COO-2982-67

CONF-810237--1

Report presented at the
FOURTH ANNUAL WOOD ENERGY
PROGRAM AND CONTRACTOR
REVIEW MEETING, USDOE,
Washington, D.C.,
February 9-12, 1981

MASTER

CONVERSION OF WOOD RESIDUES TO DIESEL FUEL

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DISCLAIMER

SUMMARY

1. **Title:** CONVERSION OF WOOD RESIDUES TO DIESEL FUEL

2. **Contractor:** Arizona State University

3. **Principal Investigator:** Dr. James L. Kuester
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4. **Contract Number:** DE-AC02-76CS40202
Contract Period: June 1, 1980 to May 31, 1981
Funding Level: $204,377 (current period); total funding from ERDA/DOE since June 1, 1976 = $421,709.

5. **Previous Contracts:**

   a. U. S. Navy/EPA, January 1976 - December 1976
   b. ERDA/DOE, June 1976 - May 1978
   c. DOE, June 1978 - May 1979
   d. Arizona Solar Energy Research Commission, September 1978 - May 1979
   e. DOE, June 1979 - May 1980
   f. Arizona Solar Energy Research Commission, October 1979 - June 1980
   g. USDA, June 1980 - May 1983
   h. Arizona Solar Energy Commission, October 1980 - June 1981

6. **Objectives and Anticipated Results:**

   Develop a process to produce quality liquid hydrocarbon fuels equivalent to those derived from petroleum for a variety of cellulosic type feedstocks at economically viable conditions.

7. **Work Statement Outline and Schedule:**

   a. integrated runs - continuous operation from the solids feeder through the liquefaction step with direct measurement of product yields.
   b. factor studies - improvement of process performance.
   c. alternate feedstocks - assessment of materials of commercial and/or scientific interest (with extrapolation of results to commercial materials).

   The above tasks are addressed in parallel.

INTRODUCTION

The project 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 basic approach is indirect liquefaction, i.e., thermal gasification followed by catalytic liquefaction. The indirect approach results in separation of the oxygen in the biomass feedstock, i.e., oxygenated compounds do not appear in the liquid hydrocarbon fuel product. The general conversion scheme is shown in Figure 1. The process is capable of accepting a wide variety of feedstocks. Potential products include medium quality gas, normal propanol, paraffinic fuel and/or 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 2. A fluidized bed pyrolysis system is used for gasification. 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 due to the accumulation of low molecular weight paraffins.

Progress in the laboratory scale system has been documented elsewhere (see PUBLICATIONS). In general, the system is capable of producing a high quality product from a wide variety of biomass feedstocks. Demonstration of attractive yields for feedstocks of short term commercial interest is the major objective of studies in progress.

