79	3.24	4.62	2.15
C_3+olefins	3.04	6.49	4.16	5.67
C_3H_8	0.16	0.25	0.19	0.24
C_4+olefins	0.83	2.65	1.45	1.67
C_4H_{10}	0.08	0.21	0.02	0.11
C_5+olefins[3]	3.58	12.88	3.96	7.02
Total Unsaturated (mole%):	22.30	38.73	20.60	26.10
H_2/CO Ratio (mole%):	0.92	2.25	0.64	0.43

---

[1] S-steam, RPG-recycled pyrolysis gas

[2] water, N_2 free basis

[3] C_5=, C_6+ backflush peak assumed to be predominately C_5 olefins

Table 19.

Summary of Feedstock Analyses, Operating Conditions, and Gasification Results

	FEEDSTOCK ANALYSIS[1]		PYROLYSIS REACTOR PERFORMANCE								
			Operating Conditions[2]			Composition (mole%)[3] Summary					
FEEDSTOCK	Ash (wt%)	Extraction Fractions (wt%)	Fluidizing Gas (Btu/lb)[5]	Temp. (°F)	Res. (sec)	H_2	CO	H_2/CO	C_2H_4	Total Olefins	Paraffins
Jojoba	3.04	25.3,13.0,9.2,0.1	23RPG	1320	4.35	11.96	37.56	0.32	9.75	13.39	26.69
Water Hyacinth	18.97	7.8, 6.1,1.0,0.4	19RPG	1270	4.6	23.00	42.43	0.54	3.52	4.56	16.02
Raw Guayule	5.14	4.3, 8.9,2.3,10.4	19RPG	1310	4.6	17.28	34.98	0.49	5.54	10.61	28.58
Russian Thistle	15.45	9.2, 3.1,0.8,0.2	20RPG	1280	4.5	26.37	36.08	0.73	3.21	4.98	17.96
Guayule Cork	3.53	6.2, 6.6,6.0,2.3	19RPG	1210	4.6	14.32	22.73	0.64	11.03	20.60	34.58
Guayule Cork	3.53	6.2, 6.6,6.0,2.3	22RPG	1300	5.0	20.57	22.14	0.92	14.80	22.30	31.06
Guayule Cork	3.53	6.2, 6.6,6.0,2.3	95S+5RPG	1200	1.3	24.51	10.87	2.25	16.67	38.73	14.65
Sugar Sumac	5.3	3.7,16.3,2.8,nil	22RPG	1200	4.1	28.89	31.88	0.90	5.75	10.42	18.25
Wright Silktassel	3.2	1.8, 4.6,2.6,0.38	22RPG	1320	4.6	25.64	30.69	0.72	7.30	11.89	18.32
Utah Juniper	4.2	3.4, 6.7,1.3,0.19	22RPG	1300	4.5	28.83	39.54	0.73	6.56	7.33	17.86
Creosote Bush	3.8	6.4, 5.7,0.5,0.08	22RPG	1380	4.5	25.99	39.43	0.65	6.48	10.24	16.61
Hairy Mountain Mahogany	3.1	4.8, 8.1,1.2,0.14	22RPG	1380	4.2	27.61	37.84	0.72	10.26	12.83	16.91
Point Manzanita	1.7	2.0,10.4,0.9,0.33	22RPG	1380	5.2	24.46	35.50	0.68	5.64	12.85	16.28
Scrub Live Oak	3.1	4.6, 7.4,1.0,0.09	22RPG	1400	5.2	27.99	41.28	0.67	5.56	8.13	18.00
Pringle Manzanita	2.2	2.1,11.4,0.6,0.27	22RPG	1400	4.0	24.99	40.68	0.61	6.29	11.11	16.42
Arizona Cypress	4.5	1.6, 0.5,2.0,nil	22RPG	1350	4.5	26.64	38.40	0.69	6.40	10.34	17.52
Pinion Pine	3.3	2.6, 5.0,3.0,0.26	22RPG	1420	5.3	25.82	41.78	0.61	6.33	10.00	17.56
Mesquite	4.4	6.5, 4.8,0.96,0.08	21RPG	1690	3.5	33.01	44.35	0.74	2.61	5.01	18.46
Commercial Cork	2.76	7.7, 3.2,2.2,0.1	30S+5RPG	1180	4.9	14.18	33.07	0.42	11.74	26.80	22.18
Tartarian Honeysuckle	5.19	10.2,15.8,3.4,1.77	45S+5RPG	1400	3.2	44.01	28.41	1.55	8.47	9.86	8.33
Sassafras	3.14	8.9,14.4,5.7,0.23	45S+5RPG	1190	4.0	31.87	36.00	0.89	7.30	14.00	10.78
Tall Boneset	6.51	8.6,10.8,5.9,0.56	30S+5RPG	1140	4.7	20.32	35.15	0.58	8.22	15.30	19.49
Silver Maple	4.71	16.3,19.8,2.4,0.39	30S+5RPG	1080	5.0	15.89	44.64	0.36	4.39	13.55	16.99
Rosin Weed	9.35	6.2, 7.0,2.8,0.79	30S+5RPG	940	5.2	9.91	52.32	0.19	1.07	4.99	21.32
Giant Ragweed	11.45	11.4, 4.4,8.3,0.60	30S+5RPG	1420	4.1	37.14	28.49	1.30	7.79	9.95	13.29
Tall Goldenrod	7.47	---, 5.7,2.8,0.92	35S+5RPG	1260	4.3	37.02	29.29	1.20	2.78	8.78	16.95
Smooth Sumac	---	---,20.2,5.9,0.21	30S+5RPG	1350	4.9	34.98	25.36	1.38	9.83	14.54	13.67
Pokeweed	---	15.5, 5.9,3.4,0.17	30S+5RPG	1260	5.0	37.52	24.45	1.53	7.66	13.67	9.41
Coralberry	---	5.9,11.1,2.3,0.81	30S+5RPG	1200	5.3	28.37	31.33	0.90	6.58	12.87	14.75
Wild Bergamot	7.15	---, 6.9,2.4,1.24	30S+5RPG	1220	5.2	36.85	24.14	1.52	6.01	10.57	16.93

