atmosphere, pyrolysis to basic chemicals (hydrogen, methane, etc.) occurs. Thermal conversion does require much higher temperatures than those for biological conversions; however, with thermal conversion, an enormous reduction in processing time (seconds) is achieved along with a substantial decrease in control sensitivity problems. Additionally, anaerobic and hydrolysis biological conversions take place in a water wet slurry (less than ten percent solids in water) while the thermal approach for the most part requires a relatively dry feedstock. Therefore, generally, with a wet feedstock (sewage, sludge, etc.) and/ or a low production rate requirement a biological route can suffice, but with a dry feedstock (forest residues, agricultural sources, municipal refuse, etc.), and interest in a faster and larger volume throughput, a thermal approach seems preferable.

Reaching one step further, for thermal conversion via pyrolysis, efforts have been undertaken to carry the processing beyond the gasification stage, i.e., conversion of the pyrolysis gas into materials with higher value and enhanced market flexibility. The analogy to the relatively new coal liquefaction process technology is apparent (Reference 9). Projects within this category are all in the research and development stage at the present time and include among them the subject project, "Conversion of Cellulosic Wastes to Liquid Fuels. There is a considerable body of recently published technical literature on fluidized bed combustion, gasification, and liquefaction, especially as related to coal (References 25, 26, 27, and 28).

The project has been under development since 1975 with funding provided by ERDA/DOE, the U.S. Navy, USDA, Arizona Solar Energy Commission and Arizona State University. The basic concept (although somewhat more complex due to the available feedstocks) is analogous to the indirect coal liquefaction technology used by SASOL (South African Coal, Oil and Gas Corporation, Limited) in their commercial plant in South Africa (Reference 9). A summary of the project's administration is included in Table A-1.

B.   PROCESS SUMMARY

Indirect liquefaction is comprised of two basic process systems — thermal gasification (pyrolysis), followed by catalytic liquefaction. The process is being tested with and seems capable of handling a diversified group of feedstocks. Due to the positive test results to date, the project technologists anticipate its adaptability to 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 conditons and needs. To date, the research and development interest has narrowed its focus to industrial diesel type fuels for tranportation vehicles (trucks, farm machinery, etc.).

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TABLE A-1.   ASU PROJECT ADMINISTRATION

PROJECT NAME: CONVERSION OF CELLULOSIC WASTES TO
                               LIQUID FUELS

PRIME CONTRACTOR: COLLEGE OF ENGINEERING AND APPLIED SCIENCES
                               ARIZONA STATE UNIVERSITY
                               TEMPE, ARIZONA 85281

PRINCIPAL INVESTIGATOR: DR. JAMES L. KUESTER
                               PROFESSOR
                               DEPARTMENT OF CHEMICAL ENGINEERING
                               COLLEGE OF ENGINEERING AND APPLIED SCIENCES
                               (602) 965-5071/3313

PROGRAM MANAGER: MR. BRUCE CRANFORD
                               DEPARTMENT OF ENERGY
                               FORRESTAL BUILDING
                               1000 INDEPENDENCE AVENUE
                               WASHINGTON, D.C.   20585
                               (202) 252-2366

              NOTE: PROGRAM MANAGER AUTHORITY DELEGATED FROM
                               DR. JEROME F. COLLINS TO MR. BRUCE CRANFORD
                               AS OF JUNE 1980

PROJECT MONITOR: MR. ED LYNCH
                               ARGONNE NATIONAL LABORATORY
                               9700 SOUTH CASS AVENUE
                               ARGONNE, IL

              NOTE: PROJECT MONITOR AUTHORITY DELEGATED FROM
                               DR. JEROME F. COLLINS TO MR. ED LYNCH AS
                               OF OCTOBER 1978

CONTRACT NUMBER: DE-AC02-76CS-40202

              NOTE: OLD CONTRACT NUMBER
                               EY-76-S-02-2982

DOE FUNDING HISTORY: BA THROUGH FY 1979 - $196,332
                               BA, FY 1980   - $204,377

A fluidized bed pyrolysis system is used for gasification. Unseparated pyrolysis gases from the gasification process are used as feed to the liquefaction process where the pyrolysis gases are put through a modified Fischer-Tropsch reactor. The liquid condensate from the reactor consists of a normal propanol-water phase and a paraffinic hydrocarbon phase that seems suitable for use as a diesel fuel. The reactor can be operated to optimize for either product. If a high octane gasoline is desired, initial results show that it can be obtained by processing of the paraffinic hydrocarbon phase through a conventional catalytic reformer. The normal propanol could be used as a fuel extender (with adequate water separation) if blended with the hydrocarbon fuel products.

