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ENERGY & ENVIRONMENT DIVISION

BIOMASS LIQUEFACTION EFFORTS IN THE UNITED STATES

Sabri Ergun

February 1980

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LBL-10456

BIOMASS LIQUEFACTION EFFORTS IN THE UNITED STATES

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February 1980

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BIOMASS AS A SOURCE OF SYNCRUDE

Assessments made for the Department of Energy place the total annual biomass resource availability at over 57 x 10^{15} Btu's. Assuming a thermal efficiency of 72% in converting biomass to oil and assigning a heating value of 6 x 10^6 Btu's to a barrel of oil, the total biomass resource potential corresponds to 6.8 x 10^9 bbls/year. This is roughly equal to the total crude oil used annually in the United States.

Estimates of recoverable or surplus biomass source, on a renewable basis, average about 8.6 quads. A modest goal of 25% utilization of the recoverable biomass resource for oil synthesis corresponds to 260 million barrels of oil ($7.8 billion) per year or about 8% of imported oil. It is obvious that a serious effort to develop technology for converting biomass to oil is warranted.

INSTITUTIONS ENGAGED IN RESEARCH

Bureau of Mines, U.S. Department of the Interior

The Pittsburgh Energy Research Center of the Bureau of Mines (now of the Department of Energy) was engaged in biomass research in the late 1960s. Their effort culminated in the design and start of construction of a process development unit located at Albany, Oregon. The facility was primarily designed for the development of a process (BOM process) conceived by the Bureau researchers. This mission was transferred to ERDA (now DOE) early in 1975. No research has been conducted at Pittsburgh since then.

Battelle Pacific Northwest Laboratories

Since 1977 PNL has been engaged in exploratory and supporting research for the development program undertaken at Albany, Oregon. A modest program of basic in-house research is also being done.

University of Arizona

The University of Arizona is primarily interested in developing extruders for the injection of biomass into high pressure vessels. Work on this project was started about three years ago.

Naval Weapons Center, China Lake, California

With funds provided by EPA, NWC investigated rapid pyrolyses of organic wastes followed by rapid quenching to produce ethylene and other olefins. The olefins are converted catalytically into gasoline; this is an established technology. This work has now been transferred to SERI. Presently the cost effectiveness of this process is doubtful.

SRI International

Recently SRI undertook a feasibility study on new processes for fuels from biomass. Currently they are investigating the effectiveness of alkali salts of molybdenum as catalysts for the hydrogenolysis of biomass.

Lawrence Berkeley Laboratory, University of California

Since October 1977, LBL has had the responsibility of technical management of liquefaction projects sponsored by DOE. Most of the LBL effort has been devoted to providing engineering analysis of the development activity and directives for the test runs conducted at Albany and analysis of results.

In October 1978, LBL undertook an experimental program to evaluate various biomass liquefaction schemes for further development at Albany. This effort paid a quick dividend in that a process scheme conceived at LBL has been tested at Albany and has been found to be technically and economically feasible. About six barrels of crude oil have been produced at Albany. The process will be discussed under a separate heading.

LBL researchers are investigating other process concepts that involve solvolysis of wood followed by selective hydrogenation of dissolved wood. LBL has constructed a bench scale continuous liquefaction unit for engineering analysis of promising catalytic liquefaction schemes. The unit is expected to be operational by March 1980.

Tech-Air Corporation and Georgia Institute of Technology

The Engineering Experimental Station of GIT has developed a process for production of oil from wood by thermal decomposition in an oxygen deficient atmosphere. The process is under development on a pilot scale plant by Tech-Air Corporation with private and public sponsorship.

Energy Resources Company, Inc.

ERC, Inc. is developing for EPA a process for pyrolysis of municipal wastes using fluid bed technologies investigated originally by Occidental Research Corporation.

Mobil Oil Company

Mobil developed a catalytic process for converting methanol directly to gasoline. Since wood is believed to be the most likely source of methanol in the future, this development has been publicized as a wood-to-gasoline process.

Universities

Biomass liquefaction is becoming increasingly popular as a subject for graduate research in departments of chemistry and chemical engineering. Such research is being conducted at the University of California, Berkeley, the University of Kansas and Texas A & M University among other academic institutions.

BIOMASS LIQUEFACTION FACILITIES

Biomass Liquefaction Test Facility, Albany, Oregon

This facility was designed to develop a process conceived by Bureau of Mines researchers in 1972 based on the results obtained in batchwise experiments in autoclaves. The plant construction was completed in December 1976. Bechtel National, Inc. was contracted to make the modifications, alterations and additions necessary to commission the facility. Bechtel was charged with the operation of the facility until mid-1978. They encountered numerous equipment failures and mechanical as well as operational difficulties. They were able to conduct a limited number of experimental runs for the BOM process. The results obtained were not encouraging.

The next contract to run the facility to develop a workable biomass liquefaction process was awarded (June 1978) to Wheelabrator Cleanfuel Corp. through its subsidiary, Rust Engineering Company, which had designed the facility. After conducting several test runs, Rust concluded that the BOM process needed to be modified by incorporating a light ends stripper and vacuum distillation unit. The unit has been designed, constructed and installed and is undergoing shakedown tests.

Rust Engineering Company has conducted a number of test runs according to directives provided by LBL to test the chemical and technical feasibility of the LBL process under steady state flow conditions. About six barrels of oil were produced within a short time. The current contract with Rust expires at the end of June 1980.

Facts about the Albany Facility

Construction completion: January 1977

Cost of Construction: About $4,000,000 (excluding land and design)

Features: See Figures 1 and 2.