---

[1] dry wt. basis

[2] fluidizing media: sand, operating pressure 0.8 - 1.0 psig

[3] water, N_2 free basis; balance of analysis = CO_2

[4] protein, polyphenol, oil, hydrocarbon fractions

[5] S-steam, RPG-recycled pyrolysis product gas

characterization data currently being accumulated include heating value and ash content. The data will be analyzed by regression analysis techniques (reactor performance as a function of operating conditions and feedstock analysis) in an attempt to relate feedstock analysis data to reactor performance. A further breakdown of the extracted fractions may be required to achieve the desired relationship. This effort continues into the new contract period. The ultimate goal is to predict a priori the liquid fuel production capability of a given biomass specie from feedstock characterization data.

CONTINUING RESEARCH

The Work Statement for the renewal period from June 1, 1981 to May 31, 1982 consists of the following tasks: (1) staged reaction system development, (2) alternative feedstock development, (3) alternative products development, (4) gasification system regenerator analysis, and (5) factor studies.

Staged Reaction System. The objective is to develop a two stage reaction system within a single vessel where the first stage serves as the gasifier and the second stage is the liquefaction reactor. A prototype system is presently being developed with "seed" funds from the Arizona Solar Energy Commission. The virtues are considerable process simplification with elimination of separate reactors with an intermediate compressor. The major obstacle is development of suitable catalysts whereas both stages can be operated at the same pressure. Success with this task will result in a significant reduction in the capacity required for a commercial plant to be economically viable.

Alternative Feedstocks. A number of feedstocks have been investigated through the gasification step. A few have been processed through the gasification-liquefaction system. The list includes cellulosic materials, synthetic polymers, preprocessed municipal refuse and peat. Many requests are received from industry, government laboratories and other university projects. It is anticipated that this role will be continued with increased emphasis on utilizing the "total" waste materials from an industrial process (say leaves, bagasse, resins from a plant extraction process). Thus liquid feed capabilities will be added to the system for waste oils and resin type materials. Compound analysis of feedstocks is anticipated in this task area.

Alternative Products. The product emphasis to date has been centered on paraffinic liquid fuel (e.g., diesel) and high octane gasoline. Other products are possible with the same basic equipment, e.g., olefins, oxygenated hydrocarbons. Again, the major development effort will be on alternative catalysts to optimize for desired products.

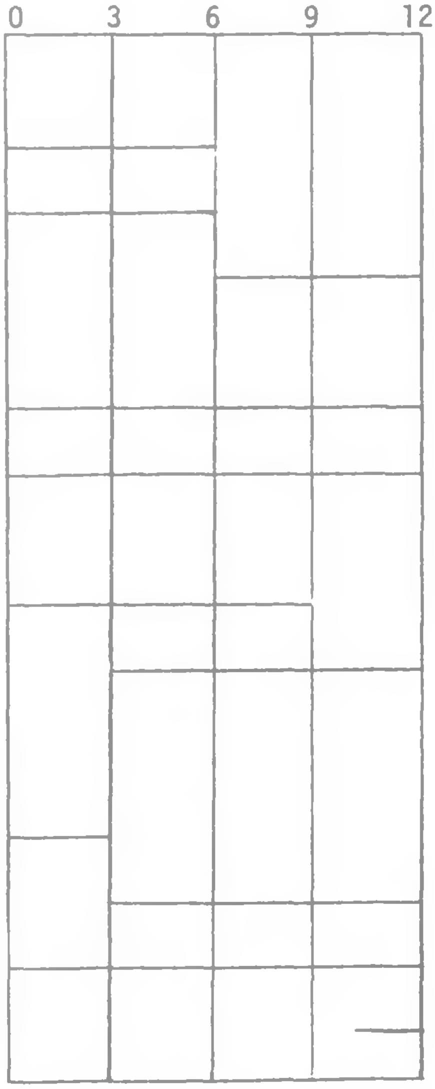
Gasification System Regenerator Analysis. All work to date has involved fueling the regenerator with propane. On a commercial scale, the fuel will be char, recycle gas and/or solid feedstock. This task will implement, characterize and assess a realistic commercial heating mode.

Factor Studies. Factor studies are a continuing phase of any chemical process development project. Thus any alternative feedstock and/or product will require adjustment of process conditions to optimize process performance. The normal factor candidates are reactor temperature, pressure, residence time, reactant composition and/or geometry and catalyst type and composition.

A task schedule is attached.