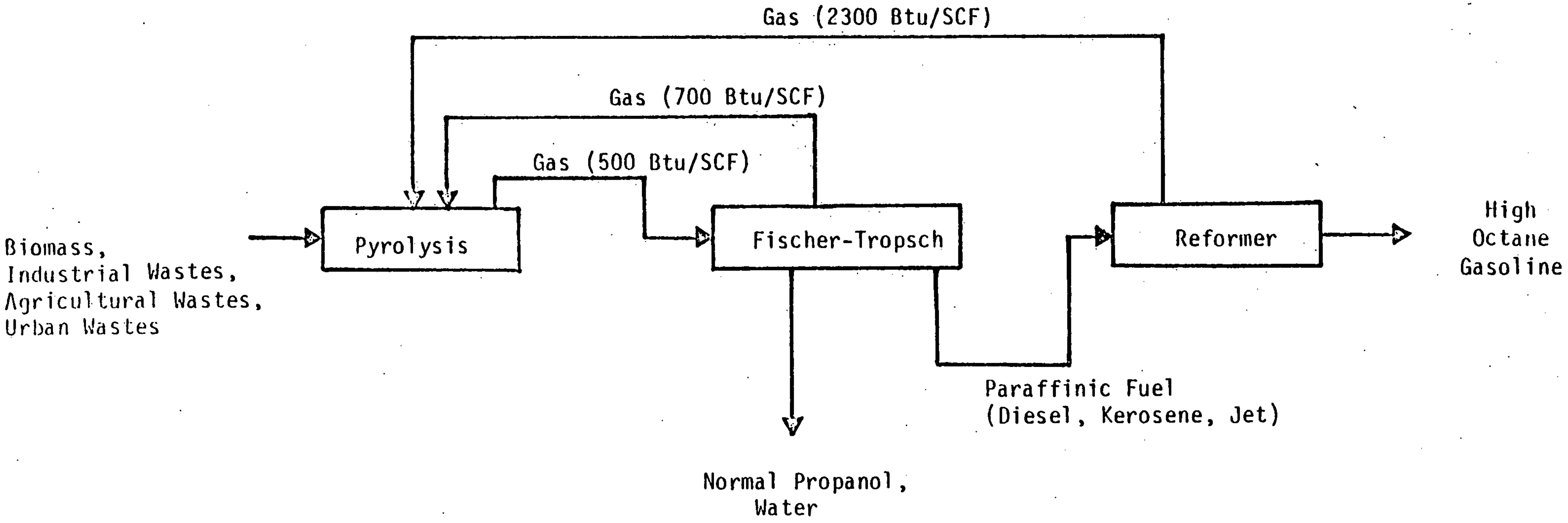

Figure 1.
Basic Chemical Conversion Scheme

CONVERSION SYSTEM SCHEMATIC

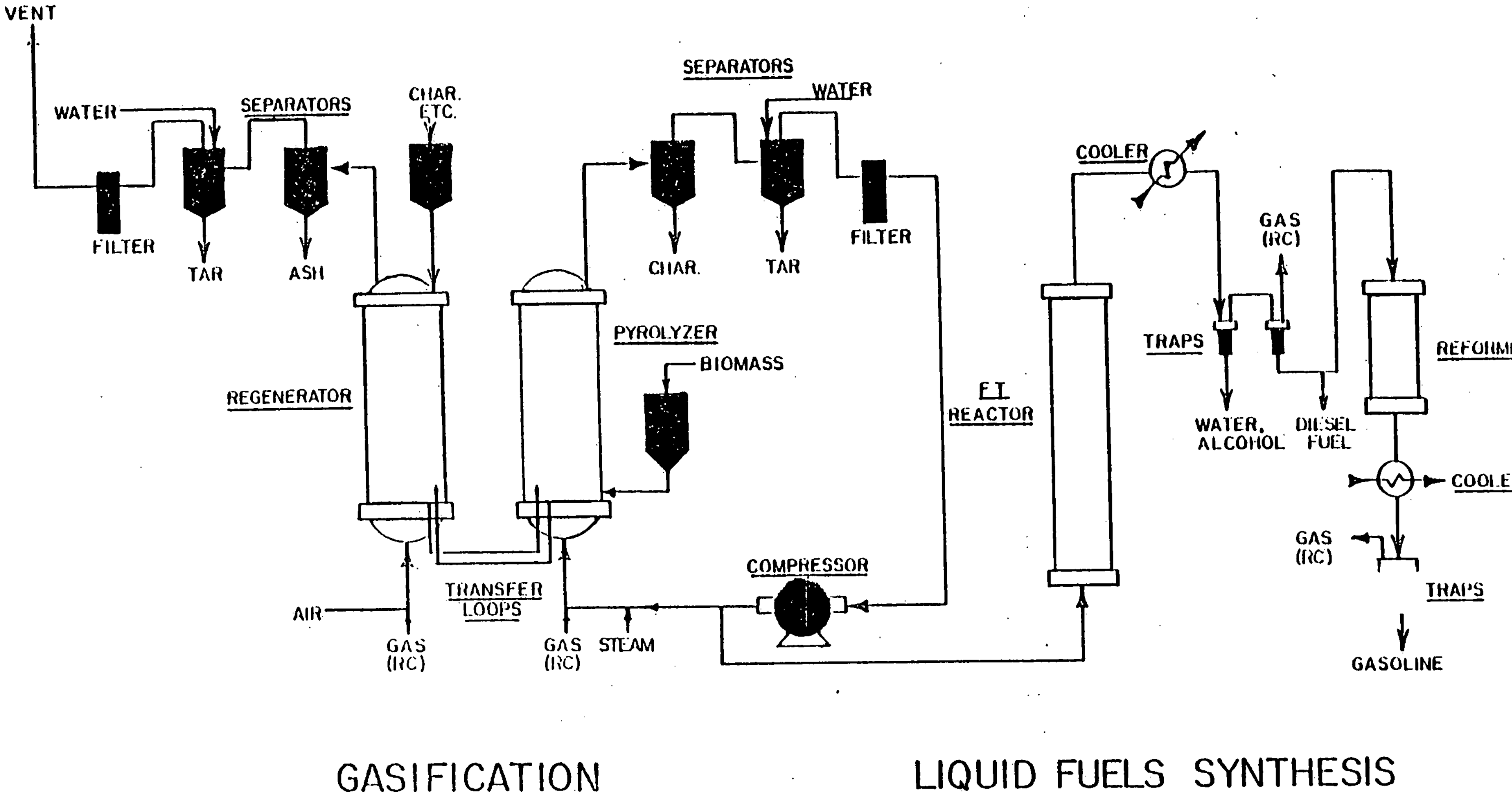

Figure 2.

PRESENT STATUS

The work statement for the current contract period (June 1, 1980 to May 31, 1981) contains the following tasks: (1) integrated runs, (2) factor studies, and (3) alternate feedstocks.

The objective of the first task is an assessment of performance with the system operated in a continuous mode from solids feeding through the liquefaction step. The desired product is diesel fuel and thus the reformer is not used. The effort has concentrated on a limited number of feedstocks. Integrated run data for two feedstocks, almond prunings (from cultivated California orchards) and guayule bagasse (from native bushes in Mexico), are shown in Tables 1-3 and Figure 3. 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 3) 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 experimental liquid hydrocarbon product with commercial materials is given in Table 4. The experimental samples represent the broad range capabilities of the liquefaction system. 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 measurement (volume product/wt. feedstock) have not been possible due to a inconsistent scale of the gasification system (larger) and the liquefaction system. Thus some generated pyrolysis gas is vented. A larger liquefaction reactor is being constructed to allow for a direct measurement. An indication of maximum possible yields for several assumptions as a function of pyrolysis gas H_2/CO ratio and olefin content are given in Tables 5 and 6. The 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 amd CH_4 could also be converted to product. Optimum yields for each assumption are listed with corresponding 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.

Product yield improvement tools presently under consideration are listed in Table 7. The major factor studies in progress or planned are lowering of the pyrolysis reactor residence time, fluidization of the pyrolysis reactor with steam + recycle gas from the liquefaction reactor, the use of catalysts in the gasification step and alternative catalysts in the liquefaction step. While product composition is of high quality and relatively insensitive to feedstock type, pyrolysis gas composition (and thus liquefaction yields) can vary with feedstock type. Thus, as shown in Table 8, a material such as guayule cork will produce an oustanding synthesis gas for maximizing liquid hydrocarbon yields. The reasons for this is a current area of investigation (feedstock compound analysis vs. reactor performance).

A number of alternate feedstocks are under investigation. A listing of materials presently on location is given in Table 9. Suppliers are industrial concerns, government laboratories (U.S. and Mexico) and sponsored projects at other institutions. The status of testing is as indicated. A large number of the materials in Table 9 have been processed through gasification and reported previously (see COO-2982-57). 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. An assessment of the current alternative feedstock candidates will be included in the interim report for the current funding period.