Additional Equipment (exclusive of pumps, compressors, storage tanks, etc.): two autoclaves (400 gallons each), 2 lock hoppers (4,000 psi design) to feed wood flour into the reactor

Additions to the facility since construction completion: machine shop, electrical shop, wood storage shed, analytical laboratory, light ends stripper and vacuum distillation unit, magnetic drive for the reactor.

Estimated cost of additions (including labor) over $1,000,000.

Design capacity: 3TPD wood chips (40% moisture) or near 6 bbl oil/day using the BOM process.

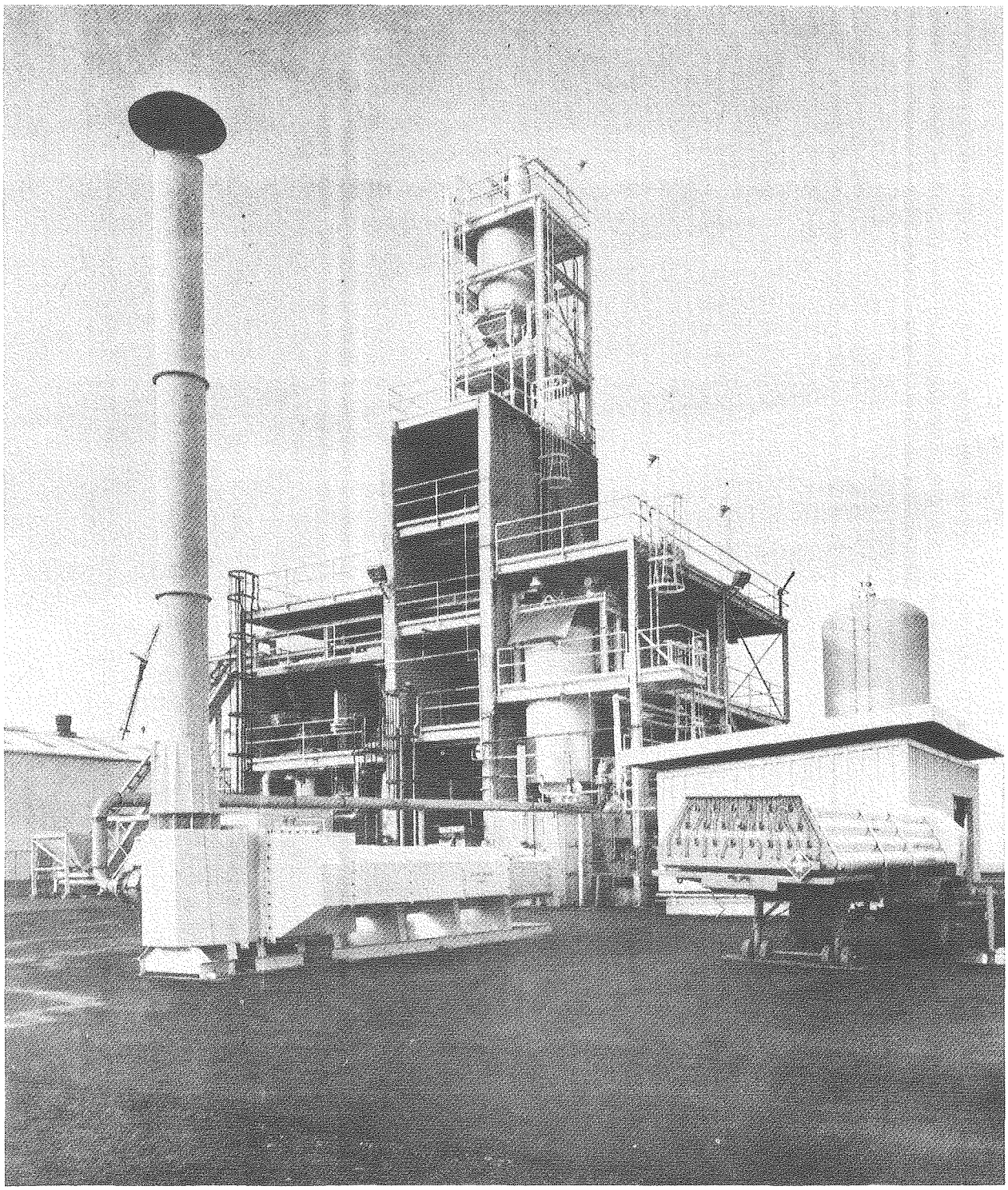


FIGURE 1

THE BIOMASS LIQUEFACTION PROCESS DEVELOPMENT UNIT ALBANY, OREGON, U.S.A.