1. Gasification. The gasification system consists of a dual fluidized bed vessel arrangement where one bed serves as the pyrolysis reactor and the other as a combustor. The combustor is used to heat a solid medium that is continuously transferred between the combustor and the pyrolyzer. The lab scale combustor is fueled by a propane-oxygen mixture. On a commercial scale it is anticipated that the combustor would use recycle char, liquefaction off gas (of high quality due to the accumulation of low molecular weight paraffins), pyrolysis gas and/or biomass as fuel. However, no tests have been made to date and there are no current plans to implement these alternate feeds on the lab scale.

The advantage of the fluidized beds is their efficient heat tranfer. Because the combustor feed charge is kept separate from the pyrolyzer, the pyrolysis gas is kept relatively free of combustion products (although small amounts of entrained char are transferred with the fluidized heat medium) minimizing the need for extensive gas cleanup steps.

In the pyrolysis reactor, feedstock is fed continuously by a feeding device into the bed operating at a controlled temperature in the $1000-2000^\circ oF$ range and a slight positive pressure. The lab scale pilot plant is currently using a vibrating screw conveyor and a rotary type valve with a pressurized hopper and sparge gas (pyrolysis gas) being used in conjunction with each device. Because feedstocks with above 15 percent moisture content could not be tested in the pyrolyzer, due to the clogging problems exhibited by the current feed system, a new system designed to handle the higher moisture content of various feedstocks will be implemented.

As the feedstock enters the pyrolyzer it is flashed to a gas. The gas passes through an overhead cleaning system (essentially the same for the combustor) which consists of a cyclone separator (to remove char and other particulate), scrubbing system (to cool the gas and remove tars, etc.), filter (to remove solid fines) and a compressor (where it is compressed to the pressure requirements of the Fischer-Tropsch reactor). From the compressor the gas is split

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into two streams. One stream is used as a recycle to satisfy the pyrolysis reactors fluidizing and sparge gas requirements for the lab scale pilot plant. The other stream is the feed stream to the liquid fuels synthesis (liquefaction) system. Storage tanks are = made available so that the generated pyrolysis gas can be contained allowing operation of the liquid fuels reactor (modified Fischer-Tropsch reactor) independent of the gasification system.

2. **Liquefaction.** Liquefaction of the pyrolysis gas occurs in the modified Fischer-Tropsch catalytic reactor system. The reactor is fed raw pyrolysis gas (primarily hydrogen, ethylene, carbon monoxide, methane, ethane and carbon dioxide). The most successful catalyst tested thus far is a cobaltalumina catalyst. The bed is fixed to achieve temperature control with significant exothermic heat of reaction. For the lab scale, a resistance wire heater temperature control system is used but for the larger pilot plant scale, a hot oil system is recommended.

The gas product off the top of the reactor is sent through a cyclone where catalyst particulate is removed and returned to the reactor. The gas is then cooled, producing two liquid phases — a hydrocarbon phase and an alcohol-water phase. Uncondensed gases with significant amounts of methane and ethane are available for processing or recycle (with the possibility of usage as a combustor fuel). The hydrocarbon water phase ratio is about 10/1 on a volumetric basis but can be adjusted to give a higher water phase yield if desired. The water phase contains about 15 percent (wt) low molecular alcohols (primarily n-propanol). The hydrocarbon phase is paraffinic in nature with some branched compounds, olefins and aromatics. This phase can be tailored to match light commercial fuels such as diesel oil (References 14, 15, 16, 17, and 18).

C. **PROJECT SUMMARY**

1. **Equipment Design and Development.** Equipment modifications, improvements and automation have been in steady progress since the start of the contract (June 1976). In many cases, commercial equipment is not available at this scale thus requiring local fabrication. This is true for essentially all of the processing vessels (reactors, cyclones, scrubbers, traps, etc.). Other items (instrumentation, compressors, feeders, analyzers, etc.) have been purchased. The gasification system is the most complex due to extensive solids handling (feeding, hot solids transfer, tar removal). No unsurmountable operational problems remain although appreciable adjustments are often required when exploring new conditions (new feedstocks, new operating condition ranges, etc.). Some of the equipment would not be practical on a commercial scale however (resistance wire heaters, manual decanting). It is assumed that these steps would be improved at the next scale of development. An unplanned shutdown in these reactors would probably be due to a catalyst problem (low activity, carbon formation, etc.).