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

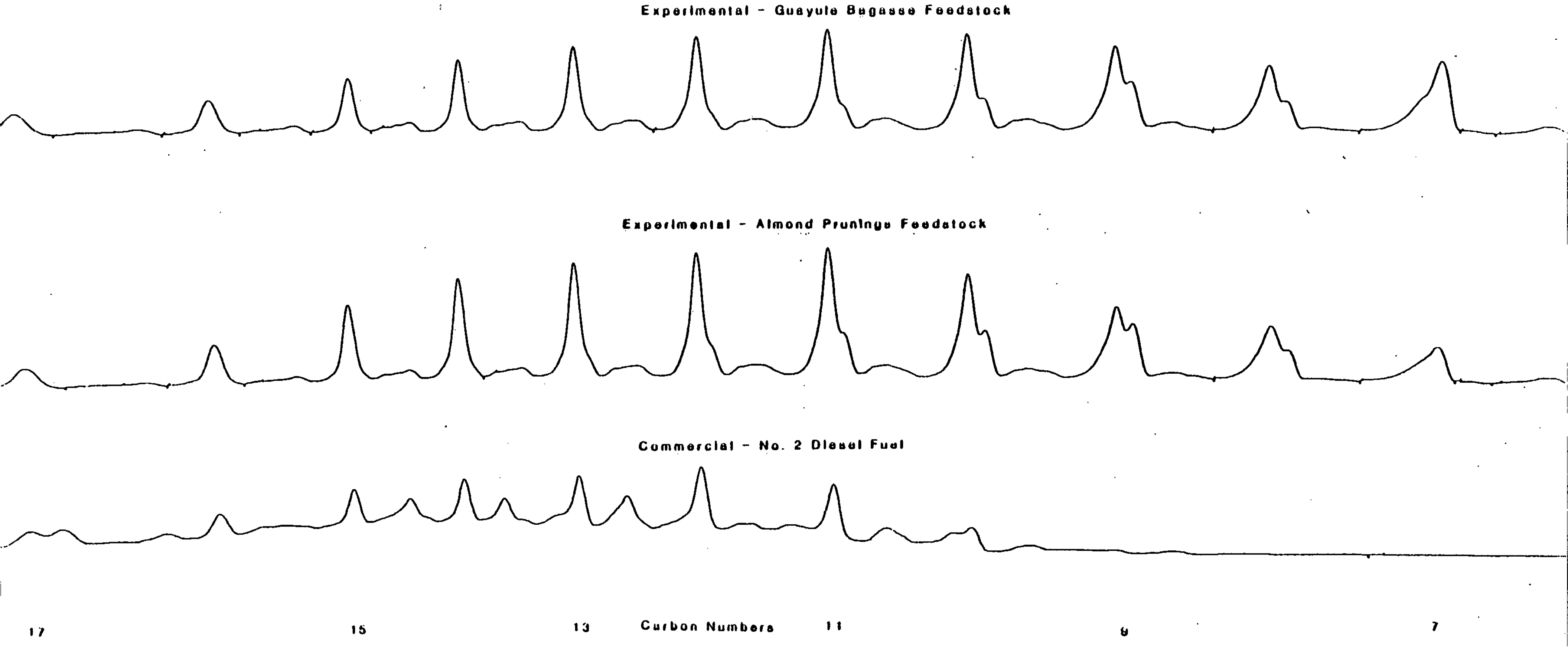

Figure 3.
LIQUID FUELS REACTOR HYDROCARBON PHASE COMPOSITION
INTEGRATED RUNS

Table 4.