PERC PROCESS SCHEMATIC

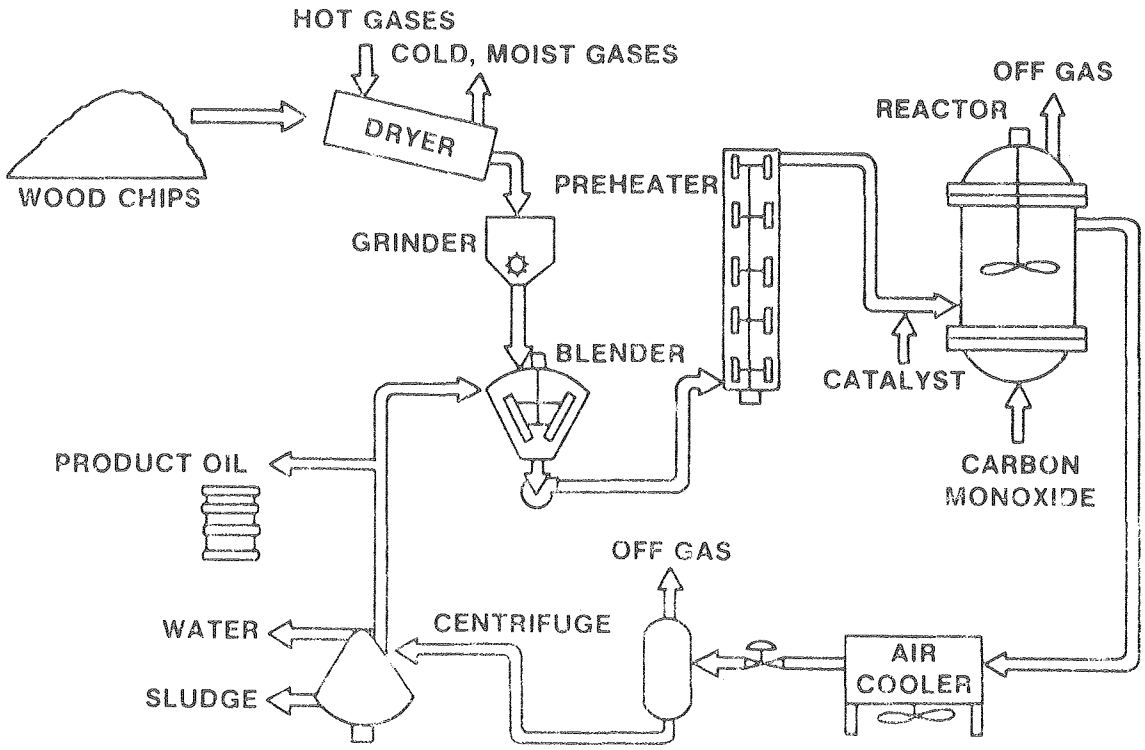


FIGURE 2

Deficiency: The existing reactor can not be scaled to commercial size.

Opportunities the facility provides: It can be utilized to test and develop liquefaction processes under study at various institutions by incorporating a reactor specifically designed for the process and auxiliary equipment if necessary. The cost of a reactor is small compared to the cost of a facility of this size.

Example: The LBL process. By incorporating a continuous hydrolyzer and reactor (under design at LBL) the facility can be used to develop the LBL process.

The end result of the facility operation: Data that would permit the design of a demonstration or a commercial plant (2,000 TPD) and a firm cost estimate of the process.

Continuous Process Evaluation Unit - LBL

Features: See Figure 3. In many ways it simulates the Albany Facility except that the reactor designed (tubular coil) simulates reactors used in large scale coal liquefaction facilities.

Design, fabrication and installation period: October 1978 - January 1980.

Current Status: Under shakedown tests (through February 1980).

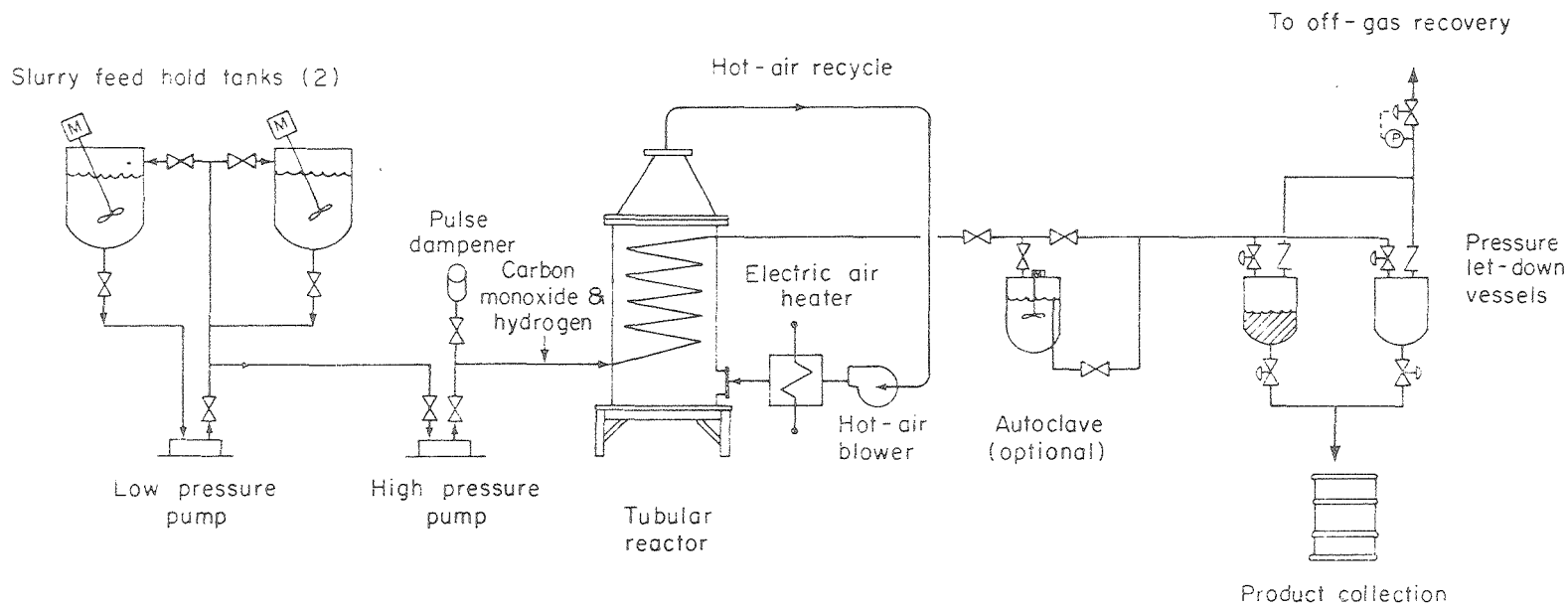
Capacity: About 7-8 liter/hr feed, 0.12 to 1 liter/hr oil.

Purpose: Investigation of liquefaction chemistry as a function of temperature, pressure, residence time, CO/H_2 ratio, synthesis gas/wood ratio, and reactor design under a continuous steady state flow mode of operation.

