Title
REVIEW OF BIOMASS LIQUEFACTION EFFORTS

Permalink
https://escholarship.org/uc/item/4921g45g

Author
Ergun, S.

Publication Date
1981-12-01

LBL-13957
UC-61a

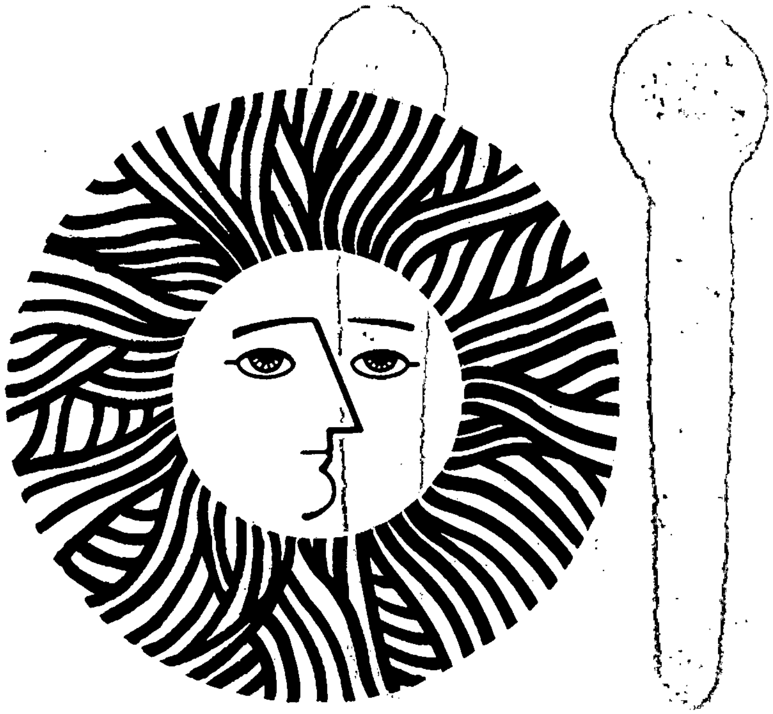
Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

REVIEW OF BIOMASS LIQUEFACTION EFFORTS

Sabri Ergun

December 1981



Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

DISCLAIMER

LBL-13957

REVIEW OF BIOMASS LIQUEFACTION EFFORTS

Sabri Ergun

Energy and Environment Division, Lawrence Berkeley Laboratory

University of California, Berkeley, California 94720

This work was supported by the Assistant Secretary for Conservation and Solar Energy, Office of Solar Applications for Industry, Biomass Energy Systems Division, of the U. S. Department of Energy under Contract DE-AC03-76SF00098. It was funded through Battelle Pacific Northwest Laboratory, Lead Laboratory for the Biomass Energy Systems Division Thermochemical Conversion Program under Contract No. DE-AC06-76LO-1830.

This manuscript was printed from originals provided by the author.

CONTENTS

TABLES

FIGURES

Section I

INTRODUCTION

The use of biomass as an energy source offers many benefits, because there are large supplies of biomass including current wastes and potential energy crops; it is a renewable and nondepletable indigenous resource. In 1900, wood supplied 25 percent of the total energy in the United States; as late as 1940, 20 percent of homes used wood for space heating.[136] Today wood contributes less than 1.5 percent of all U.S. energy, or about the equivalent of 1/2 million barrels of oil per day. It has been estimated that the potential supply of energy from commercial forest lands in the U. S. that are available for fuel would be about 3 million bbl/day of oil equivalent. It is also estimated that biomass could provide 6 percent of U. S. energy needs by the year 2000.[147]

As an energy source biomass can be used in a number of ways, which include:

- Direct combustion to produce heat, steam or electricity
- Pyrolysis to produce char, combustible liquids, and combustible gases
- Selective hydrolysis of its cellulosic component to produce sugars and subsequent fermentation of sugars to ethanol
- Gasification (i.e., incomplete combustion) to produce power gas (low or medium BTU gas)
- Gasification to produce synthesis gas as a raw material for the synthesis of methanol, ethanol, Fischer-Tropsch liquid fuels, or other liquid fuels
- Direct liquefaction to produce oils.

This review concerns only direct liquefaction efforts sponsored in recent years by the Department of Energy. Development of other technologies for wood utilization, and in prior years for some aspects of energy production, has been the responsibility of the Department of Agriculture through its regional field station - the Forest Product Laboratory at Madison, Wisconsin, for example. Serious efforts to convert wood into a clean liquid fuel date back to World War II. Prompted by the gasoline shortage prior to and during World War II, the Federal Government encouraged the production of alcohol from grain, beets, etc. and undertook a development program at the Forest Products Laboratory to produce alcohol from wood by hydrolysis and fermentation. No serious effort was made to convert wood into oil.

In the late 1960s the precarious state of energy resources in the United States and indeed in the world became of much concern to most knowledgeable persons. The formation of a cartel by the petroleum exporting countries, OPEC, was ominous. However, neither this concern nor an anticipation of an energy crisis was the primary reason for the modest effort undertaken at the Pittsburgh Coal Research Center of the Bureau of Mines, Department of the Interior;

it was instead the scarcity of land-fills for urban waste, especially in the northeastern United States. Since the bulk of the garbage collected was paper, the Bureau of Mines was consulted regarding the options for utilizing the organic matter of municipal waste as a source of energy, directly or indirectly. One of the options considered at Pittsburgh was direct liquefaction, which eventually led to the Waste-to-Oil liquefaction program.

Escalations in the price of oil by the OPEC cartel encouraged the Bureau of Mines to explore the potential of forest, agricultural, and animal wastes, and wood itself in addition to municipal wastes, as a source of raw material for liquefaction. Having found that renewable biomass resources are not insignificant, the Bureau of Mines put the Waste-to-Oil program on a fast track by deciding to design and construct a process development unit capable of processing 3 tons of wood chips daily.

Rapid rises in the price of crude oil sold by the OPEC countries led the United States to review and evaluate the Federal efforts in energy production. The evaluation, and in particular the Arab Oil Embargo, led to the establishment of the Energy Research and Development Administration (ERDA) early in 1974. The Waste-to-Oil program of the Bureau of Mines was transferred to ERDA's Solar Energy Division (later Division of Distributed Solar Technology). Biomass production and conversion were considered a solar technology because living plants absorb solar energy and convert it to biomass through photosynthesis. The biomass conversion program of ERDA aimed to exclude municipal wastes, but also to include renewable resources such as forests and crops grown specifically for their energy content, i.e., energy forests and energy farms. During 1977 the Department of Energy (DOE) was formed to assume the responsibilities of ERDA and other Federal agencies engaged in activities concerning energy. As far as thermochemical conversion of biomass to fuels and feedstocks is concerned, the ERDA-to-DOE transition did not result in radical changes in the program.

The process development unit (PDU) contemplated by the Bureau of Mines was originally intended to be located adjacent to its Pittsburgh Energy Research Center (PERC). The Center was expected to undertake the necessary supporting research for development of the method (the PERC process) for which the PDU was designed. The PDU location was later changed to Albany, Oregon. Its detailed design was completed early in 1974, and its construction was authorized as originally planned by the Bureau of Mines. Soon afterward, ERDA was officially formed, and the Albany facility under construction was transferred to ERDA. Planning, staffing, and other activities naturally took time. ERDA then authorized studies of the PERC process andof the PDU by a research institution, Battelle Pacific Northwest Laboratories (PNL), and by an engineering firm, Bechtel Corporation. On their recommendation, ERDA decided to proceed with PDU construction and to formulate supporting research projects. Construction was completed in December of 1976, only six months later than planned by the Bureau of Mines. Bechtel Corporation was awarded a one-year contract, on a sole-source basis, to commission the facility and operate it. The contract to operate the facility and develop the PERC process was awarded in June 1978 to the Wheelabrator Cleanfuel Corporation through its subsidiary, Rust Engineering Company. Rust Engineering operated the facility from July 1978 through June 1981, and since then has been responsible for maintaining the facility on a stand-by basis. At the beginning of 1977, Battelle Pacific Northwest Laboratories (PNL) contracted to provide analytical support to Bechtel Corporation in their effort to evaluate the PDU development of the PERC process. PNL also undertook supporting research and development activity to elucidate the roles of certain process parameters, such as type and the amount of the alkali metal used as catalyst, residence time, pressure, and temperature. This activity, along with product characterization, continued as long as the facility was operated by Wheelabrator/Rust.

It was anticipated in the mid-1970s that injection of biomass into vessels operating at pressures of 100 atm or higher, at concentrations of 30 percent or higher, might present difficulties. In 1977 the University of Arizona proposed investigation of the use of extruder-type devices for injecting biomass flour into high-pressure vessels, and undertook a modest-scale study. Inasmuch as the design of a reactor must conform to the state of the feed material, or vice versa, the results from this effort must be considered in relation to the progress made in reactor design.