TASK SCHEDULE

1. Staged Reaction System
   - a. catalyst development
   - b. fabrication
   - c. testing
2. Alternative Feedstocks
   - a. compound analysis
   - b. processing
3. Alternative Products
   - a. catalyst development
   - b. process testing
4. Gasification System: Regenerator Analysis
   - a. fabrication
   - b. testing
5. Factor Studies
6. Report



ECONOMICS

A comprehensive economic assessment of the project was performed during the past contract period by Energetics, Inc. (21). The report includes an assessment of cellulosic waste availability and cost, ASU process feedstock cost ceiling analysis, potential petroleum energy savings and cost impacts of the ASU process and a cost comparison of various emerging thermochemical conversion to liquid fuels technologies. Tables 20, 21, and 22 display, for illustration, some of the detailed capital cost estimates developed for 1985, 1990, and 1995 plant starts respectively. These tables show the total capital requirement for a 1000 TPD (dry feedstock equivalent) capacity plant. Working capital and start-up expenses are varied with product yield and feedstock moisture as noted in the tables. Plant operating costs, revenues, and the derivation of the feedstock delivered cost ceiling for the 1000 TPD plant are shown for illustration in Tables 23, 24 and 25.

Table 26 illustrates a cost comparison for various proposed direct and indirect liquefaction systems to convert biomass to liquid fuels. As indicated, the only process that produces a product that is less costly than the ASU product is Tech-Air's pyrolytic oil. However, further refining of pyrolytic oil would be required before direct substitution for petroleum based products is feasible.

Table 20.

Capital Cost Estimation, 1985 Start (21)

Dry Feed Capacity: 1000 TPD
Operation Start Date: 1985 (Constant dollar base year)
Plant Factor: 90%

COSTS-MILLIONS OF BASE YEAR DOLLARS

Feedstock Moisture Content

	20%				35%				50%			
	Yield (gal/dry ton)				Yield (gal/dry ton)				Yield (gal/dry ton)			
	40	60	80	100	40	60	80	100	40	60	80	100
Installed Costs[a]	31.90	31.90	31.90	31.90	33.15	33.15	33.15	33.15	35.05	35.05	35.05	35.05
Construction Indirects at 41%	13.08	13.08	13.08	13.08	13.59	13.59	13.59	13.59	14.37	14.37	14.37	14.37
Engineering at 8%	2.55	2.55	2.55	2.55	2.65	2.65	2.65	2.65	2.80	2.80	2.80	2.80
Installed Facilities	47.53	47.53	47.53	47.53	49.39	49.39	49.39	49.39	52.32	52.32	52.32	52.32
Project Contingency at 15%	7.13	7.13	7.13	7.13	7.41	7.41	7.41	7.41	7.85	7.85	7.85	7.85
Capital Investment	54.66	54.66	54.66	54.66	56.80	56.80	56.80	56.80	60.17	60.17	60.17	60.17
Land at 3.8% of Installed Costs	1.21	1.21	1.21	1.21	1.26	1.26	1.26	1.26	1.33	1.33	1.33	1.33
Total Investment	55.87	55.87	55.87	55.87	58.06	58.06	58.06	58.06	61.50	61.50	61.50	61.50
Working Capital[b]	.65	.91	1.20	1.49	.99	1.27	1.56	1.85	1.55	1.84	2.13	2.43
Interest Expenses During Construction[c]	4.71	4.71	4.71	4.71	4.89	4.89	4.89	4.89	5.18	5.18	5.18	5.18
Less Investment Tax Credit[d]	(5.59)	(5.59)	(5.59)	(5.59)	(5.81)	(5.81)	(5.81)	(5.81)	(6.15)	(6.15)	(6.15)	(6.15)
NET CAPITAL REQUIREMENT	55.65	55.90	56.19	56.48	58.13	58.41	58.70	58.99	62.08	62.37	62.66	62.96
Start-up Expenses[e]	1.52	1.84	2.18	2.54	1.94	2.28	2.63	2.99	2.62	2.97	3.33	3.68
TOTAL CAPITAL REQUIREMENT	57.16	57.74	58.37	59.02	60.07	60.69	61.33	61.98	64.70	65.34	65.99	66.64

NOTES:
- a. At 9% price escalation per year.
- b. Working capital at 45 days net cash operating expenses, 15 days' feed at $20.00/ton.
- c. At 15%, net of 48.16% income tax reduction.
- d. Assumed continued at 10% of total investment.
- e. Start-up estimated at two month's operating expenses, including feedstock supply at $20.00/ton (1985).

SOURCE: Mittelhauser Corporation, and EIA, "Annual Report to Congress, 1979."

Table 21.

Capital Cost Estimation, 1990 Start (21)

Dry Feed Capacity: 1000 TPD
Operation Start Date: 1990 (Constant dollar base year)
Plant Factor: 90%