Optimization of process operating conditions within the framework of technical feasibility and cost factors.

Analysis of the performance of critical process units that are available commercially or technologically feasible to construct:

Continuous hydrolyzer
Homogenizers, blenders or delumpers
Progressive cavity recirculation pumps
High pressure positive displacement pumps
Tubular reactor
Pressure let-down vessels and auxiliary equipment
Continuous distillation columns.



Biomass liquefaction process evaluation unit

LBL process

XBL 7910-4293

FIGURE 3.

Acquisition of engineering data for pilot scale reactor

- Design (as a function of process variables)
- Pressure drop
- Heat transfer
- Mass transfer
- Reaction stoichiometry
- Reaction rate

Acquisition of design data for a continuous prehydrolyzer considering such factors as

- Nominal chip size
- Variations in the moisture content of chips
- pH
- Residence time
- Temperature (which dictates the pressure)
- Mechanical shear requirements

FACTS ABOUT THE LBL PROCESS

BACKGROUND

It was well-known to Bureau of Mines researchers that a wood flour-water paste could be converted into oil at 350°C under synthesis gas pressure (2,000 psi) using sodium carbonate as a catalyst. Wood flour, however, swells when mixed with water and the paste is not pumpable when its wood content exceeds 8%. Even if vaporization of water can be prevented, the heat required to raise the temperature of 11.5 parts of water from 25 to 350°C amounts to over 86 percent of the heating value of one part wood flour. Realizing these facts, Bureau of Mines researchers proposed mixing wood flour with a vehicle oil, anticipating that slurries containing as much as 30% wood could be injected into high pressure vessels using a positive displacement pump, i.e., a vehicle/wood ratio 2.33 instead of 11.5. Experience at Albany showed that commercially available pumps undergo frequent failures if the wood content of an oil slurry exceeds 20%. Unfortunately, even using this low concentration it has not been possible to obtain a pure wood-derived oil at Albany. Plugging occurs when the concentration of the substance dissolved in or mixed with the start-up oil (anthracene) exceeds 50%.

PREHYDOLYSIS OF WOOD

LBL researchers focused their attention on the prehydolysis of wood to cut down swelling so that wood-water slurries containing as much as 25% wood by weight (dry basis) could be circulated by the conventional pumps. They found that this could be achieved by treating the wood with water containing 500/ppm sulfuric acid at 180°C for about 45 minutes. They also noted that converting wood chips to a flour requires drying and milling, two costly operations. They used moist chips, added enough water to bring the total water content to about 75% by weight and sufficient sulfuric acid to acidify the total water to a pH of 2. Using a 10 gallon stirred autoclave they found that the wood chips disintegrated into fine particles and some courser but friable particles. When the resultant sludge passed through a disc refiner, a slurry that appeared to be pumpable was obtained.

A slurry recirculation loop apparatus was constructed, cf. Figure 4, consisting of a mixer (blender), a progressive cavity pump (Moyno type), a high pressure pump, and 80 ft coil stainless steel tubing (6 mm ID) to test the performance of these commercially available pumps in handling prehydrolyzed wood slurries and to obtain engineering data regarding pressure loss as a function of wood concentration, slurry temperature, and flow rate. The test proved that prehydrolyzed-refined wood slurry could be pumped continuously for days without plugging or pump malfunction.