In 1978 SRI International was commissioned to make feasibility studies of large-scale thermal conversion systems using wood as a feedstock. Direct liquefaction of wood was one of the systems to be included in the studies. Later SRI International contracted to undertake basic chemistry and mechanism studies for direct liquefaction of biomass and Catalytica Associates, Inc., was commissioned to conduct supporting systems studies. In particular, Catalytica proposed to make a systematic assessment of the role of catalysis in thermochemical gasification and liquefaction, and to examine the potential impact of new concepts under development in other areas, such as coal conversion catalysis and reactor technology, on biomass conversion. In October 1977, Lawrence Berkeley Laboratory (LBL), University of California, was given the responsibility of providing technical evaluation and monitoring services of projects sponsored by DOE pertaining to direct liquefaction of biomass, specifically the development activity at the Albany, Oregon facility. A year later, LBL was authorized to undertake an experimental program to evaluate biomass liquefaction options for further development at Albany in addition to the PERC process or in place of the PERC process should it prove to be not feasible. A liquefaction scheme conceived by the LBL researchers was tested at Albany, Oregon, early in May 1979 with moderate success. Soon after, LBL undertook the construction of a bench scale process evaluation unit capable of operating various process units under flow conditions for the PERC, LBL and other processes that may evolve from the ongoing research activity; and at that time it was designated the lead laboratory. Concurrent with that, PNL and LBL were selected to provide program management services to the Biomass Energy Systems Program of DOE, the former for the project dealing with combustion and gasification, and the latter for the direct liquefaction of biomass. A year later the program management services were consolidated; and the PNL was selected to provide those services. This step established the present administrative structure.

The purpose of this report is to review the biomass liquefaction activities in the United States. A brief overview of the chemical structure and reactivity of wood and wood components, and their significance for hydrogenation and hydrogenolysis, is provided in Section 3 along with a discussion of liquefaction based largely on the results of studies made before the "energy crisis". Studies undertaken at the Bureau of Mines have been reviewed separately in Section 4, because they constituted a concerted effort to develop a process, and because they culminated in the construction of the pilot-scale PDU. The "energy crisis" served to accelerate the program and bring it quickly to pilot-scale development. Section 5 deals with the evaluations authorized by ERDA of the direct biomass liquefaction program which it inherited from the Bureau of Mines.

Section 6 deals with the commissioning and efforts to operate the Albany facility by Bechtel Corporation, who had the opportunity to evaluate the potential of the process for which the facility was designed and built as well as the facility itself. Section 7 deals with the efforts of Rust Engineering Company to develop the PERC process and to evaluate the technical feasibility of a companion process. It was Rust Engineering Company who was awarded the detailed design of the Albany facility based on the conceptual design provided by the Dravo Corporation.

Early in 1980, four studies were authorized by DOE concerning the operation of the Albany facility, feasibilities of the processes investigated at Albany, assessment of the facility, and the role of the plant in the development of a commercial process. These studies were the result of a large scale reorganization in DOE; the whole biomass program of DOE had been in a state of flux. An overview of these evaluations is given in Section 8.

Finally, the prospects of oil from biomass are discussed in Section 9 along with some general recommendations.

Although it is widely recognized that the light crude oil reserves of the United States are not inexhaustible and that dependence on foreign oil has its pitfalls, the "energy crisis" of the mid-1970s is, as of now, regarded as solved, for the most part by conservation and by increased exploration activities for gas and oil. Whether or not the crisis is over, it is prudent to review the difficulties encountered in the programs devoted to technology development, the progress made, and to analyze the prospects of commercialization. Such a review of the wood-to-oil program has been the aim of this report.

Section 2

SUMMARY

Crude oil reserves of the United States are not sufficient to meet the nation's demands for oil. Wood liquefaction has the potential of lessening somewhat the dependence of the United States on oil imports, because wood is a major indigenous, renewable resource with a potential liquid fuel contribution of up to 6 million barrels per day.[147] The conclusion reached in the course of preparing this review is that direct biomass liquefaction efforts should be continued; it would be a mistake to discontinue or emasculate the program, because most of what has been learned would, for all practical purposes, be lost.

The liquefaction program of DOE was initiated in an atmosphere of "energy crisis". In order to put the program on a fast track, a PDU was designed and constructed at Albany, Oregon, for a specific process, inspite of the fact that the stoichiometry of the reactions taking place had not been established. The author does not consider that the decision to build a PDU was wrong, because a PDU enables the development of technology common to many liquefaction schemes that can be envisaged. Indeed DOE early recognized the importance of technology development in deciding to commission and operate the facility which it had inherited from the Bureau of Mines.

Check-out commissioning of the PDU was beset with innumerable mechanical difficulties, mostly the result of improper material selection, equipment design, and quality control. Due to the transfer of the facility from BOM to the then ERDA, the design, construction, and layout of the PDU did not receive input from any team well qualified for process development. These difficulties upset the task schedules, and technology development efforts suffered, because oil production received far more attention than detailed analysis of the performance of the plant's various prototype units.

The PERC process for which the PDU was built called for injection of a feed slurry containing 30 percent wood flour and 70 percent recycle oil, in order for the process to approach economic feasibility.[20,30,57] The recycle oil obtained at Albany was very viscous; this limited the amount of the fresh wood to less than 10 percent, resulting in a very low productivity per cycle of about 5 percent wood oil. In spite of this and many other operational difficulties, about 30 drums of oil were obtained at Albany in the final run (TR-12).[166] Consistent recycle operation was shown, but not economic feasibility.

LBL researchers conceived a modification of the PERC process, which involved an alternative wood feed slurry preparation/feeding technique.[65] Trial of this concept at Albany under makeshift conditions resulted in the production of about 30 gallons of pure wood-derived oil. This achievement early in May of 1979 was a breakthrough in many respects:

- After two years of trials, it was still not possible to obtain pure wood-derived oil using the PERC process. Those critical of the wood-to-oil program were advocating closing the facility because no breakthroughs had occurred during two years of operation.
- It provided opportunity to compare the properties of such oil with those from other liquefaction systems; for example, the oxygen content (11 percent) of the oil produced was far less than the oxygen content (33 percent) of pyrolytic oil derived from the pyrolysis of municipal solid waste.[191] Other pertinent data were obtained on heating value, viscosity, distillation characteristics, types of compounds contained, burning characteristics, etc.
- The data permitted design of a tubular heater and a distillation column that were later constructed at the facility.
- It stimulated supporting research and development efforts.

After some alterations, about eight barrels of oil were obtained at Albany by wood hydrolysis and refining prior to liquefaction. This modified process appears to be chemically and technically feasible; however, the yields range from 30 to 40 percent,[73a] and even 40 percent may not be high enough for economic feasibility. Lower yields correspond to larger production of water-solubles, including organic acids.[54a] The author's conclusion regarding further work on this process scheme is that the emphasis should be placed on the conversion of organic acids into marketable products, preferably oil.

Recently Ergun and Yu[69] discovered that the wood oil produced at Albany is a very effective solvent for wood, and that the solubilized wood when hydrogenated with oxides of copper and chromium as a catalyst produce a stable oil, more fluid than, and as effective a wood-solvolysis as, the oil produced at Albany. Based on these discoveries, they have conceptualized a process now under study.

From the point of view of technology development, valuable experience has been gained at Albany that risks being lost. Our recommendation is that an in-depth study be made of the operation of the Albany PDU to design and specify critical process units as if it is intended to build a biomass liquefaction test facility, andto recommend equipment performance tests (to be conducted at Albany) if needed for equipment selection and design of the hypothetical BLTF. The author suggests, as an example, testing the lock-hopper system (designed and constructed to operate at 4,400 psi at a cost of one-third of the entire plant) and the centrifuge.

The Albany PDU had a stimulating influence upon basic research for biomass liquefaction. Its operation as a large-scale research and development facility under the conditions of previous arrangements has been expensive. However, at relatively low expense, it would be possible to maintain the facility in a state ready to operate, and to operate it on a when-needed basis. The author believes that it would be a mistake to mothball the facility.

Section 3

STRUCTURE AND CHEMISTRY OF WOOD AND WOOD COMPONENTS

3.1 Structure of Wood

Wood is composed of three major components; cellulose (30-50 weight percent), hemicellulose (10-35 weight percent) and lignin (15-35 weight percent). The chemistry of wood can be described for the most part by the chemistry of these constituents.

Cellulose is formed from D-flucose blocks joined by β-1, 4-flucosidic bonds. Wood cellulose occurs as polymeric molecules with molecular weights generally in the range of 80,000 to 340,000. The structure of cellulose is shown in Fig. 1.

Hemicelluloses are complex molecular chains of xylose or arabinose backbones. Xylans combined with substantial amounts of uronic acids often predominate. Glucose, mannose, and other sugar structures are found in some wood species.

Lignin is a polymeric substance whose complexity results from the variety of ways in which constituent phenyl propane and other building blocks can be linked. Several models have been proposed for the structure of lignin. One such model, by Freudenberg,[75] is shown in Figure 2. The molecular weight of lignin polymers in wood ranges from 8,000 to 11,000 (or higher) corresponding to a degree of polymerization of 35 to 55.

A conventional composition of Douglas fir wood is given in Table 1.