COSTS-MILLIONS OF BASE YEAR DOLLARS

Feedstock Moisture Content

	20%				35%				50%			
	Yield (gal/dry ton)				Yield (gal/dry ton)				Yield (gal/dry ton)			
	40	60	80	100	40	60	80	100	40	60	80	100
Installed Costs[a]	49.08	49.08	49.08	49.08	51.00	51.00	51.00	51.00	53.93	53.93	53.93	53.93
Construction Indirects at 41%	20.12	20.12	20.12	20.12	20.91	20.91	20.91	20.91	22.11	22.11	22.11	22.11
Engineering at 8%	3.93	3.93	3.93	3.93	4.08	4.08	4.08	4.08	4.31	4.31	4.31	4.31
Installed Facilities	73.13	73.13	73.13	73.13	75.99	75.99	75.99	75.99	80.35	80.35	80.35	80.35
Project Contingency at 15%	10.97	10.97	10.97	10.97	11.40	11.40	11.40	11.40	12.05	12.05	12.05	12.05
Capital Investment	84.10	84.10	84.10	84.10	87.39	87.39	87.39	87.39	92.40	92.40	92.40	92.40
Land at 3.8% of Installed Costs	1.86	1.86	1.86	1.86	1.94	1.94	1.94	1.94	2.05	2.05	2.05	2.05
Total Investment	85.96	95.96	85.96	85.96	89.33	89.33	89.33	89.33	94.45	94.45	94.45	94.45
Working Capital[b]	.92	1.40	1.92	2.46	1.54	2.05	2.58	3.12	2.56	3.09	3.62	4.16
Interest Expenses During Construction[c]	7.25	7.25	7.25	7.25	7.53	7.53	7.53	7.53	7.96	7.96	7.96	7.96
Less Investment Tax Credit[d]	(8.60)	(8.60)	(8.60)	(8.60)	(8.93)	(8.93)	(8.93)	(8.93)	(9.44)	(9.44)	(9.44)	(9.44)
NET CAPITAL REQUIREMENT	85.53	86.01	86.53	87.07	89.44	89.98	90.51	91.05	95.53	96.06	96.59	97.13
Start-up Expenses[e]	2.22	2.81	3.44	4.10	2.98	3.60	4.24	4.90	4.21	4.87	5.51	6.17
TOTAL CAPITAL REQUIREMENT	87.75	88.82	89.97	91.17	92.45	93.58	94.75	95.95	99.74	100.93	102.10	103.30

NOTES:
- a. At 9% price escalation per year.
- b. Working capital at 45 days net cash operating expenses, 15 days' feed at $20.00/ton.
- c. At 15%, net of 48.16% income tax reduction.
- d. Assumed continued at 10% of total investment.
- e. Start-up estimated at two month's operating expenses, including feedstock supply at $20.00/ton (1985).

SOURCE: Mittelhauser Corporation, and EIA, "Annual Report to Congress, 1979."

Table 22.

Capital Cost Estimation, 1995 Start (21)

Dry Feed Capacity: 1000 TPD
Operation Start Date: 1995 (Constant dollar base year)
Plant Factor: 90%

COSTS-MILLIONS OF BASE YEAR DOLLARS

	Feedstock Moisture Content											
	20%				35%				50%			
	Yield (gal/dry ton)				Yield (gal/dry ton)				Yield (gal/dry ton)			
	40	60	80	100	40	60	80	100	40	60	80	100
Installed Costs[a]	75.75	75.52	75.52	75.52	78.48	78.48	78.48	78.48	82.98	82.98	82.98	82.98
Construction Indirects at 41%	30.96	30.96	30.96	30.96	32.18	32.18	32.18	32.18	34.02	34.02	34.02	34.02
Engineering at 8%	6.04	6.04	6.04	6.04	6.28	6.28	6.28	6.28	6.64	6.64	6.64	6.64
Installed Facilities	112.52	112.52	112.52	112.52	116.94	116.94	116.94	116.94	123.64	123.64	123.64	123.64
Project Contingency at 15%	16.88	16.88	16.88	16.88	17.54	17.54	17.54	17.54	18.55	18.55	18.55	18.55
Capital Investment	129.40	129.40	129.40	129.40	134.48	134.48	134.48	134.48	142.19	142.19	142.19	142.19
Land at 3.8% of Installed Costs	2.87	2.87	2.87	2.87	2,99	2.98	2.98	2.98	3.15	3.15	3.15	3.15
Total Investment	132.27	132.27	132.27	132.27	137.46	137.46	137.46	137.46	145.34	145.34	145.34	145.34
Working Capital[b]	1.22	2.11	3.06	4.05	2.35	3.29	4.27	5.25	4.20	5.19	6.17	7.15
Interest Expenses During Construction[c]	11.15	11.15	11.15	11.15	11.59	11.59	11.59	11.59	12.25	12.25	12.25	12.25
Less Investment Tax Credit[d]	(13.23)	(13.23)	(13.23)	(13.23)	(13.75)	(13.75)	(13.75)	(13.75)	(14.53)	(14.53)	(14.53)	(14.53)
NET CAPITAL REQUIREMENT	131.41	132.30	133.25	134.24	137.65	138.59	139.57	140.55	147.26	148.25	149.23	150.21
Start-up Expenses[e]	3.15	4.23	5.39	6.59	4.53	5.67	6.85	8.06	6.78	7.98	9.17	10.37
TOTAL CAPITAL REQUIREMENT	134.56	136.53	138.64	140.83	142.18	144.26	146.43	148.61	154.04	156.23	158.40	160.58

NOTES:
- a. At 9% price escalation per year.
- b. Working capital at 45 days net cash operating expenses, 15 days' feed at $20.00/ton.
- c. At 15%, net of 48.16% income tax reduction.
- d. Assumed continued at 10% of total investment.
- e. Start-up estimated at two month's operating expenses, including feedstock supply at $20.00/ton (1985).

SOURCE: Mittelhauser Corporation, and EIA, "Annual Report to Congress, 1979."

Table 23.