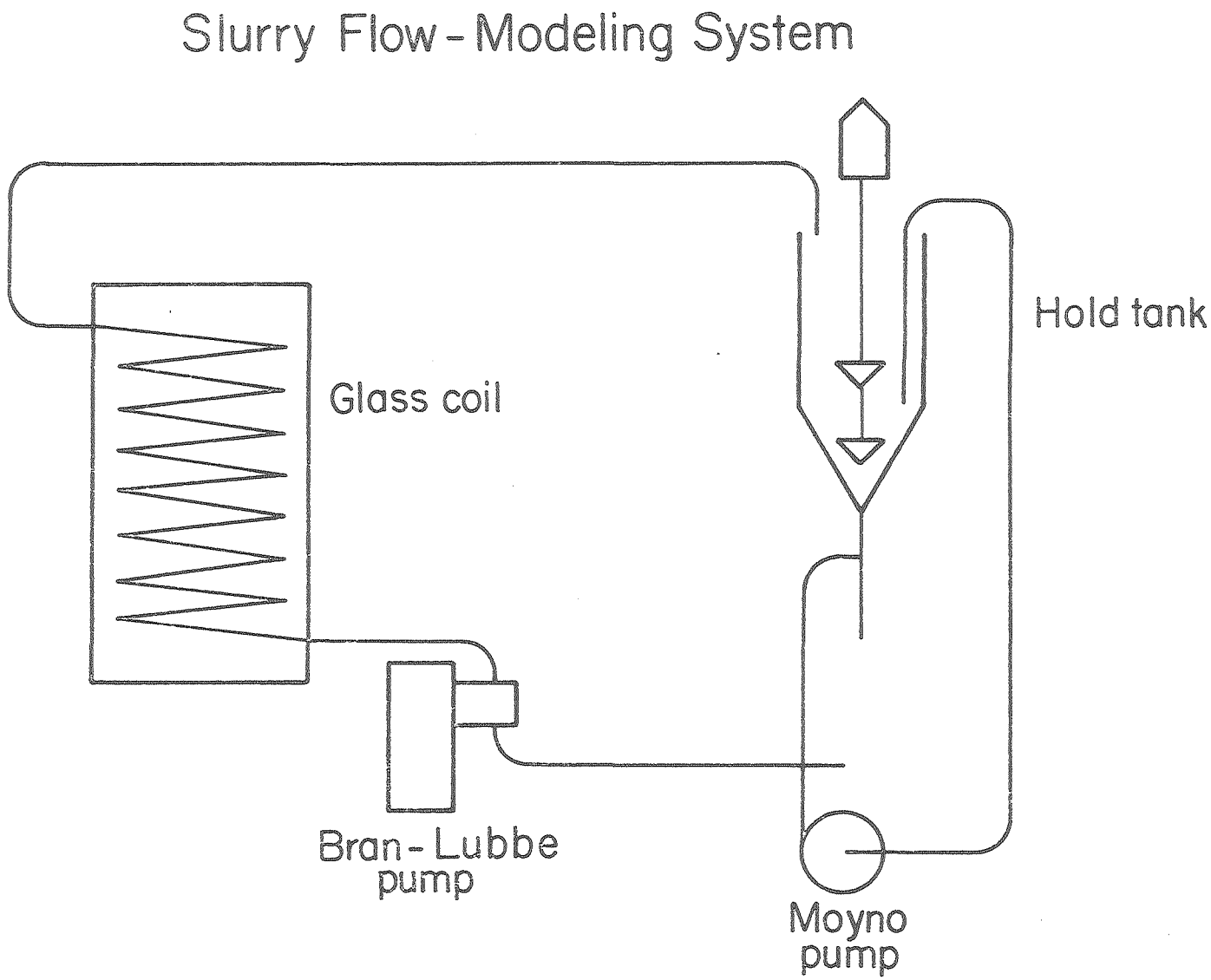


FIGURE 4.

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Attention was next focused on the quality and yield of oil produced from prehydolyzed vs. those obtained using wood flour-water pastes and wood flour-carrier oil pastes. It was found that prehydrolyzed wood gave as good results as untreated wood, if not better.

The LBL team then issued a number of operating directives to test their process scheme at the Albany, Oregon Facility step-by-step. Since the Albany Facility was not designed with this process in mind, some alterations and improvisations had to be made. Within three months (including the modifications) about six barrels of oil were obtained at Albany. The technical and chemical feasibility of the LBL process thus became established less than a year after its inception.

CHEMICAL PREHYDROLYSIS

Chemical and physical analyses of prehydolyzed wood revealed that prehydrolysis results in converting a large fraction of hemicellulose portion of wood (20-30% depending upon wood) into sugars (hexoses and pentoses). This evidently unglues the wood and makes it susceptible to size degradation.

THE OVERALL PROCESS

The overall process is shown schematically in Figure 5.

DESIGN BASES POSTULATED (1979)

Input to prehydrolyzer:

Wood chips	= 100 lb (dry basis)
Water	= 335 lb (total)
H_2SO_4	= 0.17 lb

Wood composition (weight percent):

C	= 48.7
H	= 6.1
O	= 44.3 (by difference)
N	= 0.1 ($\pm$ 0.10)
Ash	= 0.85

Heat of combustion:

7833 Btu/lb (moisture free)

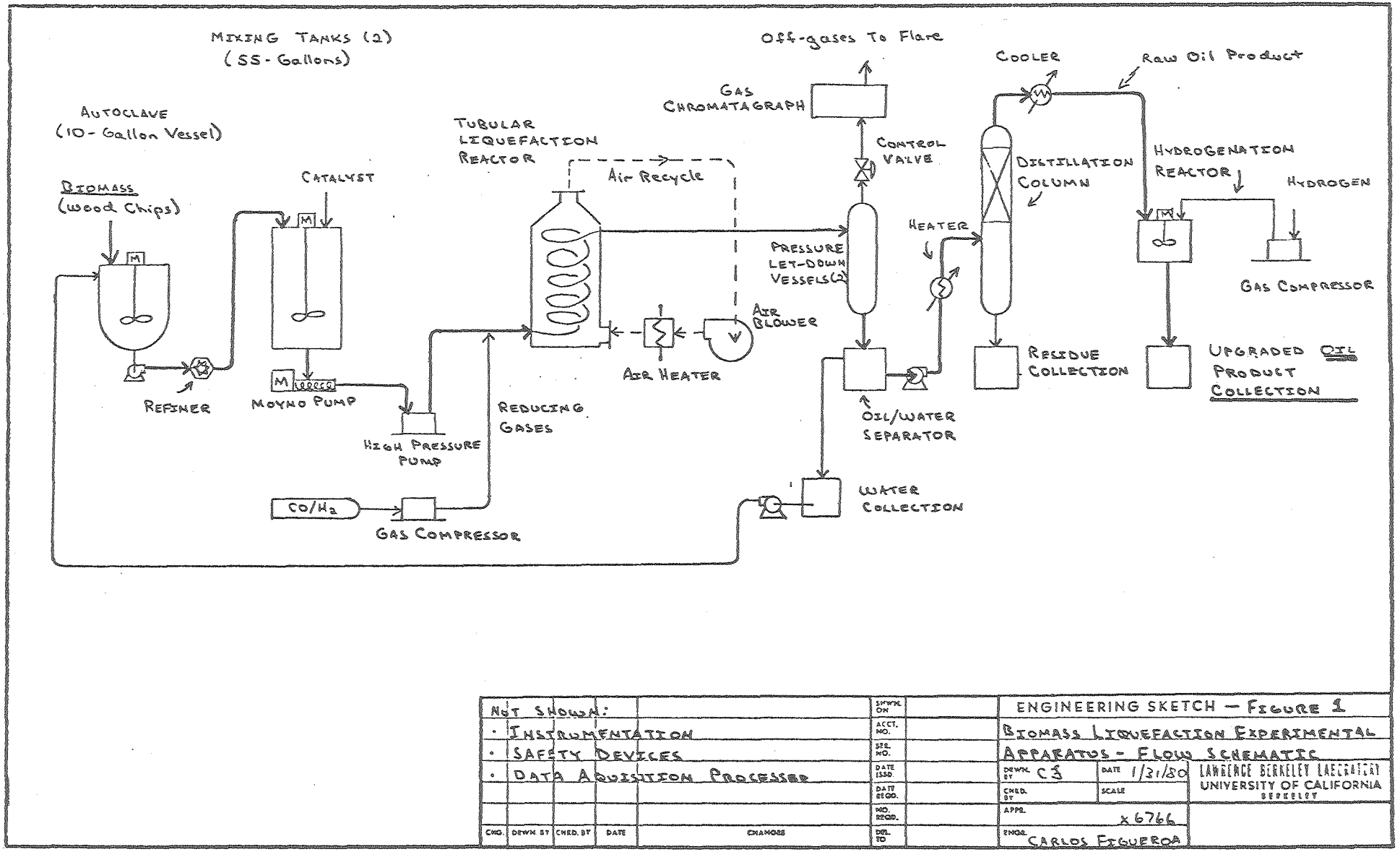
MIXING TANKS (2)
(55-Gallons)
AUTOCLAVE
(10-Gallon Vessel)
BIOMASS
(wood Chips)
CATALYST
REFINER
MOYNO PUMP
HIGH PRESSURE PUMP
CO/H2
GAS COMPRESSOR
REDUCING GASES
TUBULAR LIQUEFACTION REACTOR
Air Recycle
AIR HEATER
AIR BLOWER
PRESSURE LET-DOWN VESSELS(2)
GAS CHROMATAGRAPH
Off-gases To Flare
CONTROL VALVE
HEATER
OIL/WATER SEPARATOR
WATER COLLECTION
DISTILLATION COLUMN
RESIDUE COLLECTION
COOLER
Raw Oil Product
HYDROGENATION REACTOR
HYDROGEN
GAS COMPRESSOR
UPGRADED OIL PRODUCT COLLECTION
NOT SHOWN:
· INSTRUMENTATION
· SAFETY DEVICES
· DATA AQUISITION PROCESSOR
ENGINEERING SKETCH — FIGURE 1
BIOMASS LIQUEFACTION EXPERIMENTAL APPARATUS - FLOW SCHEMATIC
DRWN. BY C.J.
DATE 1/31/80
CHKD. BY
SCALE
APPR.
x6766
ENGR. CARLOS FIGUEROA
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY

FIGURE 5.

Conditions of prehydrolysis:

Heat up period	= 12 to 15 min
Temperature	= 356°F
Pressure	= 130 psig
Residence time	= 45 min
Agitation	= vigorous

Hydrolysis Products

Insoluble solids	= 72 lb (16.6%)
Soluble solids	= 21 lb (4.8%)

Expectations:

Size degradation	= suitable for pumping
Viscosity	= 30 cp at 70°F
Settling velocity	= less than linear flow rate

Input for liquefaction:

Prehydrolyzed charge	= 435 lb
Sodium carbonate	= 5 lb
Synthesis gas	= 1.30 lb moles

Synthesis gas composition (mole percent):

H_2	= 40.3
CO	= 40.3
CO_2	= 19.4

Liquefaction conditions

Temperature	= 680°F
Pressure	= 3,000 psi (inlet)
Residence time	= 45 min

Overall liquefaction stoichiometry

$$\underset{\text{(wood)}}{C_6H_{8.9}O_{4.09}} + 0.509\ CO + 0.509\ H_2 =$$

$$\underset{\text{(oil)}}{0.612\ C_6H_{6.9}O_{0.6}} + \underset{\text{(residue)}}{0.329\ C_6H_{4.23}O_{1.08}} + 0.863\ CO_2 + 2.152\ H_2O$$

Gasifier input:

Solid residue	= 21.0 lb
Oxygen	= 17.6 lb
Steam	= 13.5 lb

Gasification stoichiometry (at 1290°F)

$C_6H_{4.23}O_{1.08} + 2.46\ O_2 + 3.35\ H_2O =$

$4.06\ CO + 4.06\ H_2 + 1.94\ CO_2 + 1.41\ H_2O$

Synthesis gas produced (100 lb dry wood basis)
1.82 moles ($CO + H_2$)

Synthesis gas consumed:
0.695 lb moles

Liquefaction vent: 1.125 lb moles
contains 37% ($CO + H_2$)
63% CO_2

About 110 Btu gas

PROPERTIES OF OIL PRODUCED

Composition of oil phase (weight percent)

Solids	= 0.6
Water	= 7.1
Oil	=92.3 (acetone soluble)

Composition of oil (weight percent)

Carbon	=81.2
Hydrogen	= 7.9
Nitrogen	= 0.1
Oxygen	=10.8 (by difference)

Additional properties

Heating value	= 15,800 Btu/lb
Specific gravity	= 1.09
Viscosity	= 40 cp at 210°F
Distillate yield	= 70% (275°C at 3 mm Hg)
Distillate equivalency	= between No. 2 and No. 4
No. 2 equivalent yield	= 40%
No. 4 equivalent yield	= 30%
Raw oil equivalency	= No. 6 fuel oil

ECONOMIC FEASIBILITY

Rust Engineering Company and SRI made, independently, an economic feasibility analysis of the LBL process in comparison with the BOM process. The LBL process compared favorably. From a small plant processing 1,000 TPD wood (dry basis) the cost of the oil produced (equity financing) was placed at $48/bbl by SRI.

Very recently (January 25, 1980) SRI International made a comparative study of the economic feasibilities of six processes, under various stages of development, for producing hydrocarbon liquids and heavy oil from biomass. The product revenue requirements estimated by SRI are shown in Table 1. It is seen that the LBL process fares well.