TABLE 1

Typical Composition of Douglas Fir Chips - Dry Basis[136]

A. Elemental	Wt. %	B. Type	Wt. %
Carbon	53.2	Cellulose	41
Hydrogen	5.6	Hemicellulose	26
Nitrogen	0.13	Lignin	28
Sulfur	0.05	Other	5
Ash	0.5		
Oxygen (by difference)	40.5		

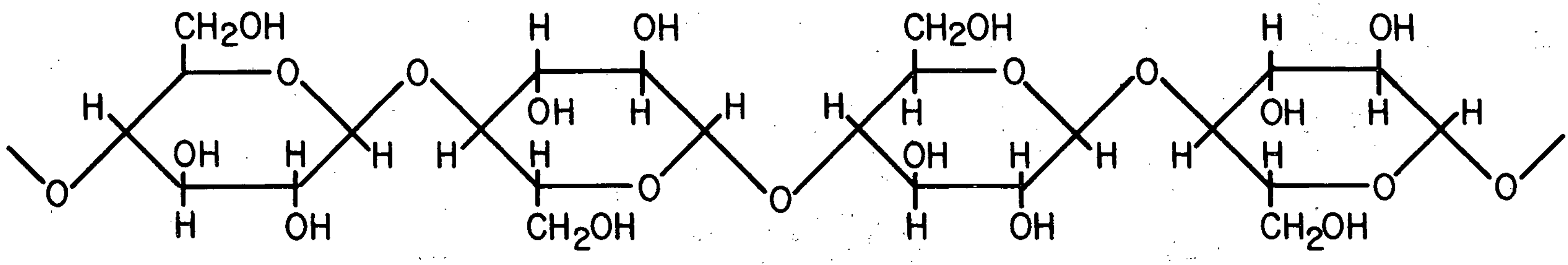


Figure 1. Structure of Cellulose

XBL 795-1647

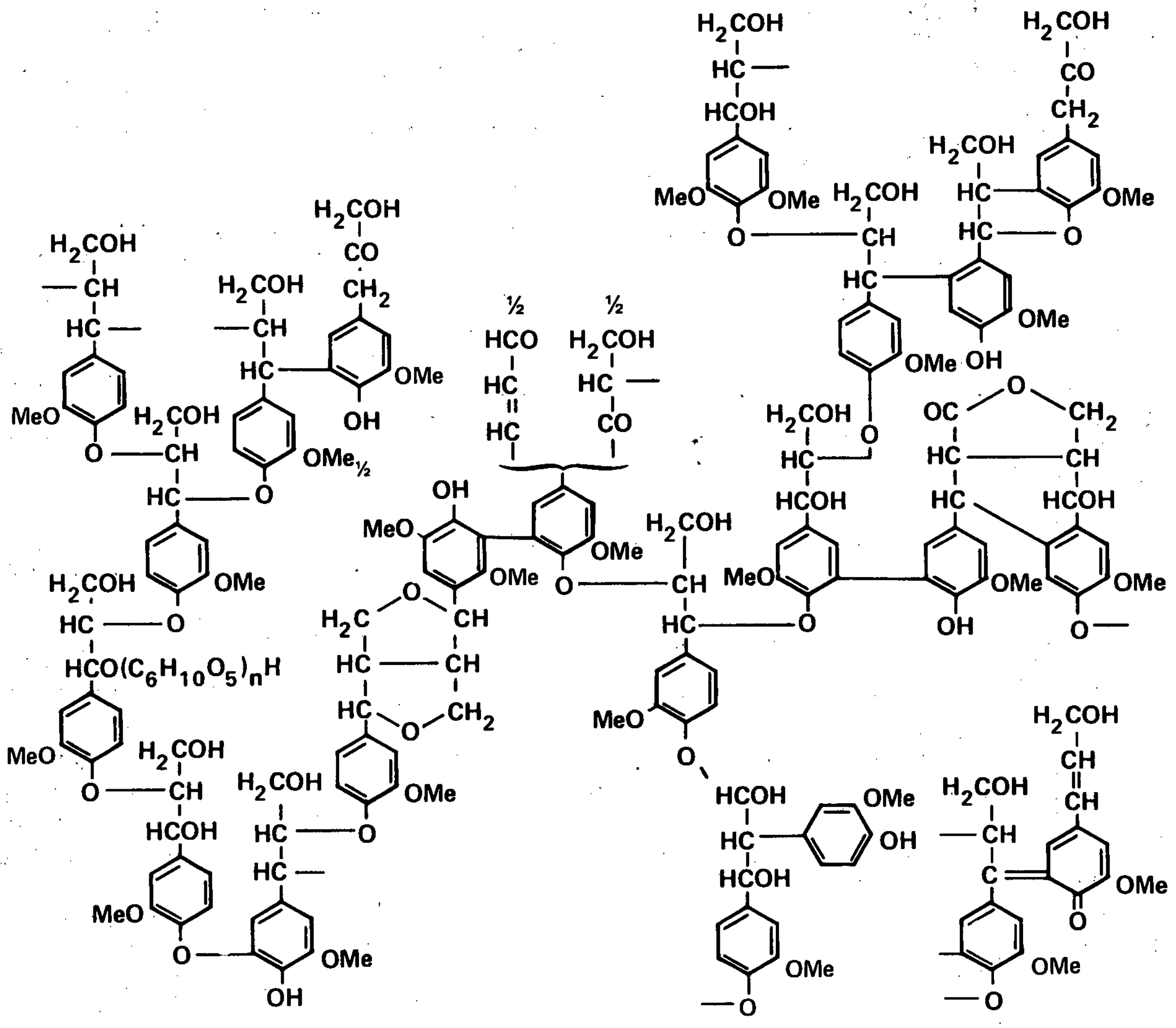


Figure 2. Structure of Lignin

XBL 795-1648

3.2 Chemistry of Wood and Wood Components

Several areas of wood chemistry have been well explored. Pulping of wood for the manufacture of paper is probably the most studied and best understood area of wood chemistry.[49,154] The hydrogenation and hydrogenolysis of wood, lignin, and cellulose, too, have been extensively studied. Substantial information also exists on the selective hydrogenation of carbohydrate materials such as cellulose, sugars, and polyhydric alcohols.

Review of the various methods of degradation and hydrogenolysis of wood and wood components suggested that four major chemical routes to liquefaction offered promise: 1. Treatment with inorganic salt solutions, as in paper manufacture; 2. Treatment with hydrocarbon hydrogen-donor solvents; 3. Solvolytic degradation with water or alcohols in an acidic medium; 4. Hydrogenation (or reduction), perhaps aided by homogeneous organometallic complexes as catalysts, in dilute aqueous acids. To these we may add solvolysis of wood in oils derived from wood[199] followed by chemical treatment of solubilized wood.[54b,69 199a]

Hydrolysis of wood has been studied by numerous investigators. An earlier review was provided by Harris.[96] Hydrolysis is facilitated by the addition of acids, as well as by an increase in reaction temperature. Above 100°C hemicellulose is rapidly attacked by dilute mineral acids (2 to 3% sulfuric or hydrochloric acid). The cellulose is attacked more slowly, probably because of its crystalline nature. Typical hydrolysis conditions range from 70% acid at 20°C for 2 hours, to 0.4% acid at 190°C for 20 minutes.[167] Some loss of sugars occurs during hydrolysis because of reversion reactions and degradation to furan-type compounds.[16] The hydrolysis of polysaccharides has been found to be first-order in acid.[49] Also it has been established that the energy of activation of hydrolysis of polysaccharides is considerably higher than that of decomposition ofthe sugars formed. Since the interest in hydrolysis stems from the sugars that it yields, and maximum sugar yields are obtained at high temperatures and low residence times, a limitation to large-scale operations is imposed by the achievable heating and cooling rates. The ultimately desired product from hydrolysis is ethanol, obtainable by fermentation. Whereas acidic conditions tend toconvert cellulose into soluble sugars, alkaline conditions tend to convert lignin into soluble salts. The objective of solubilizing lignin and leaving cellulosic parts intact (as fibers) is to produce pump for paper manufacture. In one of the most commonly used pumping processes, wood chips are treated with a calcium bisulfite solution at 130 to 150°C and 60 to 160 psig for 7 to 25 hours. Lignin is converted to water-soluble sulfite salts, and the cellulose is recovered mechanically. Alternately wood is digested with sodium hydroxide, or a mixture of sodium hydroxide and sodium sulfite at temperatures of 170 to 180°C for 7 to 12 hours, to recover cellulose as a pulp.

Whether acidic or alkaline conditions are imposed, the pentosans or hemicellulose generally appear to be attacked first.

3.3 Hydrogenation and Hydrogenolysis of Wood and Wood Components

More relevant to this review are studies concerning hydrogenation and hydrogenalysis of wood in general, and of its components. Upon pyrolysis, with oxygen excluded, wood produces gases, liquids (including water and tars), and a residue referred to as char or charcoal. If this pyrolysis is carried out in an enclosed vessel, pressure will build up. The final pressure and the yields and the composition of final products will depend upon many factors, e.g. composition of the wood employed, ratio of free volume in the vessel to the weight of the wood charged, rate of heating, final temperature of heating, retention time at final temperature, and rate of cooling. If in addition the vessel is pressurized with inert gas, say nitrogen, the yields and composition of the products will depend as well on the pressure initially imposed. In general there will be an increase in the yields of condensable liquids or tarry products. We can surmise that pyrolysis of wood under special conditions has much in common with liquefaction of wood; however, pyrolysis per se is beyond the scope of the present study. Suffice it to say that early pyrolysis efforts can be traced to 1871[110], and that factors influencing products obtainable from wood pyrolysis influence those obtainable upon hydrogenation. The distinction is that heating carbonaceous mater at, e.g. wood or coal, in an autoclave initially pressurized with hydrogen is regarded as hydrogenation, whereas the same treatment in an inert atmosphere at low or moderate pressures is regarded as pyrolysis.

Pioneering studies of catalytic hydrogenation of wood were provided by Rautola[163] and Lindblad.[134] Rautola reported that sawdust liquefaction was promoted by hydroxides of copper, cobalt and iron; nickel formate; ammonium molybdate; or ammonium chromate; resulting in oil yields as much as 35% by weight. Lindbald investigated systematically the effects of impregnating sawdust with hydroxides of copper, cobalt and nickel; sulfides of cobalt, nickel and iron; molybdic acid; and zinc chloride. The relative effectiveness of the various caralysts was measured by the yields of oils distillable at temperatures below 180°C. He reported that wood impregnated with cobaltous sulfide (7.5% based on wood) absorbed 6.6% hydrogen, yielding 40.5% oils of which 67% distilled below 180°C.