2. Factor Studies and Optimization. The overall process objective is to maximize liquid fuel yields subject to constraints on product quality (composition, physical properties) and operating conditions (factors). The factors available for manipulation are those associated with any typical chemical reactor system -- temperature, pressure, residence time, feed composition, catalyst composition and characteristics. In addition, reactor mixing and solid contact patterns can play important roles in achieving desired process performance.

About forty feedstocks have been explored including paper chips, Eco-Fuel II (Combustion Equipment Associates) and kelp waste. The paper chips and Eco-Fuel II appear to be similar in performance. The kelp waste (Kelco Co.) was dropped from consideration due to the large amount of inert filter aid (Perlite) present in the material.

Although the process is similar in concept to indirect coal liquefaction, it presents several, more complex problems. With the indirect liquefaction of coal, the pyrolysis gas is a composition of hydrogen gas (H_2) and carbon monoxide gas (CO). This gas contains very small amounts of other organics and impurities which are separated from the gas before it enters the Fischer-Tropsch reactor. Because the Fischer-Tropsch reactor produces its highest yields with a H_2 to CO ratio for the feed gas in the range of 1.5:1 to 3:1, and the coal pyrolysis gas ratio is below the bottom limit, the coal pyrolysis gas undergoes a water gas shift process which optimizes the H_2:CO ratio prior to the gas entering the Fischer-Tropsch reactor.

With the cellulosic waste pyrolysis, hydrogen and carbon monoxide are not the only major constituents in the pyrolyzer gas. A large percentage of the gas is composed of olefins, predominantly ethylene. Technically, the olefins could be separated in a gas separation step, but this step would be costly in terms of equipment required and the small amounts of olefins produced (the primary use for olefins is in the plastics industry) would have to be disposed of or sold. Therefore, efforts now focus on development of catalysts in both the pyrolyzer and modified Fischer-Tropsch reactor that will maximize liquid fuel yield with the gas that is produced.

Catalyst development initially was concentrated on the liquefaction reactor. An extensive effort was made to develop a catalyst to use in conjunction with the mixed pyrolysis gas feed stream. A modified Fischer-Tropsch type was finally selected (colbalt-alumina). Additionally, several commercial reforming catalysts were tested. The use of water gas shift and tar cracking catalysts in the pyrolysis reactor are currently under investigation.

TABLE A-2. FEEDSTOCKS TESTED BY A.S.U.

Industrial Wastes

Sawdust
firbark
guayule bagasse
guayule cork
jojoba meal

almond hulls
almond shells
paper chips
polyethylene
polypropylene

Forest Residues

creosote bush
sugar sumac
Arizona cypress
pringle manzanita
Wright silktassel
pointleaf manzanita

shrub live oak
hairy mountain mahogany
Utah juniper
pinion pine
mesquite

Urban Wastes

Eco-Fuel II

Agricultural Wastes

almond prunings

Energy Crops

Russian thistle
raw guayule
water hyacinth
peat

Source: Reference 15.

Results to date are as follows:

	Pyrolysis	Fischer-Tropsch
	CO = 35-55 mole %	35 gals/ton cellulose
Present:	H_2 = 10-20	
	C_2H_4 = 5-10	
	CO = 21 mole %	100 gals/ton cellulose
Optimal:	H_2 = 28	
	C_2H_4 = 21	

Thus, the "optimal" feed gas composition to the modified Fischer-Tropsch step requires less carbon monoxide, more hydrogen and more ethylene. The major thrust to achieve improved pyrolysis gas composition is the use of catalysts.

The dual fluidized bed gasification system is set up for the use of catalysts to manipulate the pyrolysis reactions. Candidates include a tar cracking catalyst, water gas shift catalyst (to adjust the CO and H_2 content) and dolomite (to strip CO_2 in an exothermic reaction).