LBL originally (June, 1979) provided SRI a conservative data base. For example, water/wood ratio was given as 3.35. Experiments conducted since June 1978 revealed that this ratio could be reduced to nearly 2.0 resulting in a 40% reduction in reactor heat requirements and a 31% reduction in the number of reactors for a fixed oil production capacity. These translate into a minimum of 25% reduction in the operating costs. A second conservative data base provided concerns the synthesis gas utilization. Additional studies revealed that by adjusting the H_2/CO ratio in the synthesis gas introduced, the net synthesis gas consumption can be reduced to less than one half of the original estimates.

It is anticipated that sufficient data will be generated at LBL by the end of April 1980, using the continuous process evaluation unit, to warrant an updating of the cost estimates of the process (by SRI).

TECHNICAL FEASIBILITY OF CONTINUOUS PREHYDROLYSIS

Prehydrolysis at Albany, Oregon was performed batchwise using one of the two 400 gallon autoclaves. The resulting slurry was refined using the laboratory refiner at Oregon State University. If this unit operation can be done continuously, the economics of the process can be assured. Engineers familiar with pulp and paper technology point out that modern pulping machines operate under higher pressures (250 psig) than those required for prehydrolysis (130 psig) and at higher temperatures. They foresee no difficulty in designing and constructing a unit capable of processing 2,000 TPD (smaller than modern pulpers).

COMMERCIALIZATION POTENTIAL

The LBL team believes that sufficient data can be obtained at LBL and Albany by the end of April 1981 to design a demonstration or commercial plant (2,000 TPD) and a firm cost estimate of the process. The target dates set are given below:

- Design of a reactor capable of producing 10-20 bbl oil/day. May 1, 1980 (by LBL)

- Fabrication and installation of the reactor at Albany May-August 1980

TABLE 1.

ESTIMATED PRODUCT REVENUE REQUIREMENTS -
LIQUID PRODUCTS FROM WOOD

Basis: 2,000 Tons/Day Green Wood Plant
Mid-1979 Dollars
Industrial Producer (15% DCF ROR, 100% Equity)

Process	PERC	LBL	Pyrolysis	Methanol	Mobil	China Lake
Product	Heavy Oil	Heavy Oil	Pyro. Oil	Methanol	Gasoline[4]	Polymer Gas.
Product Cost Components	Dollars per Million Btu					
Capital-related	4.04	3.22	4.08	8.81	11.31	12.86
Feedstock	1.99	2.24	4.34	2.23	2.45	5.85
Labor-related	1.41	1.31	1.79	2.57	3.20	4.34
Operating supplies	0.09	0.33	--	0.20	0.24	0.01
Maintenance supplies	0.29	0.23	0.29	0.65	0.80	0.94
Fixed costs[1]	0.66	0.51	0.65	1.46	1.88	2.10
Purchased utilities	0.08	0.14	0.04	0.29	0.07	0.06
By-product credit	--	--	(2.33)[3]	--	--	--
Total Product Revenue Required	8.56	7.98	8.86	16.21	19.95	26.16
Utilities Financing[2]	(6.82)	(6.59)	(7.09)	(12.42)	(15.10)	(20.62)

1. Excluding depreciation
2. 65/35 debt/equity with return at 9%/15%
3. Char selling price at $1.50/MM Btu
4. Price parity is assumed for gasoline and LPG; Royalty for Mobil catalyst not included

- Acquisition of a continuous hydrolyzer (20 TPD) and installation at Albany
  May-August 1980

- Shakedown tests of the reactor and hydrolyzer
  September-November 1980

- Test runs at Albany
  December-January 1981

- Basic engineering data generation and integrated plant concept development
  May-January 1981 (LBL)

- Design of a commercial size plant
  February-April 1981.

Regarding the next to the last item, LBL is continually evaluating various integrated plant concepts. An example of an integrated process concept is shown in Figure 6. The novel feature of the concept is a reactor for both gasification and liquefaction. The conceptual design is shown in Figure 7.