Catalysis of hydrogenation of wood or wood components by the oxides and sulfides of transition metals has been investigated by many researchers, notably Hachihama and coworkers,[89-92] Kashima and coworkers,[116,120] Harris et al.,[96,102] and Hibbert and coworkers[39,53,85,108,109]. The catalysts investigated included copper chromate, Raney nickel;[92,160] iodine and hydrogen iodide;[83] tin iodides; nickel formate;[134] carbonyls of cobalt, nickel, and iron;[168-171] ruthenium components; and many other preparations.

Wood or wood components in powdered form are usually suspended or dissolved in a liquid (vehicle) before they are placed in an autoclave. The most commonly used vehicle is, of course, water. Other vehicles tried include dioxane,[89-92,98] phenol,[36,89-92] cresol,[116-120,148,149] tetralin,[36,116-120] decalin,[188] cyclohexanol,[116-120,124,148,149] x-pinene,[124] methanol,[100] ethanol,[160] and hydrogenated oil.[31] In some experiments the vehicle is a hydrogen donor.[31,36,124,188]

As seen from the foregoing, wood hydrogenation has not been neglected. However, hydrogen treatment has mainly been applied to wood hydrolysates, acidic or more often basic, rather than to wood. In making pulp for paper, the interest is in solubilizing lignin and in utilization of the lignin solubilized. some researchers focused their attention directly on the catalytic hydrogenation of Kraft spent liquor[22,31,132,140] where many others investigated catalytic hydrogenation of lignin in alkali media[89,92,130,132] in some cases including ethanol in the mixture.[132] Since lignin is a by-product of acidic hydrolysis of wood in converting cellulose to glucose, many researchers investigated hydrolysis of lignin in acid media.[93,168-171] Oshima et al.[149] described a process for the conversion of lignin into a relatively few monophenols. Mixtures of iron sulfide with cupric hydroxide, nickel hydroxide or sulfide, or zinc sulfide were used as catalysts. Goheen[85] described a process for the conversion of lignin into a relatively few monophenols. Mixtures of iron sulfide with cupric hydroxide, nickel hydroxide or sulfide, or zinc sulfide were used as catalysts. Goheen[85] described conditions that were found to be optimum, e.g., 450°C, 15 min. residence time, for the conversion of lignin into material boiling under 240°C with 55% yields. In one experiment with wood flour, high yields of water, gas, and "neutral oils" were reported.

3.4 Liquefaction Prospects

Although the structure of wood components and their reactions has been investigated extensively, the mechanism of their liquefaction by hydrogenation is not fully understood. However, the nature and distribution of products may be estimated from an analysis of the depolymerization products of cellulose and lignin. A partial list of cellulose and lignin decomposition products is shown in Figures 3 and 4, together with their estimated boiling points and solubilities in water.

It is reasonable to assume that depolymerization of wood in reducing atmospheres results in formation of products of progressively lower oxygen content and polarity. The lignin largely decomposes to form water-insoluble high-boiling products, whereas cellulose decomposition results in the formation of water-soluble products having lower boiling points. This is a rather simplified view of wood liquefaction, since it ignores the possibility of formation of polymeric materials from condensation and degradation reactions. However, it does permit estimation of the physical properties of process streams, and selection of possible separation processes.

Seth et al.[183] suggested a slurry medium consisting of two partially immiscible liquid phases. The light aqueous phase would contain added process water and water from wood dehydration, together with dissolved low-molecular-

	Example	Boiling Point	Solubility in water
Cellulose			
↓			
Oligomers			Insoluble
↓			
Sugars	Glucose	-	Soluble
↓			
Polyalcohols	Sorbitol	295(@ 3.5mm Hg)	Soluble
↓	Glycerol	290	v. Soluble
Alcohols	Propanol	98	v. Soluble
↓	Ethanol	79	v. Soluble
Alkanes			

Figure 3. Products of Cellulose Decomposition[136]

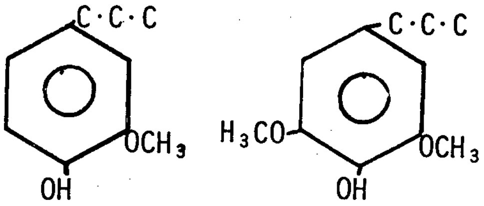
		Boiling Point (°C)	Solubility in water
Lignin			Insoluble
Oligomers			
Phenylpropanes		265-400	
	4-methoxy-2 methyl phenol	252	Insoluble
Substituted phenols and cresols	Cresolol Ethyl phenol	249 207	
Phenols	Phenol	182	Soluble
Cyclohexanols	Methyl cylohexanol	155	Insoluble
Cyclohexanes	Cyclohexane	81	Insoluble

Figure 4. Products of Lignin Decomposition[136]

weight oxygenated products. Higher-molecular-weight wood-derived oils and any non-polar organic slurrying solvents could be expected in the heavy organic phase. The organic phase would also contain any unreacted wood or high-molecular-weight condensation and degradation products or char. Distribution of products between oil and water phases could depend upon the relative amounts of the two phases present.

Selection of a chemical approach, from among the published methods of wood liquefaction, that may have the potential of being technically and economically feasible is by no means easy. We may dismiss the results involving excessive residence times or those dealing with the byproducts of pumping or ethanol production processes. We may further eliminate those approaches involving expensive solvents as a vehicle and expensive catalysts that present recovery problems, (e.g. iodine). Since wood is a solid, improved heat and mass transfer and reaction selectivity is expected if the wood can be suspended or solubilized in a carrier liquid; hence selection of the carrier is an important factor. Moreover we also find that thermal treatment of wood in a hydrogen atmosphere without catalyst invariably results in the formation of chars and gaseous products; therefore, the selection of catalyst is also a decisive factor. Having narrowed the scope of the field, we may legitimately ask if we can choose a chemical approach, from among those published, for process development. In the opinion of this writer the answer is, "not without further screening."

There are several reasons for this conservative approach. One is that researchers generally investigate the relative effectiveness of catalysts or of solvents under some standardized conditions. To do otherwise would require finding the optimum conditions of effectiveness for each catalyst or solvent selected, which is a formidable task. If, on the other hand, one has to rely on comparing the results reported by different researchers, the task is equally difficult. To illustrate the difficulty, we need to list the variables involved in a batch liquefaction experiment using an autoclave, and to consider the number of permutations for selecting the optimum condition, among the following:

- Biomass selected (its physical condition)
- Capacity of the autoclave
- Weight of the biomass charged
- Carrier vehicle
- Vehicle/biomass weight ratio
- Composition of the gas phase imposed
- Its initial pressure
- Catalyst used (its physical state)
- Catalyst/biomass ratio
- Stirring or mixing of the contents of the autoclave
- Rate of heating
- Final temperature of heating
- Retention time
- Rate of cooling

It is readily recognized that each factor is not equally important, and that we may dismiss some. On the other hand, it is impossible to change one variable and keep everything else the same. For example, it is impossible to heat the contents of a one-gallon autoclave as rapidly as the contents of a 250 ml autoclave.

Our conclusion is that selection of a promising chemistry will not be easy, and may require screening. Homogeneous and heterogeneous catalysts, organic and aqueous carrier solvents, and separation methods that could be combined into integrated processes must be conceived and evaluated. Wood is more reactive than is coal; its reactivity offers possibilities for creative process development.

Section 4

STUDIES UNDERTAKEN AT THE BUREAU OF MINES

4.1 Batch Autoclave Experiments

The Bureau of Mines studied the liquefaction of a variety of cellulosic wastes to heavy oils. These studies were an outgrowth of the liquefaction of low rank coals by carbon monoxide and steam at high pressures and supercritical conditions.[8] Most of the experimental work was conducted batchwise in a 500-ml autoclave, heated in a furnace and fitted with a rocking mechanism. A municipal waste containing 30 percent moisture required no water when treated at 380°C (supercritical) with carbon monoxide. A 20-minute residence time (exclusive of heat-up and cool-down period) was sufficient to reduce char to 6 percent. It was further observed that hydrogen was far less effective than carbon monoxide, oil yield being 18 percent (maf waste) versus 41 percent when carbon monoxide was used. In addition, the oil produced with hydrogen contained more oxygen.

The Bureau of Mines made similar studies of a variety of cellulosic materials, e.g. sawdust, manure, sewage sludge, pine needles and twigs, newsprint, and cellulose. The stated objective of the investigations was "... to determine the scope of the reaction and elucidate the chemistry involved." (References 9, 10, and 11 contain detailed discussions of the several aspects of the liquefaction reactions). Sodium carbonate, 5 to 10 percent by weight based on dry organic matter, was found to be an effective catalyst. In some experiments cobalt molybdate (on alumina) catalyst was used with sodium carbonate; the product obtained was less viscous and contained less oxygen. In a series of experiments, softwood sawdust was converted to oil at 250°C and 68 atmospheres, using cresol as solvent and formic acid or sodium formate as a catalyst (as low as 2 percent by weight) in the absence of carbon monoxide. In another series of experiments, the effect of various organic solvents was investigated. Several organic solvents were found to be very effective, and nearly complete liquefaction was achieved at lower pressures and temperatures. The objective of these experiments was to investigate the use of recoverable solvents, and to explore process conditions that would yield an oil product unable as a recycle solvent. In addition, the reduction of acetophenone and the liquefaction of sucrose and pure cellulose were investigated. Carbon monoxide consumption was found to range from as high as 50 weight percent of waste converted at 380°C, to less than 10 percent at 300°C. Inasmuch as hydrogen is a byproduct of the reaction and synthesis gas is much cheaper than pure carbon monoxide (especially if the raw gas is to be obtained by the oxy-gasification of waste), a 1:1 synthesis gas was used under a variety of conditions. An oil yield loss of 2 to 4 weight percent of moisture- and ash-free waste was observed when synthesis gas was substituted for carbon monoxide.