3. <u>Feedstock Studies</u>. The development effort is limited to cellulosic waste with emphasis on wood wastes. A large number of feedstocks were investigated through the gasification step (Table A-2. The industrial wastes refer to by-products of industrial processes. The forest residues tested are all cut by the U.S. Forest Service in the southwestern United States for water conservation purposes and burned in the field. Environmental pressures will preclude burning in the future. Eco-Fuel II is a preprocessed municipal refuse. Almond prunings are cut and burned in the almond orchards and thus represent an environmental problem. Russian thistle (tumbleweeds), raw guayule, water hyacinth and peat represent materials that might be harvested deliberately for energy production purposes. With the pyrolysis result, efforts to characterize feedstocks (chemical analysis, etc.) with gasifier yields and composition were made. The carbon, hydrogen, oxygen and nitorgen compositions are similar for the biomass materials. The sulfur content is very low except for preprocessed municipal refuse (Eco-Fuel II). The ash content does vary significantly for the materials, ranging from negligible for the synthetic polymers to over 15 percent for a few materials (e.g., Eco-Fuel II, Russian thistle, water hyacinth).

All the cellulosic feedstc .s yield a gas with a heating value of about 500 Btu/SCF. The ga; from the synthetic polymer has a much higher heating value due to the absence of oxygenated compounds. The gas composition results, although masked somewhat by the variation in operating conditions for the different runs, did show that:

(1) The more cellulosic type feedstocks yield the lowest total olefin content (generally in the 5-15 mole % range).

(2) Materials containing hydrocarbon materials (e.g., oils, latex, synthetic polymers) result in total olefin yields in the 10-25 mole % range.

(3) Hydrogen/carbon monoxide mole ratios of 0.25 to 0.95 are encountered for dry feedstocks without steam addition (excluding the synthetic polymers).

(4) H_2S was not detected for any feedstock, including high sulfur materials such as Eco-Fuel II. H_2S can be detrimental to catalyst activity; therefore, this is of significance with regard to potential effects on catalyst activity downstream.

Experimental optimal pyrolysis gas composition for maximizing liquid hydrocarbon fuel yields is 20 + mole % olefins and a H_2/CO ratio of 1-1.5. Although selected feedstocks are capable of producing the desired amounts of olefins (e.g., guayule cork), without steam addition, all the materials (except the synthetic polymers) result in a suboptimal H_2/CO mole ratio.

4. **Waste Stream Characterization.** The waste streams of concern are the pyrolysis reactor scrubber effluent, combustor off gas, combustor scrubber effluent, gasification system ash and Fischer-Tropsch reactor water phase. Thus far, no emphasis has been placed on analysis of gas stream effluents from the gasification and liquefaction processes. Tar and ash samples were collected but analytical results have been limited to moisture, ash, volatile matter and fixed carbon only.

The Fischer-Tropsch water phase normally approaches a binary of normal propanol in water, but other lower molecular weight alcohols are also present in small quantity. The normal propanol, to be considered a by-product stream and not a waste stream product, would require water separation. The water from this stream plus that from the gasification system scrubbers could be treated and recycled to the system on a commercial scale.

5. **Liquefaction Studies.** A feed composition study has been reported for the Fischer-Tropsch step, using a synthetic feed gas for the factor studies. The objective for the project has been to maximize the liquid hydrocarbon product yield.

A limiting feed composition study was also performed (hydrogen and carbon monoxide, nitrogen and ethylene). Large amounts of pure water were produced for the (H_2/CO) run. No alcohols were produced in the three limiting runs. Relatively low molecular weight hydrocarbons were observed in the organic phase for the (H_2/CO) run. No alcohols were produced in the three limiting runs. Relatively low molecular weight hydrocarbons were observed in the organic phase for the (H_2/CO) run while relatively high molecular weight hydrocarbons were detected for the (N_2/C_2H_4) and (H_2/C_2H_4) runs. Olefins were not detected in the hydrocarbon product for these three runs. The results indicate the necessity for all three reactant types to maximize liquid hydrocarbon yields.

A run with activated alumina only in the reactor (120 psig, 260°C, 30 SCFH, feed mole % = 31.71 H_2, 29.90 C_2H_4, 5.00 CH_4, 11.33 CO_2) produced pure water only (no liquid hydrocarbons). Thus, the synthesized hydrocarbons are apparently formed by catalysis with the cobalt oxides (not via alumina or by thermal reaction).

Although several runs were performed using actual pyrolysis gas, the lab scale compressor performance limited the Fischer-Tropsch operating pressure to atmospheric, resulting in low organic product yields. Product quality remained high and similar to that obtained from a synthetic feed gas.