O&M Cost Estimation and Feedstock Cost Ceiling, 1985 Start (21)

Dry Feed Capacity: 1000 TPD
Operation Start Date: 1985 (Constant dollar base year)
Plant Factor: 90%

ANNUAL COSTS --- THOUSANDS OF BASE YEAR DOLLARS

Feedstock Moisture Content

	20%				35%				50%			
	Yield (gal/dry ton)				Yield (gal/dry ton)				Yield (gal/dry ton)			
	40	60	80	100	40	60	80	100	40	60	80	100
Payroll[a]	1360	1360	1360	1360	1396	1396	1396	1396	1396	1396	1936	1396
Operating Supplies at 15% Oper. Payroll	89	89	89	89	94	94	94	94	94	94	94	94
Maintenance Supplies at 2.25% Capital Investment	1230	1230	1230	1230	1278	1278	1278	1278	1354	1354	1354	1354
Total Supplies[a]	1319	1319	1319	1319	1372	1372	1372	1372	1448	1448	1448	1448
Electricity[b]	442	442	442	442	457	457	457	457	478	478	478	478
Purchased Gas Fuel (By-Product Credit)[c]	(2340)	(416)	1652	3792	0	2030	4146	6286	3878	6016	8132	10272
Outside Services[d]	93	93	93	93	93	93	93	93	93	93	93	93
Local Taxes and Insurance at 3% Total Investment[e]	1676	1676	1676	1676	1742	1742	1742	1742	1845	1845	1845	1845
TOTAL ANNUAL O&M EXPENSES EXCLUDING FEEDSTOCK	2550	4474	6542	8682	5060	7090	9206	11346	9138	11276	13392	15532
Annual Capital Cost (CRF=.16)	9146	9238	9339	9443	9611	9710	9813	9917	10352	10454	10558	10662
Income Tax at 48.16%[h]	5668	5739	5817	5897	5973	6049	6129	6209	6460	6538	6618	6699
Gross Revenue[f]	18790	28186	37580	46976	18790	28186	37580	46976	18790	28186	37580	46976
Feedstock Cost at 0.160 CRF[g]	1426	8735	15882	22954	(1854)	5337	12432	19504	(7160)	(82)	7012	14083
1985 Feedstock Cost in dollars/dry ton	4.34	26.59	48.35	69.87	(5.64)	16.25	37.84	59.37	(21.80)	(0.25)	21.35	42.87

NOTES:
a. Escalated at 9.0% per year.
b. Escalated at 8.6% per year, base price 6.13 cents/kWh in 1985.
c. Escalated at 12.9% per year, base price \$5.96/10^6 Btu in 1985 for purchased fuel; \$5.36/10^6 Btu in 1985 for excess by-product gas credit.
d. Escalated at 8.0% per year (assumed rate of general inflation).
e. Fixed annual expense.
f. Sale of product at refiner's price, distillate fuel oil; escalated at 10.5% per year, base price \$1.43/gal in 1985.
g. 15% ROI, 20 year investment life; feedstock cost assumed to escalate at 8.0% per year.
h. Income Taxes = 48.16/51.84 x (Annual Capital Recovery - 1/20 (Capital Investment + Startup + Interest Expense)

SOURCE: Mittelhauser Corporation, February 15, 1980, and DOE/EIA, "Annual Report to Congress, 1979."

Table 24.

O&M Cost Estimation and Feedstock Cost Ceiling, 1990 Start (21)

Dry Feed Capacity: 1000 TPD
Operation Start Date: 1990 (Constant dollar base year)
Plant Factor: 90%

ANNUAL COSTS --- THOUSANDS OF BASE YEAR DOLLARS

	Feedstock Moisture Content											
	20%				35%				50%			
	Yield (gal/dry ton)				Yield (gal/dry ton)				Yield (gal/dry ton)			
	40	60	80	100	40	60	80	100	40	60	80	100
Payroll[a]	2092	2092	2092	2092	2148	2148	2148	2148	2148	2148	2148	2148
Operating Supplies at 15% Oper. Payroll	314	314	314	314	322	322	322	322	322	322	322	322
Maintenance Supplies at 2.25% Capital Investment	1892	1892	1892	1892	1966	1966	1966	1966	2083	2083	2083	2083
Total Supplies[a]	2206	2206	2206	2206	2288	2288	2288	2288	2405	2405	2405	2405
Electricity[b]	678	678	678	678	690	690	690	690	722	722	722	722
Purchased Gas Fuel (By-Product Credit)[c]	(4292)	(763)	3030	6956	0	3724	7605	11530	7113	11035	14916	18842
Outside Services[d]	137	137	137	137	137	137	137	137	137	137	137	137
Local Taxes and Insurance at 3% Total Investment[e]	2578	2578	2578	2578	2680	2680	2680	2680	2833	2833	2833	2833
TOTAL ANNUAL O&M EXPENSES EXCLUDING FEEDSTOCK	3399	6928	10721	14647	7943	11667	15548	19473	15358	19280	23161	27087
Annual Capital Cost (CRF=.16)	14040	14211	14395	14587	14792	14973	15160	15352	15958	16149	16336	16528
Income Tax at 48.16%[h]	8697	8828	8970	9117	9194	9334	9478	9625	9968	10115	10259	10406
Gross Revenue[f]	30956	46435	61911	77390	30956	46435	61911	77390	30956	46435	61911	77390
Feedstock Cost at 0.160 CRF[g]	4820	16468	27825	39039	(973)	10461	21725	32940	(10328)	891	12155	23369
1990 Feedstock Cost in dollars/dry ton	14.67	50.13	84.70	118.84	(2.96)	31.84	66.13	100.27	(31.44)	2.71	37.00	71.14
1990 Feedstock Cost in 1985 dollars/dry ton	9.98	34.12	57.65	80.88	(2.01)	21.67	45.01	68.24	(21.40)	1.84	25.18	48.42