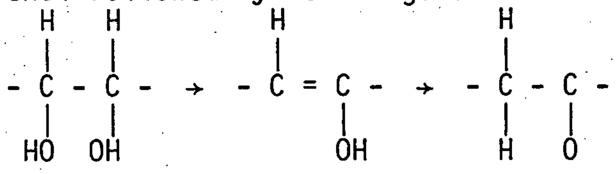
The Bureau of Mines investigated the conversion to heavy oils of a great variety of wastes, and studied the influence of a great number of experimental factors (residence time, temperature, pressure, feed gas, solvent, and catalyst) on the conversion. The number of experiments necessary to deduce the partial influences of all of the factors involved on the product quality, product yield, syngas or carbon monoxide consumption, etc., would literally run into hundreds; as such, the extent of the Bureau of Mines investigations cannot be regarded as exhaustive. In order to attain the optimum operating conditions, the Bureau of Mines investigators conducted a modest number of experiments to elucidate the mechanism of the reaction. The complexity of the chemistry needs no elaboration, for the conversion involves several reactions such as depolymerization, decarboxylation, and dehydration, of which each in turn is complex.

Some key experiments by the Bureau of Mines proved very illuminating. For example, experiments with formic acid and sodium formate as catalyst, using no carbon monoxide, furnished a plausible explanation of the role of sodium carbonate as a catalyst. Hydrogen formation at supercritical conditions could be explained by the classical water-gas shift reaction requiring catalysis of oxygen exchange between reducing (CO and H_2) and oxidizing (CO_2 and H_2O) gases on the solid surfaces. Hydrogen formation in reactions occurring at least partially in liquid phase was a matter of conjecture. Noting that sodium formate was an effective catalyst, that it could be formed from carbon monoxide and water with sodium carbonate at elevated pressures and mild temperatures, and that its decomposition could lead to the formation of hydrogen, carbon monoxide, and sodium carbonate, the Bureau of Mines researchers were able to explain the hydrogen formation in a catalyzed liquid-phase reaction. The following reaction mechanism was proposed:

1. Production of sodium formate:

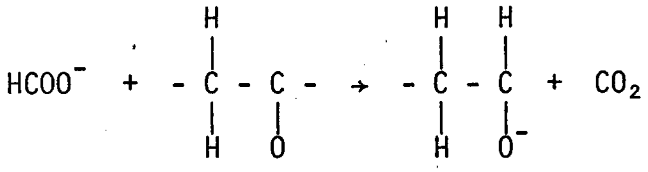
   $Na_2CO_3 + 2\ CO + H_2O \rightarrow 2\ HCONa + CO_2$

2. Formation of ketones by dehydration of adjacent hydroxyl groups to an enol followed by rearrangement to a ketone:

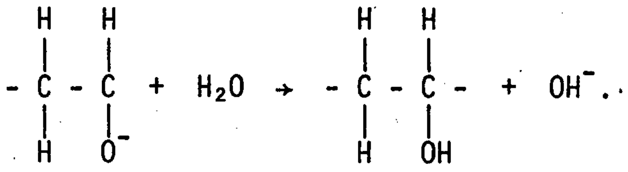


$$-\overset{H}{\underset{HO}{C}}-\overset{H}{\underset{OH}{C}}- \rightarrow -\overset{H}{C}=\underset{OH}{C}- \rightarrow -\overset{H}{\underset{H}{C}}-\underset{O}{C}-$$

3. Reduction of this carbonyl group to formate ion and water:



$$HCOO^- + -\overset{H}{\underset{H}{C}}-\underset{O}{C}- \rightarrow -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{O^-}{C}} + CO_2$$



$$-\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{O^-}{\overset{H}{\underset{|}{\overset{|}{C}}}} + H_2O \rightarrow -\underset{H}{\overset{H}{\underset{|}{\overset{|}{C}}}}-\underset{OH}{\overset{H}{\underset{|}{\overset{|}{C}}}}- + OH^-.$$

Two other important reactions were suggested. First, the aldol condensation between two or more carbohydrate molecules could lead to the formation of high molecular weight products. Second, if two carbonylic groups were formed in one molecule, these would migrate to adjacent carbon atoms and then split off as carbon dioxide.

4.2 Bench-Scale Flow Experiments

To conduct exploratory engineering studies for development of a continuous process, a bench-scale continuous unit capable of processing 1 lb/hr organic refuse to oil was constructed.[76] The oil yield obtained from an urban refuse was 23 weight percent of dry refuse at 350°C and 4000 psig (CO + steam) for a residence time of two hours.[76] We may compare the above results with an oil yield of 41 percent at 380°C and 4200 psig for a hold-up residence time of 20 minutes in a batch operation (cf. Tables 3 and 6 of Reference 10). It is readily recognized that in the batch operation cited, a supercritical condition is reached and the effects of the heat-up and cool-down periods cannot be well predicted; nevertheless, the performance of the continous unit could not be regarded as encouraging. The greatest operational difficulty encountered in the small bench-scale continuous unit is the pumping of the waste slurry. A larger continuous process development unit capable of processing 10 to 20 lbs/hour of slurry was later constructed at the Pittsburgh Energy Research Center of the Bureau of Mines. No results from the larger units were reported, probably because of the transfer of the program to a different division.

4.3 Bases for Reaction Stoichiometry and Process Concept

Data reported by the Bureau of Mines on the conversion of municipal wastes are shown in Table 2. The first two rows involve autoclave experiments that reached the supercritical stage during the hold-up time. The third row corresponds to an autoclave run conducted at relatively mild conditions; the product oil has a high oxygen concentration. The fourth row represents the results obtained in a continuous unit. Considering that oil yield was poor for a residence time of 120 minutes (compare rows 1 and 4), the results from the continuous unit are discouraging. The last row represents the expectations in a continuous operation under the conditions listed.

(Organic Waste) (Synthesis Gas) Catalyst

$CH_{1.517}O_{0.678}S_{0.00185}N_{0.00493}$ + $0.07566\ CO + 0.02788\ H_2$ —

(Oil) (Solubles)

$0.871\ CH_{1.165}O_{o.207}S_{0.00121}N_{0.0015}$ + $0.0357\ CH_{3.0}\ 0.0454$ +

$0.000796\ H_2S$ + $0.003624\ NH_3$ + $0.16896\ CO_2$ + $0.21924\ H_2O$.

Bureau of Mines researchers became convinced that biomass impregnated with sodium carbonate could be converted into a heavy oil, with the oil produced in the process serving as a vehicle oil.

Table 2

U.S. BUREAU OF MINES DATA ON LIQUEFACTION OF MUNICIPAL WASTE

(Data taken from the tables indicated in Reference 18)

Table No.	Temperature °C	Pressure psig	Residence Time Min.	Approximate Formula [a] of Product	Oil Yield Percent
3[b]	380	4200	20	$CH_{1.50}O_{0.079}$	41
4[b]	380	5000	?	$CH_{1.55}O_{0.064}$	?
5[b]	250	1500	60	$CH_{1.66}O_{0.20}$	37
6[c]	350	4000	120	$CH_{1.66}O_{0.090}$	23
Expected[d]	300	2500	40	$CH_{1.61}O_{0.15}$	58

[a] S and N have been omitted

[b] Batch operation

[c] Continuous operation

[d] Reference

4.4 Technical and Economic Feasibility Analysis

The Blaw-Knox Chemical Plants Division of Dravo Corporation was contracted by the Bureau of Mines to evaluate the technical and economic feasibility of commercial plants converting manure and waste wood to oil, based on the bench scale experimental results obtained at the Pittsburgh Energy Research Center. If the process appeared to be reasonably close to being economically feasible, the contract called for the conceptual design and cost estimate of a process development unit to develop the process.

In the Blaw-Knox report,[30] it was stated that "...the process for converting wood to oil is shown to approach economic feasibility, whereas the process for converting manure to oil is not feasible," It was also stated: "Sufficient data for translating laboratory findings to commercial plant design are not available," In the feasibility study, the break-even price of oil, taken alone, was found not to be competitively acceptable as of the date of issue of the report (June 22, 1973), the price being in excess of $7.00 per barrel. The recommendation was that "...a large-scale pilot plant be constructed and evaluated, to improve the process and to obtain a better basis for the design and selection of equipment for a commercial plant,"

4.5 PDU Design and Construction

In the Blaw-Knox study, injection of biomass into the high-pressure reactor received a great deal of attention. In one method, Method A, it was proposed to dry and mill the biomass and blend it with recycle oil so that it could be injected into the reactor by means of a positive displacement pump. This technique appeared to be the simplest in that it simulated methods adopted in coal liquefaction technology. However, the economic feasibility of this technique depended on the ability of the commercial pumps to inject slurries containing 30 percent (by weight) dry biomass flour. The unknown nature of the recycle oil produced in the process led Blaw-Knox to seek other injection options.

In the second method (B), the biomass flour was directly fed into the reactor by means of lock hoppers. It was anticipated that the vehicle oil/wood flour weight-ratio could be reduced to 1 (from 2.33 in Method A), resulting in a reduction by one-third of the equipment reaction train systems in a commercial plant. The recognized disadvantages of this method were, 1) the complicated feed system, with two additional gas compressors and several gas pressure surge-and-hold tanks to take care of the large volumes of gas required for pressurization, and 2) the necessity and cost of cooling, flashing, and compressing the high-pressure gas carried into the reactor through the lock hoppers. The most discouraging aspect of this method was that lock-hopper operation had not been demonstrated (and still has not been) at the pressure of 200 atmosphere or more required for the PERC process.