Conceptual Commercial Biomass Liquefaction Flow Schematic
LBL Process

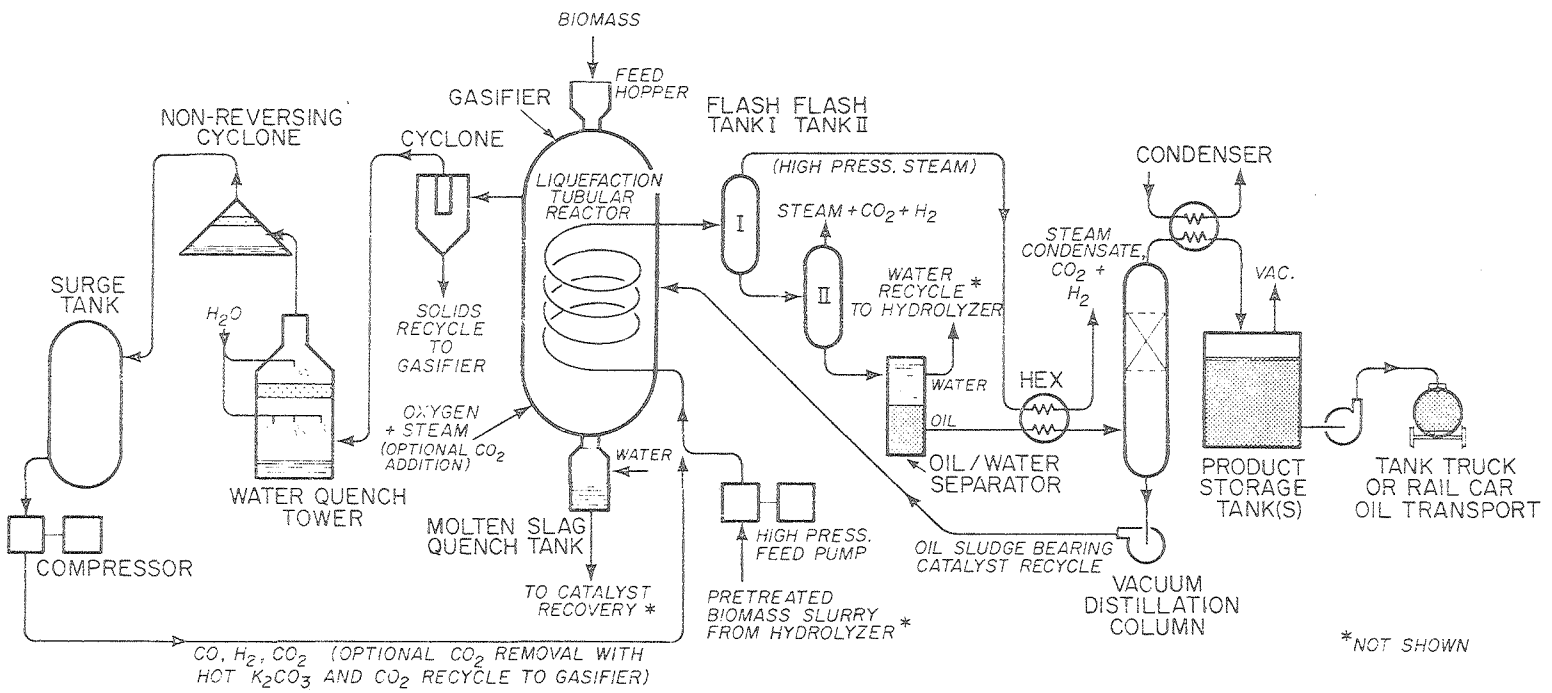

FIGURE 6

Modified Lurgi Gasifier with Liquefaction Reactor

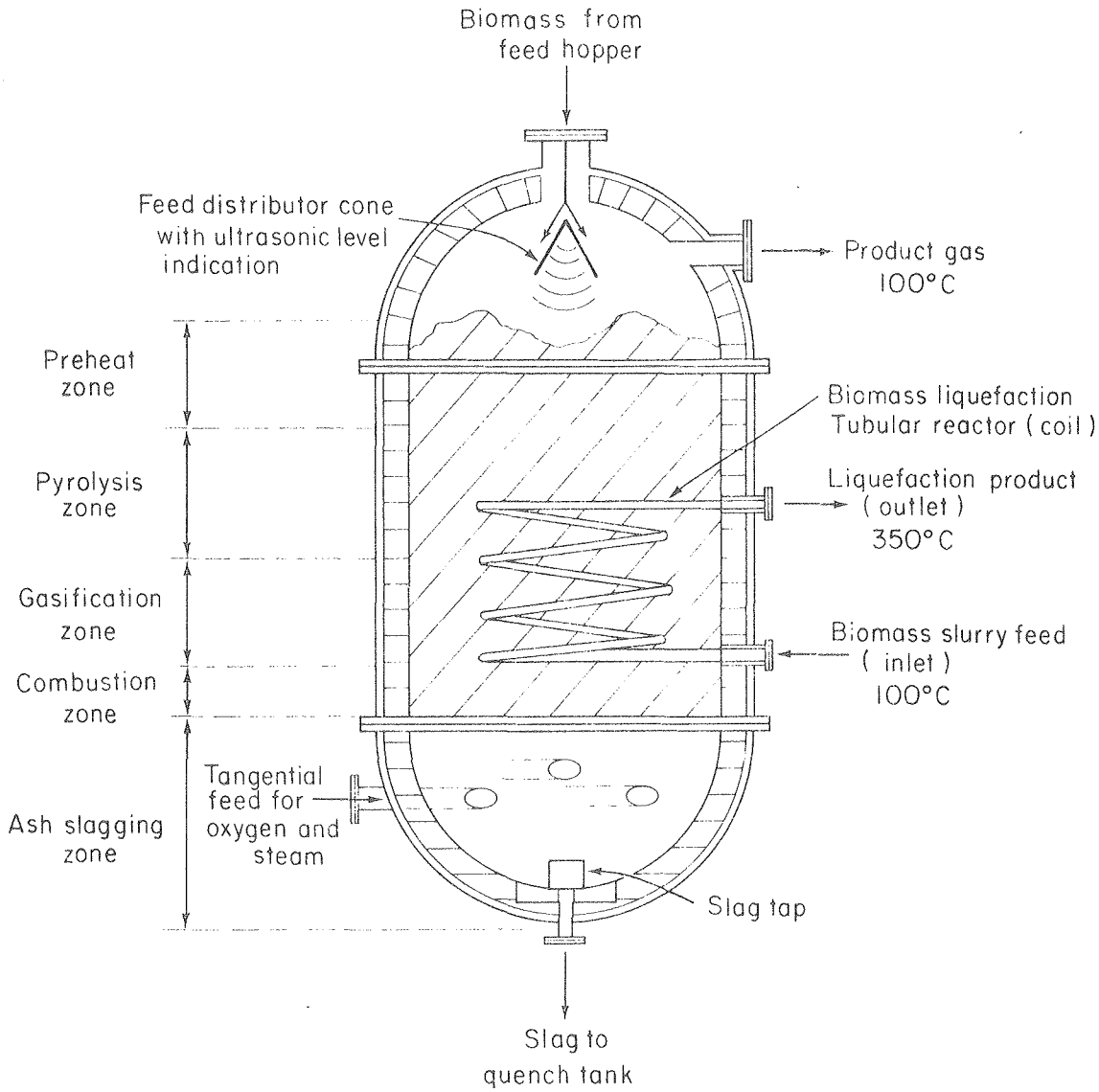

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FIGURE 7.