NOTES:
a. Escalated at 9.0% per year.
b. Escalated at 8.6% per year, base price 6.13 cents/kWh in 1985.
c. Escalated at 12.9% per year, base price $5.96/10^6$ Btu in 1985 for purchased fuel; $5.36/10^6$ Btu in 1985 for excess by-product gas credit.
d. Escalated at 8.0% per year (assumed rate of general inflation).
e. Fixed annual expense.
f. Sale of product at refiner's price, distillate fuel oil; escalated at 10.5% per year, base price $1.43/gal in 1985.
g. 15% ROI, 20 year investment life; feedstock cost assumed to escalate at 8.0% per year.
h. Income Taxes = 48.16/51.84 x (Annual Capital Recovery - 1/20 (Capital Investment + Startup + Interest Expense)

SOURCE: Mittelhauser Corporation, February 15, 1980, and DOE/EIA, "Annual Report to Congress, 1979."

Table 25.

O&M Cost Estimation and Feedstock Cost Ceiling, 1995 Start (21)

Dry Feed Capacity: 1000 TPD
Operation Start Date: 1995 (Constant dollar base year)
Plant Factor: 90%

ANNUAL COSTS --- THOUSANDS OF BASE YEAR DOLLARS

	Feedstock Moisture Content											
	20%				35%				50%			
	Yield (gal/dry ton)				Yield (gal/dry ton)				Yield (gal/dry ton)			
	40	60	80	100	40	60	80	100	40	60	80	100
Payroll[a]	3220	3220	3220	3220	3305	3305	3305	3305	3005	3305	3305	3305
Operating Supplies at 15% Oper. Payroll	463	483	483	483	496	496	496	496	496	496	496	496
Maintenance Supplies at 2.25% Capital Investment	2911	2911	2911	2911	3026	3026	3026	3026	3199	3199	3199	3199
Total Supplies[a]	3394	3394	3394	3394	3522	3522	3522	3522	3695	3695	3695	3695
Electricity[b]	1007	1007	1007	1007	1043	1043	1043	1043	1091	1091	1091	1091
Purchased Gas Fuel (By-Product Credit)[c]	(7873)	(1400)	5558	12759	0	6830	13950	21150	13048	20242	27361	34562
Outside Services[d]	201	201	201	201	201	201	201	201	201	201	201	201
Local Taxes and Insurance at 3% Total Investment[e]	3968	3968	3968	3968	4124	4124	4124	4124	4360	4360	4360	4360
TOTAL ANNUAL O&M EXPENSES EXCLUDING FEEDSTOCK	3917	10390	17348	24549	12195	19025	26145	33345	25700	32894	40013	47214
Annual Capital Cost (CRF=.16)	21530	21845	22182	22533	22749	23182	23429	23778	24646	24997	25344	25693
Income Tax at 48.16%[h]	13327	13569	13828	14099	14139	14488	14662	14931	15408	15678	15945	16214
Gross Revenue[f]	50998	76499	101995	127497	50998	76499	101995	127497	50998	76499	101995	127497
Feedstock Cost at 0.160 CRF[g]	12224	30685	48637	66316	1915	19804	37759	55443	(14756)	2930	20693	38376
1995 Feedstock Cost in dollars/dry ton	37.21	93.44	148.06	201.87	5.83	60.29	114.94	168.78	(44.92)	8.92	62.99	116.82
1995 Feedstock Cost in 1985 dollars/dry ton	17.23	43.28	68.58	93.50	2.70	27.93	53.24	78.18	(20.81)	4.13	29.18	54.11

NOTES:
a. Escalated at 9.0% per year.
b. Escalated at 8.6% per year, base price 6.13 cents/kWh in 1985.
c. Escalated at 12.9% per year, base price \$5.96/10^6 Btu in 1985 for purchased fuel; \$5.36/10^6 Btu in 1985 for excess by-product gas credit.
d. Escalated at 8.0% per year (assumed rate of general inflation).
e. Fixed annual expense.
f. Sale of product at refiner's price, distillate fuel oil; escalated at 10.5% per year, base price \$1.43/gal in 1985.
g. 15% ROI, 20 year investment life; feedstock cost assumed to escalate at 8.0% per year.
h. Income Taxes = 48.16/51.84 x (Annual Capital Recovery - 1/20 (Capital Investment + Startup + Interest Expense)

SOURCE: Mittelhauser Corporation, February 15, 1980, and DOE/EIA, "Annual Report to Congress, 1979."

Table 26.