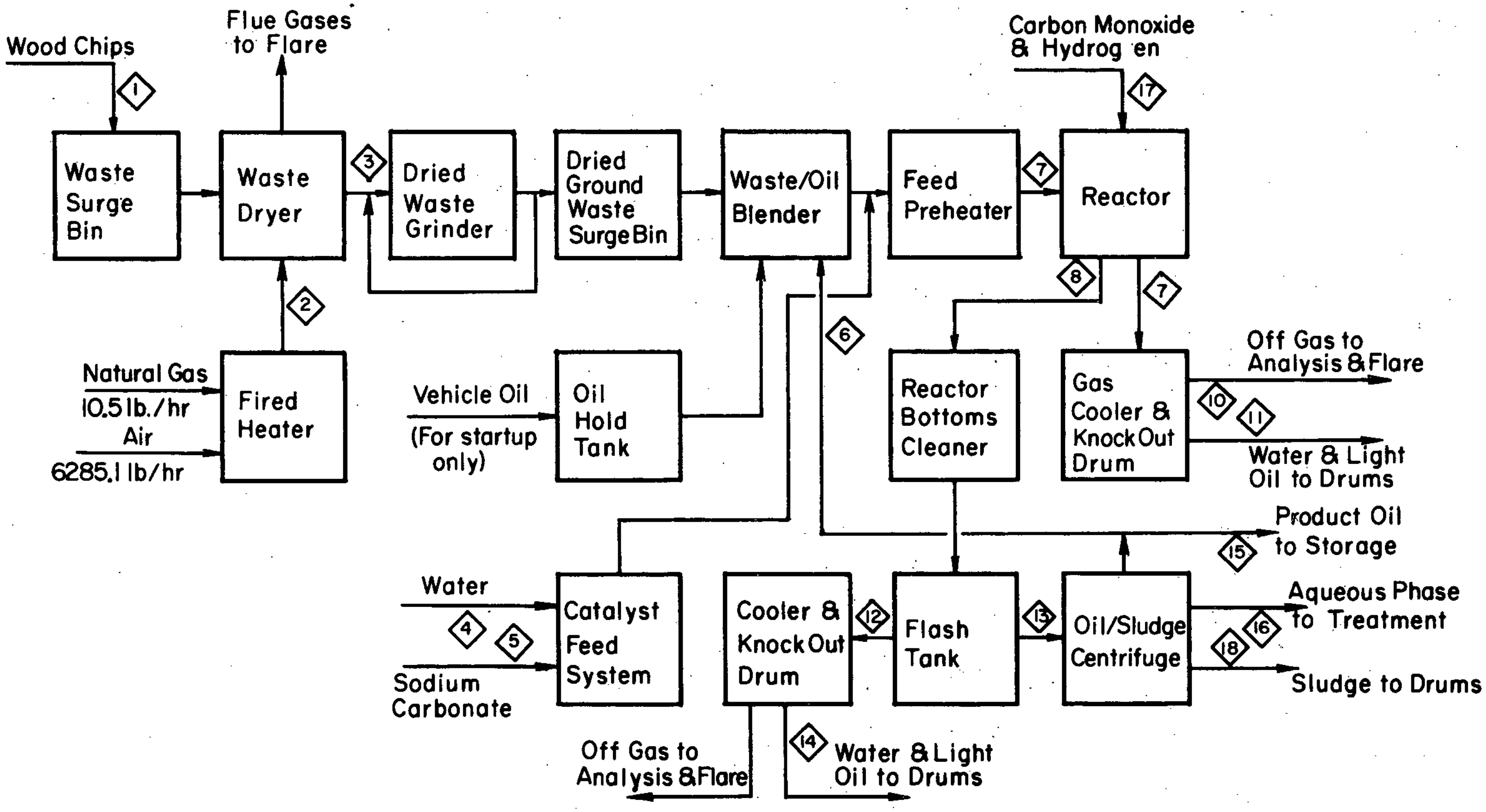
The third method (C) calls for pretreatment of the biomass before it is fed into the blender. The operative assumption is that after pretreatment of the biomass, a 50 percent biomass-oil slurry can be pumped. The pretreatment method envisaged by the PERC researchers comprises the following steps:

- Loading biomass into a preheater
- Adding process water to the preheater and heating the contents to 260°C and 750 psi with continuous stirring
- Cooling the product slurry to below 65°C by pumping it through an air-cooled heat exchanger followed by transfer to a slurry holding tank. The entire pretreatment operation will be performed batchwise as needed.
- Feeding preheated slurry continuously to a vacuum filter
- Pumping the filtrate into an aqueous waste holding tank for recycling or disposal
- Feeding solids by gravity from the vacuum filter into the dryer to reduce the moisture content to approximately 4 percent
- Grinding, storing, and processing the dried biomass as described in Methods A and B

Figures 5-7 are simplified process flow diagrams for each method. The material balances shown are based on the process flow diagrams prepared by Rust Engineering Company[164] and are reproduced from a Bechtel Report.[18] The Rust Engineering Company contracted with the Bureau of Mines to make a detailed engineering design of the pilot plant; and Maecon, Inc., was awarded the construction of the facility. The plant construction at Albany, Oregon originally scheduled for September 1976, was completed in December 1976.

4.6 Supporting Research and Development Plans

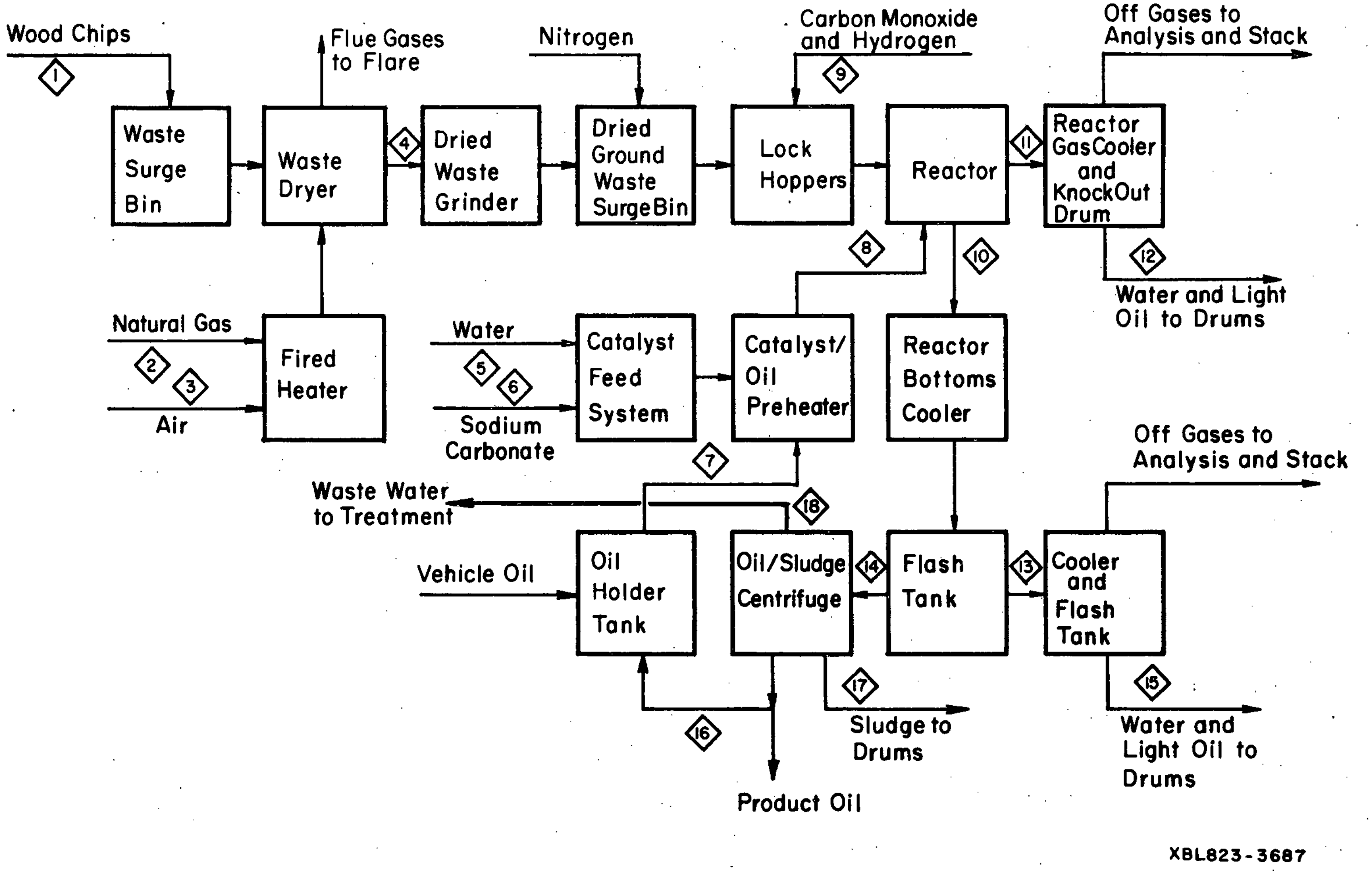
The Pittsburgh Energy Research Center of the Bureau of Mines had the facility and researchers to conduct supporting research and development for evaluating their proposed process in the process development unit. They had excellent analytical facilities, autoclaves, and a bench-scale continuous liquefaction unit capable of processing 1 lb/hr biomass, and they were constructing a larger continuous liquefaction unit capable of processing 10 to 20 lbs/hrs of slurry. This elaborate plan for research and development activity in support of the PDU stemmed from the recognition that the existing bench-scale data was not sufficient to assure technical and economical feasibility of the process. The energy crisis appeared to foster the decision to comstruct a PDU in order to speed the development of the process. Unfortunately for the planned coordination, a decision was made to construct the PDU at Albany, Oregon, adjacent to the Albany Metallurgical Research Center of the Bureau of Mines, instead of at Pittsburgh. Moreover, with anticipation of a reorganization, PERC was directed not to engage in biomass research.