Properties of Fischer-Tropsch Product and Commercial Fuel Oils

		Commercial Fuel Oils			Fischer-Tropsch Product	
		No. 2 Diesel	Kerosine	JP-4	Sample 1	Sample 2
Specific gravity		.836	.8108	.7586	.7268	.7483
Gravity, API°		37.8	43/43.4*	55/52.8*	63.1	57.6
Boiling point range, °F						
evaporated at	10%	369	336/373*	147/209*	180	140
	50%	458	410/418*	302/311*	306	279
	90%	563	479/480*	438/419*	457	475
Calculated Cetane Index		45.9	47.8/50.6*	48.3/46.6*	66.4	47.9
Heating value, Btu/lb		19383	21676	22440	20430	22113

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

Table 5.

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 6.

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

Table 7.

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

Table 8.

Steam-Residence Time-Recycle Effects
(Guayule Cork Feedstock)

	No Steam	Steam
Operating Conditions:		
temperature, °F	1300	1200
pressure, psig	0.9	0.9
residence time, sec	8	1
feed rate, lbs/hr.	5	5
heat transfer media	70 mesh sand	70 mesh sand
fluidizing gas	recycle pyrolysis gas	recycle pyrolysis gas + steam
Pyrolysis Gas Composition (mole %)[1]:		
H_2	20.57	24.51
O_2	0.17	0.47
CO	22.14	10.87
CO_2	3.77	10.76
H_2S	0.00	0.00
CH_4	26.03	10.95
C_2H_2	0.05	0.04
C_2H_4	14.80	16.67
C_2H_6	4.79	3.24
C_3 olefins	3.04	6.49
C_3H_8	0.16	0.25
C_4 olefins	0.83	2.65
C_4H_{10}	0.08	0.21
C_5H_{12}	0.00	0.00
C_5 + olefins	3.58	12.88
total unsaturated	22.30	38.73
H_2/CO ratio	0.93	2.25

1 - water, nitrogen free basis

Table 9.

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
**pokewood
*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 (to February, 1980)
(rest on hand but not yet evaluated)

FUTURE PLANS

The future for the project is projected as follows:

1. demonstrate that economically attractive yields (direct measurement) are possible in the laboratory scale unit for feedstocks of commercial interest. A proposed criteria is >40 gals. of quality liquid hydrocarbon product per ton of dry feedstock.
2. build a larger scale pilot plant (approximately 10 tons/day) for the purpose of endurance testing of equipment and catalysts and production of a sufficient amount of product for applications testing.
3. commercialization.

It is anticipated that the larger scale pilot plant will involve both federal and industrial funding with eventual commercialization to be financed by private industry. The laboratory scale system should remain active as long as it is useful (factor and optimization studies, screening of alternate feedstocks, system simplification, chemical and physical property testing of products, etc.). It should be emphasized that a larger scale facility is not economically viable for extensive experimentation, i.e., any proposed major revisions should be explored first at the laboratory scale

PUBLICATIONS

A number of publications concerning this project have been completed. These include:

Kuester, J. L., "Fluidized Bed Pyrolysis to Gases Containing Olefins," presented at the Specialists' Workshop on Fast Pyrolysis of Biomass, Solar Energy Research Institute, Copper Mountain, Colorado, October, 1980.

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).

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

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

Kuester, J. L., "Conversion of Cellulosic and Waste Polymer Material to Gasoline," 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).

Kuester, J. L., "Liquid Hydrocarbon Fuels from Biomass," presented at the Biomass as a Non-Fossil Fuel Source Symposium, American Chemical Society, Honolulu, April, 1979 (published in Preprints and Symposium Series).

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, 1980).

Kuester, J. L., "Conversion of Cellulosic Wastes to Liquid Fuels," presented at Engineering Foundation Conference on Municipal Solid Waste as a Resource: The Problems and the Promise, Henniker, New Hampshire, July, 1979 (published by Ann Arbor Press).

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

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

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

Kuester, J. L., DOE Progress Reports, COO-2982-1 to 65 (1976 to present) Contract No. EY-76-S-02-2982, DE-AC02-76CS40202.