Estimated Product Revenue Requirements for Various Thermochemical Conversion to Liquid Fuels Technologies (21)

	PERC[3]	LBL[4]	TECH-AIR[5]	MTG[7]	CHINA LAKE[8]	ASU[9]
REVENUE REQUIREMENTS[1] (\$/10^6 Btu)						
CAPITAL-RELATED CHARGES	9.8	9.7	4.1	13.5	7.3	3.6
FEEDSTOCK COSTS[2]	2.5	2.8	4.3	2.8	5.9	4.6
OPERATING COSTS	3.8	4.0	(2.0)[6]	.8	1.0	1.5
FIXED COSTS	1.6	1.2	2.4	5.2	6.4	.7
TOTAL						
Dollars Per 10^6 Btu	17.7	18.0	8.8	22.3	20.6	10.4
Dollars Per Barrel	103.0	105.0	36.5	117.0	110.0	60.6
TOTAL CAPITAL INVESTMENT (10^6\$)	106.0	97.0	25.8	135.3	60.6	39.5
PRIMARY PRODUCT	LIGHT FUEL OIL	LIGHT FUEL OIL	PYROLYTIC OIL (No.6 Fuel Oil)	GASOLINE	GASOLINE	LIGHT FUEL OIL (Diesel Oil)

---

[1] Base case is 1000 dry tons per day, 80% plant factor, 1979 dollars, 50% moisture, 15% return on investment.

[2] Wood cost assumed is \$1.25/10^6 Btu; HHV of wood = 8900 Btu/lb.

[3] Pittsburgh Energy Research Center Direct Catalytic Liquefaction Process.

[4] Lawrence Berkeley Laboratory Direct Liquefaction Process.

[5] Production of oil and char by pyrolysis of wood.

[6] By-product credit exceeds other operating costs.

[7] Mobil Methanol to Gasoline Process.

[8] Polymer Gasoline from Biomass.

[9] Conversion of Cellulosic Waste to Fuel Oil via Indirect Catalytic Liquefaction.

Source: Reference 22 (SRI) for all technologies except the ASU process. This comparative analysis is based on the SRI methodology.

BIBLIOGRAPHY

1. Jones, J. L. and S. B. Radding (ed.), Thermal Conversion of Solid Wastes and Biomass, ACS Symposium Series 130, American Chemical Society (1980)

2. Klass, D. L. (ed.), Biomass as a Nonfossil Fuel Source, ACS Symposium Series 144, American Chemical Society (1981)

3. A Survey of Biomass Gasification: Vols. I, II, III, SERI/TR-33-239, Solar Energy Research Institute (1980)

4. Bente, P. (ed.), The Bio-Energy Directory, The Bio Energy Council (1981)

5. Kuester, J. L., "Conversion of Wood Residues to Diesel Fuel," presented at the Fourth Annual Wood Energy Program and Contractor Review Meeting, USDOE, Washington, D.C. (February, 1981)

6. Kuester, J. L., Conversion of Cellulosic Wastes to Liquid Fuels, DOE Interim Report No. COO-2982-57, Contract No. EY-76-S-02-2982 (September, 1980)

7. Kuester, J. L., "Olefins from Cellulose Pyrolysis" presented at the American Chemical Society Symposium on Alternative Feedstocks for Petrochemicals, Las Vegas, Nevada (August, 1980)

8. Kuester, J. L., "An Indirect Liquefaction Process for Producing Liquid Fuels from Biomass," presented at the American Institute of Chemical Engineers Session on Conversion of Biomass to Energy and High Value Products, Portland, Oregon (August, 1980)

9. Kuester, J. L., "Conversion of Cellulosic and Waste Polymer Material to Gasoline," presented at the American Chemical Society Symposium on Thermal Conversion of Solid Wastes, Residues and Energy Crops, Washington, D. C. (September, 1979)(published in Preprints and Symposium Series)

10. Kuester, J. L., "Liquid Hydrocarbon Fuels from Biomass," Chapter 8 in Biomass as a Nonfossil Fuel Source, D. L. Klass ed, ACS Symposium Series 144, American Chemical Society, Washington, D.C. (1980)

11. Kuester, J. L., "Conversion of Cellulosic Wastes to Liquid Fuels," Chapter 15 in Design and Management for Resource Recovery: Vol. I, Energy from Waste, T. C. Frankiewicz ed, Ann Arbor Press, Ann Arbor, Michigan (1980)

12. Kuester, J. L., Conversion of Cellulosic and Waste Polymer Material to Gasoline, DOE Interim Report No. COO-2982-38, Contract No. EY-76-S-02-2982 (March, 1979)

13. Kuester, J. L., "Liquid Fuels from Biomass," presented at the AIAA/ASERC Conference on Solar Energy, Phoenix, Arizona, November, 1978 (published in Proceedings)

14. Kuester, J. L., "Urban Wastes as an Energy Source," in Energy Systems: An Analysis for Engineers and Policy Makers, Marcel Dekker (1978)

15. Kuester, J. L., "Conversion of Waste Organic Materials to Gasoline," Proceedings of the Fourth National Conference on Energy and the Environment, Cincinnati, Ohio (October, 1976)

16. Kuester, J. L., DOE Progress Reports, COO-2982-1 to 72 (1976 to present), Contract No. EY-76-S-02-2982, DE-AC02-76CS40202

17. Diebold, J. P. et al, Conversion of Organic Wastes to Unleaded, High Octane Gasoline, Final Report, EPA-IAG-DG-0781 (1979)

18. Meisel, S. L. et al, "Gasoline from Methanol in One Step," CHEMTECH 6, pp. 80-89 (February, 1976)

19. Kuester, J. L., Trip Report (Japan), COO-2982-65, USDOE (1981)

20. Bagby, M. O., R. A. Buchanan and F. H. Otey, "Multi-use Crops and Botanochemical Production," Chapter 6 in Biomass as a Non-fossil Fuel Source, D. L. Klass ed, ACS Symposium Series 144, American Chemical Society, Washington, D.C. (1981)