XBL 823-3684

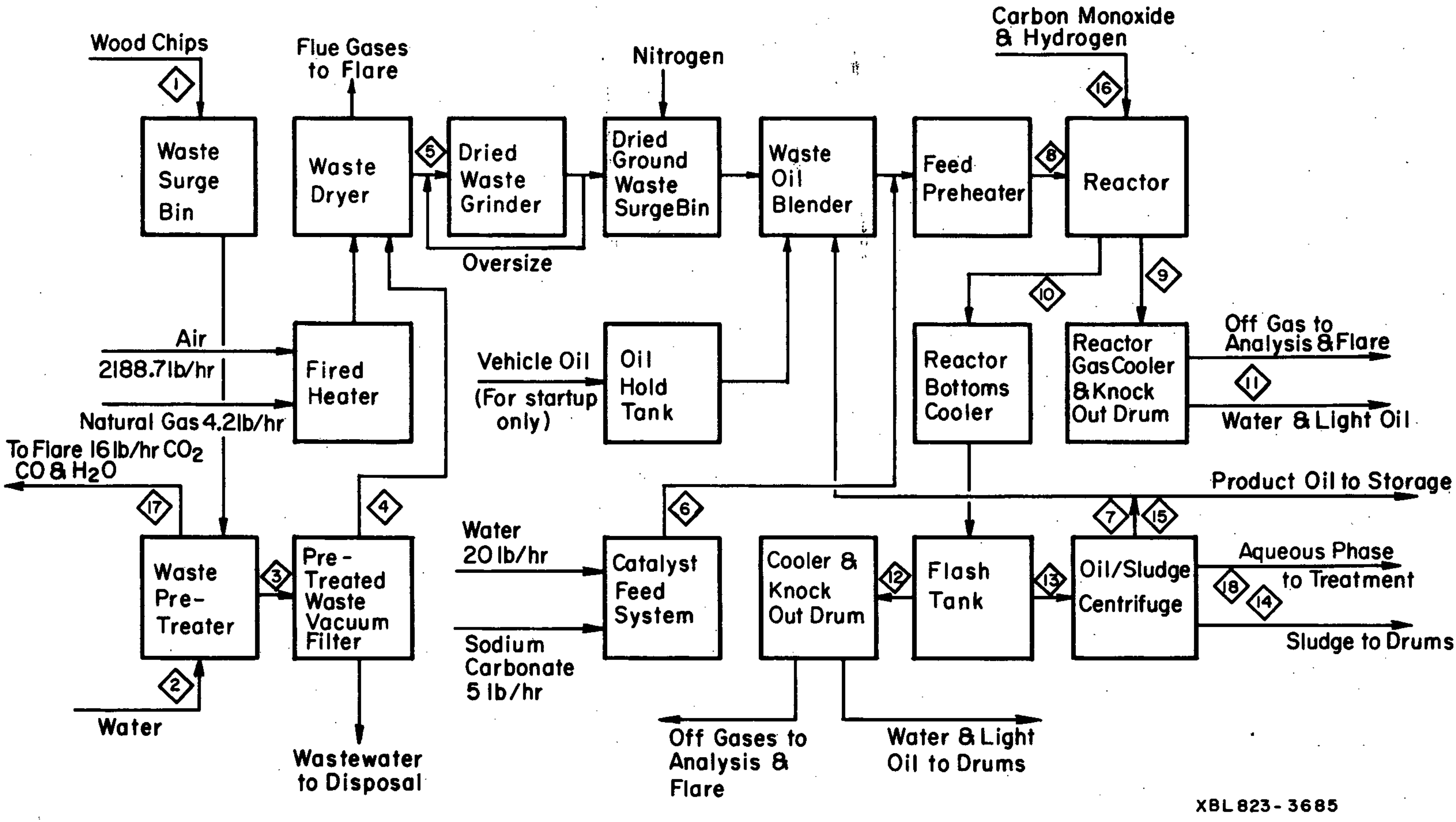
STREAM NO. / DESCRIPTION	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ASH	0.1		0.1				0.1											
CARBON DIOXIDE		27.3							15.4	15.4								
CARBON MONOXIDE									9.8	9.8							19.6	
HYDROGEN																		
METHANE																		
NITROGEN		4807.5																
OIL						421.4	340.2	421.4					421.4	NEG.	81.2			
ORGANIC SOLIDS	139.9		139.9				139.9											
OXYGEN		1413.5																
SODIUM CARBONATE					8.5		8.5	8.5					8.5	8.5				
SOLUBLE ORGANICS								4.2					4.2	4.2				
WATER	110	47.3	5.8	33.6			39.4	73.1	15.3	7.13	7.7	49.1	24.0	24.0		49.1		
TOTAL LBS/HR	250	6295.6	145.8	33.6	8.5	421.4	528.1	607.2	40.5	32.8	7.7	49.1	458.1	36.7	81.2	49.1	19.6	COMBINED
TEMP. °F	AMB.	210	185	60	60	212	630	705	680	180	180	240	240	212	212	180		WITH
PRESSURE PSIG	ATM.	1	ATM.	ATM.	ATM.	20	4000	4000	4000	5	5	10	10	ATM.	20	ATM.	4000	STREAM 14

Figure 5. Flow Diagram Using Wood/Oil Slurry Injection.



STREAM / DESCRIPTION	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ASH	0.1			0.1						0.1								
CARBON DIOXIDE		0.2									15.4							
CARBON MONOXIDE									58		67.8							
HYDROGEN																		
METHANE		9.8																
NITROGEN		0.5	4807															
OIL							146	146		227.2				227.2		87.2		
ORGANIC SOLIDS	139.9			139.9														
OXYGEN			1453															
SODIUM CARBONATE						8.5		8.5		8.5				8.5			8.5	
SOLUBLE ORGANICS										4.2				4.2			4.2	
WATER	110		25.1	5.8	34.0			34.0		34.2	54.5	24.9	34.2		34.2		NEG.	
TOTAL LB/HR	250	10.5	6285.1	145.8	34.0	8.5	146	188.5	58	274.2	137.7	24.9	34.2	240.0	34.2	87.2	12.8	COMBINED WITH STREAM 14
TEMP. °F	AMB.	60	60	185	60	60	240	630	580	705	680	180	180	286	180	212	212	
PRESSURE. PSIG	ATM.	2	1	ATM.	ATM.	ATM.	20	4000	4000	4000	4000	5	5	10	ATM.	20	ATM.	

Figure 6. Flow Diagram Using Lock Hopper Feed System.



STREAM NO. / DESCRIPTION	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ASH	0.1		0.1	0.1	0.1			0.1		0.1			0.1					
CARBON DIOXIDE									9.3								13.8	
CARBON MONOXIDE									5.9								0.5	
HYDROGEN																19.6		
METHANE																		
NITROGEN																		
OIL							132.7	84		132.7			132.7	NEG.	48.7			
ORGANIC SOLIDS	140		83.9	83.9	83.9			84										
OXYGEN																		
SODIUM CARBONATE						5				5			5	5				
SOLUBLE ORGANICS			11.5							2.5			2.5	2.5				
WATER	110	310	448.7	36	3.4	20		23.4	12.9	39.9	8.4	19.0	20.9	20.9			1.5	
TOTAL LBS/HR	250	310	544.2	120	87.4	25	132.7	196.5	28.1	180.2	8.4	19.0	161.2	28.4	48.7	19.6	15.8	COMBINED
TEMP. °F.	AMB.	60	150-500	90	185	70	212	630	680	705	180	240	240	212	212	580	140	WITH
PRESSURE PSIG	ATM.	ATM.	50-750	ATM.	ATM.	16	20	4000	4000	4000	6	10	10	ATM.	20	4100	5	STREAM 14

Figure 7. Flow Diagram Using Wood Pretreatment and Slurry Injection.

Section 5

ASSESSMENTS OF PROGRAM BY ERDA

5.1 Transition

Once the decision had been made by ERDA to consider biomass production and conversion as a solar technology, the branch now responsible for the biomass energy systems moved quickly to evaluate its programs and to initiate the new programs mandated. The biggest component of the wood-to-oil program was the Albany process development unit under construction. ERDA, therefore, had to evaluate the process for which the facility was being constructed, and the facility design and construction vis-a-vis other process options. The evaluation process had to be speeded because delays in construction schedules were rather costly, and ERDA proceeded with deliberate speed.