6. Reactions. The gasification systems primary function is pyrolysis of biomass to a synthesis gas predominately composed of hydrogen, carbon monoxide, and olefins. A cursory representation of this process is as follows:

Cellulose = (CO,H_2, olefins, paraffins, CO_2, H_2O + ($C_6H_{10}O_5$)

Char + organic liquids + tars

The thermal degradation process (pyrolysis) is comprised of various complex and interrelated reactions which are grouped as 1) primary reactions of the biomass (cellulosics) to volatile material; 2) secondary reactions of the volatile material. and 3) gasification of char

Because, for the most cellulosic feedstocks, the synthesis gas H_2 to CO ratio is suboptimal in order to achieve the desired 1.0 to 1.5, H_2 to CO ratio (prior to entrance into the modified Fischer-Tropsch reactor) a water gas shift reaction to increase the amount of H_2 is usually implemented either directly after the pyrolyzer via a water gas shift catalyst or, for some feedstocks, just through use of steam, an autocatalytic effect occurs.

The water shift reaction is:

$$CO + H_2O = CO_2 + H_2$$

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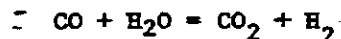
Reactions in the modified Fischer-Tropsch, although extremely difficult to isolate, do include those reactions of a conventional Fischer-Tropsch reactor used for coal liquefaction, i.e.:

$$nCO + 2nH_2 = (CH_2)n + TnH_2O$$

$$1nCO + nH_2 = (CH_2)n + nCO_2$$
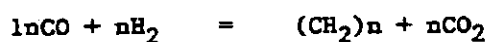
D.   Status. The laboratory project is currently addressed to additional factor studies, feedstock studies, and integrated runs with a primary objective of achieving higher product yields. The next logical step is a small pilot plant facility.

The present Second-Year Project Analysis is undertaken to assist DOE in interpreting the expected laboratory test results in determining the readiness of the process to proceed to the pilot scale.

APPENDIX B

COST COMPARISON OF EMERGING

THERMOCHEMICAL CONVERSION TO

LIQUID FUELS TECHNOLOGIES

COST COMPARISON OF EMERGING

THERMOCHEMICAL CONVERSION TO

LIQUID FUELS TECHNOLOGIES

Due to the increasing demand for liquid fuels, and their decre.. ing supply, various new process technologies for the production of ynthetic fuels are being investigated. One avenue for the production of synthetic fuels is via thermochemical conversion. Two process approaches for thermochemical liquefaction can be distinguished: direct and indirect. Direct liquefaction involves a single reaction step. The products have a relatively high percentage of undesirable oxygenated compounds. These "wood oils" require further refining before they can be directly substituted for petroleum (the refining technologies necessary are difficult and not yet state of the art). An example of the direct liquefaction process is the Tech-Air production of oil and char by pyrolysis of wood.

Indirect thermochemical liquefaction (of which ASU is one process) involves at least two reactions steps to produce a liquid product. It has comparatively low concentrations of oxygenated compound due to the two step process and does not require the extensive refining necessary for direct liquefaction products.

In the SRI Study (References 7 and 11) the major process techniques of both direct and indirect liquefaction were evaluated with the exception of the Arizona State University process. For purpose of comparison, this data appears in Table B-1 along with an SRI type evaluation of the ASU process. The only process that produces a product that is less costly than the ASU product is Tech-Air's pyrolytic oil. However, as aforementioned, further refining of pyrolytic oil is necessary before direct substitution for petroleum-based products is feasible.

TABLE B-1. ESTIMATED PRODUCT REVENUE REQUIREMENTS FOR VARIOUS THERMOCHEMICAL CONVERSION TO LIQUID FUELS TECHNOLOGIES

REVENUE REQUIREMENTS[1] ($/10^6 Btu)	PERC[3]	LBL[4]	TECH-AIR[5]	MTG[7]	CHINA LAKE[8]	ASU[9]
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	36.3	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 Catalytic Liquefaction Process.
[5] Production of oil and char by pyrolysis of wood. (Reference 23 and Reference 24)
[6] By-product credit exceeds other operating costs.
[7] Mobil Methanol to Gasoline Process. (Reference 20)
[8] Polymer Gasoline from Biomass. (Reference 22)
[9] Conversion of Cellulosic Waste to Fuel Oil via Indirect Catalytic Liquefaction.

Source: Reference 11(SRI) for all technologies except the ASU process. This comparative analysis is based on the SRI methodology

referenced and is not the approach used elsewhere in this report.