21. Second Year Project Analysis of The Arizona State University Process to Convert Cellulosic Wastes into Light Fuel Oil, Draft Final Report, prepared by Energetics, Inc. for Argonne National Laboratory under Subcontract No. 31-109-38-5869 (March 10, 1981)

22. Technical and Economic Evaluations of Biomass Utilization Processes, Technical Report No. 1, Prepared for the United States Department of Energy, Biomass Energy Systems Branch, by SRI International, Menlo Park, California (September, 1980)

APPENDIX 1

Work Statement

(June 1, 1980 to May 31, 1981)

Integrated Runs. The major outstanding item remaining at the research scale is an assessment of performance for the integrated system, i.e., continuous operation from the biomass feeder through liquefaction step. This will include a measurement of product yields (rather than a measured-calculated hybrid) and product quality for selected feedstocks. Long run lengths will be required with appropriate staffing. It is anticipated that the Fischer-Tropsch off-gas will be recycled back to the gasification system. Use of the reforming step is not anticipated, i.e., the desired product will be a paraffinic transportation fuel such as diesel. Separation and recycle of the scrubber effluent, Fischer-Tropsch water phase and pyrolysis char streams are not anticipated although these items will be addressed with regard to scale up to a commercial facility. The ultimate objective will be reliable material and energy balances for the selected feedstocks. An environmental assessment of the process will accompany the integrated run effort.

New equipment to be purchased and/or fabricated for the integrated run series includes a new compressor (to replace the Nash-Worthington sequence), new control gear (recycle streams), new solids feeder with feedback control (for more accurate yield measurements), and more efficient size reduction equipment (hammer mill, cutting mill).

Factor Studies. The system optimization problem is to maximize the liquid hydrocarbon yields subject to constraints on product quality and operating conditions. For the gasification step, the subobjective is to maximize gas phase yields subject to constraints on reactive components (hydrogen, carbon monoxide, olefins). The purpose of the liquefaction step is to achieve maximum conversion of these reactive components to quality liquid hydrocarbon products.

Factor studies anticipated for the gasification system include a continuation of studies of the effect of type of fluidizing gas (steam vs. recycle pyrolysis gas vs. recycle liquefaction system off gas), fluidized solid (inerts vs. catalysts), residence time, temperature and wet vs. dry feedstocks. New equipment to be purchased and/or fabricated for implementing the above studies include a steam generation and control system and catalyst development apparatus.

Liquefaction system factor studies will concentrate on catalyst improvements. Any new catalyst will require optimization with regard to reactor operating variables (e.g., temperature, pressure, residence time, feed composition). New catalyst testing equipment will be implemented. It should be noted that development of a liquefaction catalyst that will achieve desired conversions at lower pressures will result in considerable process simplicity.

Alternative Feedstocks. Feedstocks have been selected based on industrial and/or scientific interest. Thus some feedstocks may be outstanding in performance but are not considered to be commercially viable. The purpose in studying these materials is to elucidate the reasons for high performance and hopefully to extrapolate this information to materials of industrial interest. In this regard, an active program is anticipated (in cooperation with other laboratories) to characterize various biomass materials with regard to compound analysis and hopefully correlate this with conversion performance.

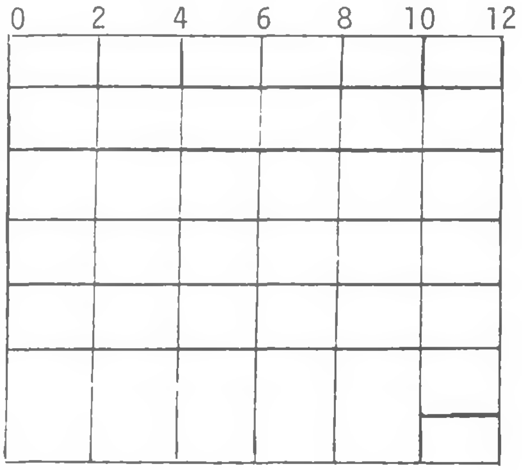
The laboratory will continue to cooperate with external concerns interested in testing feedstocks (within the constraints of budget and staffing).

A projected schedule for the new contract period follows:

Task

1. integrated runs
2. factor studies
    a. gasification
    b. liquefaction
3. alternate feedstocks
4. report

Month



As indicated, the multiple tasks will be considered a parallel effort. Thus the system will be staffed to allow for 2-3 two shift runs per week. It is anticipated that this schedule will allow for multiple objectives to be addressed within an operational period, i.e., integrated run + factor studies + alternative feedstock study.

APPENDIX 2

Equipment Revisions

Several equipment modifications were implemented during the past contract period. These include:

(1) Purchase of an Alpine cutting mill and hammer mill to aid in feedstock preparation.

(2) Purchase and installation of a SIHI liquid ring compressor to replace the previous staged Nash liquid ring-Worthington piston compressor configuration.

(3) Purchase and installation of a KTRON screw feeder system with continuous weighing and feedback control capabilities.

(4) Purchase and installation of a Chromalox steam generation and superheater system.

(5) Purchase of additional control and monitoring equipment for sparge gas flows, recycle flows, temperature monitoring, etc.

(6) Fabrication and installation of a larger fluidized bed liquefaction reactor (6" x 6') with internal heating and cooling coils.