5.2 Bechtel Study for NSF

The National Science Foundation contracted with Bechtel Corporation to study the technical and economic desirability of waste-to-oil liquefaction. The tasks to be performed by Bechtel included a review of process flowsheets, analysis of the flowsheets regarding their consistency with the available bench-scale data, assessments of the effects of waste streams on the environment and/or of the added costs if additional processing steps become necessary, and an order-of-magnitude cost estimate of a commercial-size plant. An added task in NSF's neg!tiated contract with Bechtel was the outline of an R & D program for process development. The study for Bechtel was made by S. Ergun and T. Lindemuth.[18]

They developed flow diagrams for a liquefaction facility processing 2800 tons municipal waste daily, including a gasification plant utilizing 800 tons of the waste for synthesis gas production. The flow diagrams included feed preparation, reactor, oil recovery, gas production, catalyst recovery, gas purification, gas combustion, waste water treatment and syngas recycling systems. It was concluded that "On the basis of net operating costs alone, the plant does not appear to be economically feasible. For example, without disposal fees for the municipal waste, the net cost of the plant equals $19.28/ton, or in order to break even, a selling price of $16.13/bbl for the product oil would be required." In the report it was further noted that "In larger metropolitan areas, waste disposal fees as high as $15/ton are becoming more common, and thus the combination of reasonable disposal fees plus selling price for the oil may make the operation feasible." Bechtel made a comparison of the costs of direct firing of shredded and classified waste into existing coal-fired utility boilers and of pyrolysis of unshredded waste in the Union Carbide "Purex" unit. It was found that direct firing of solid waste as a supplemental fuel to a large coal-fired utility boiler "...is by far the most economic use for the waste." Pyrolysis to gas was found to be economically on a par with waste-to-oil, the broader range of oil marketability making oil more attractive under some circumstances.

The reaction stoichiometry and reactor-operating conditions constitute two of the most important bases for flow sheet development. Regarding the operating conditions it was noted that "...the temperature and pressure chosen are 300°C (572°F) and 2500 psia, respectively. These conditions will obviously be changed when pilot plant studies are concluded. At a temperature level of 300°C, the vapor pressure of water changes greatly with changes in temperature (a steep region of the Mollier diagram), the critical temperature being 374°C. A plus or minus 25°C change in the reactor temperature (at a total pressure of 2500 psia) would change the mole percent of the steam in the gas phase from 34.5 to 70.6 percent. Such a shift radically changes the treatment (volume, enthalpy, etc.) of the gases as well as the heat requirements of the preheater and of the reactor. Such changes would alter the economic picture considerably."

Stoichiometry of the reaction is the key to the material and heat balance for the reactor because it determines the quality of the oil produced, carbon monoxide and hydrogen consumed, and the treatment accorded the gases separated and the reactor bottoms (heat recovery, purification, etc.). It was concluded that the stoichiometry in a continuous operation with oil recycled over 7 times will be very different from that furnished by the Bureau of Mines. It was noted that by changing the oil yield by ±3 percent (assuming no change in product composition), the carbon monoxide comsumption rate will be changed by a factor of four or more; such uncertainties in the stoichiometry affect heat requirements, and the sizing and selection of heat-exchanger and gas-purification systems.

An interesting observation made in the Bechtel report concerned the reaction stoichiometry given Dravo Corporation by the Bureau of Mines, see Section 4.3. They noted that if water-gas shift occurs, i.e.

$$CO + H_2O \qquad CO_2 + H_2$$

relative amounts of CO and H_2 consumed from the synthesis gas do not affect the product distribution, except for CO_2 and H_2O generated, provided CO + H_2 introduced remains the same, e.g. 0.10354 in stoichiometry shown in Section 4.3. If no hydrogen reacted, as appears likely, 0.10354 CO would result in an increase of 0.12788 moles in CO_2 formed and a corresponding decrease in H_2O formed. Conversely, if 0.10354 moles of hydrogen were fed into the system, CO_2 formed would decrease by 0.17566 moles with a corresponding increase in the amount of water formed. It was further noted that if no CO or H_2 were fed into the system, one could obtain, stoichiometrically, the same oil yield having the same composition with minor changes in amounts of solubles, CO and H_2O formed (0.002, 0.197 and 0.191, respectively.) A recent reconstruction of wood-liquefaction stoichiometry has been carried out, indicating $CH_{1.365}O_{0.632}$ and 0.141 CO as the reactants.[54a]

Other major factors which introduced uncertainties to the equipment design and selection were identified in the Bechtel report as feed-slurry properties, oil properties, heat of reaction, and synthesis-gas composition. On the basis of this analysis, it was concluded that the design bases for the PERC process were not established! Inasmuch as no bench-scale supporting research was being conducted at that time to resolve the uncertainties in the Bureau of Mines waste-to-oil liquefaction process, the necessity of completing the construction of the PDU at Albany, Oregon, came into question. The National Science Foundation then solicited an opinion from Bechtel regarding the desirability of completing the PDU and operating it. One factor in favor of construction completion was that the savings to be effected by cancellation of the contract were not very significant. A second favorable factor was that there were and still are, many unit operations peculiar to the process and to biomass handling that cannot be adequately investigated in small units. In particular it was noted that the pilot plants under construction had three different wood injection systems and that the blending, pumping, product separation, etc. called for in the process had sooner or later to be tried in a PDU. The major factor unfavorable to construction completion was that neither the reaction stoichiometry nor the operating conditions were established. In addition it was found that the pilot plant needed modifications (eight were listed) and its location, near a residential section, was not very desirable. It was also pointed out that "...pilot plant operations are by no means inexpensive"; therefore, purely research-type activity could not advantageously be conducted at Albany.

Bechtel then made an in-depth study of the flowsheets of the pilot plant and developed an outline of R & D program for the plant, considering each and every unit operation: conveying, drying, milling, feeding, blanding, preheating, reactor operation, product gas treatment, ractor bottom treatment, catalyst recovery, and sludge and waste-water treatment. Particular emphasis was placed on the development of start-up procedure. They predicted that the commissioning and shakedown operations of the facility would be beset with many difficulties, largely because of the multiplicity and complexity of the unit operatons involved and that development of any process for direct liquefaction of biomass would require a pilot plant scale process development unit. Their conclusion was that "...a large-scale pilot plant, such as the one under construction at Albany, Oregon, is needed to provide firm data and to improve the Bureau of Mines waste-to-oil liquefaction process, if it is decided to proceed to the design and selection of equipment for a commercial plant."

5.3 PNL Study for ERDA

Battelle Pacific Northwest Laboratories were commissioned by ERDA[17] "...to identify and evaluate, as a basis for decision, the available alternatives for future utilization of the (Albany, Oregon) facility." The scope of the PNL study differed considerably from that of Bechtel in many respects. The PNL study dealt with the potential contribution of the "Fuels-from-Biomass" program to the "nation's energy economy" including resources (wood wastes, food processing wastes, residues from biological conversion processes), alternative processes for liquid fuels (Fischer-Tropsch process, Bergius process, Garrett process, fermentation processes, and methanol production), and long-range research and development plans. The conclusions drawn were, like the study, organized "as a series of evaluative tasks."

Regarding the status of current technology, it was concluded that, 1) Available bench-scale data were not adequate to extrapolate to continuous process conditions; 2) "It is probable that the defined process can be simplified to improve performance by avoiding the consumption of carbon monoxide and reducing the operating pressure;" 3) The stability of the oil product, sufficient enough to serve as a recycle vehicle for feeding solids, was questionable; 4) The suitability of the oil product as a substitute for petroleum-derived fuels had not been determined.

Regarding the pilot plant, the conclusions were: 1) Judgement played a great role in the selection of process parameters used in the design of the pilot plant; 2) "The pilot plant can operate at the process conditions of the original process concept, is sufficiently flexible to accommodate significant process modifications, and can be used with little or no physical modifications to investigate alternate processes such as hydrogenation;" 3) "All unit operations critical to a thermochemical conversion process are included in the pilot plant;" 4) "The pilot plant includes no provisions for effluent waste treatment development or for product refining."

In the conclusions concerning utilization of the mechanical processes, it was recognized that the original process was not viable in the then existing economic environment; but they were favorable to undertaking a development program at Albany, because modified versions of the process appeared to be feasible and economically viable, and sufficient organic material regarded as waste was available in economically collectible concentrations. Their conslusion was that "...the Albany pilot plant should be commissioned and operated" for the purpose of potential utilization of thermochemical processes.

The conclusions drawn in the PNL report were somewhat optimistic, as illustrated in the paragraph quoted below:

> The Albany pilot plant facility may also be considered as a resource which is not now committed to a specific detailed program. As a development facility, it has some degree of flexibility and may be a valuable tool for developing a variety of conversion processes. In this context, the facility should be used to maximum advantage in the national energy Research, Design, and Development (RD&D) programs regardless of the original basis and justification for its construction.

The major feature of the PNL report was the development plan outlined. Figure 8 shows a diagram of the decision points, time spans, and activities recommended by PNL "...in developing the Albany facility." The program cost after five years was estimated to be between \$8 and \$10 million. It is most likely that the total annual cost of the program after two years would have approached \$2 million (based on the manpower estimates by PNL); and the total cost of a 102-month development program would most likely have exceeded \$17 million, not allowing for any inflation.

5.4 Bechtel Study for ERDA

The second study authorized by ERDA concerned a detailed technical evaluation of the PDU nearing construction completion at Albany, Oregon[19] Bechtel Corporation was contracted to undertake the study which comprised seven major tasks. The first task involved a detailed analysis of the modifications and additions to the facility to meet the objectives of the program that ERDA had tentatively formulated, viz.,

- To obtain sufficient data to assess the technical and economic feasibilities of the PERC process and to further develop it if found to be feasible
- To develop auxiliary unit processes that would improve the economics of the PERC process if the process approaches economic feasibility
- To evaluate the performance of special equipment available at (and those that would be incorporated in) the Albany facility with a view of technology development regardless of the nature of the process
- To develop other promising biomass-to-synfuel processes in base of unfavorable results from PERC process.

Another factor considered in the modifications was the time element. Accordingly, Bechtel divided the modifications into three groups. Group I modifications were intended to be completed before the start-up. They concerned the slurry preheater, slurry-pump checkout, product-oil yield monitoring, and high-pressure slurry sampling. Group II modifications were to be initiated after the startup, and included in the first year of commissioning and shakedown operations. Group II modifications were to be incorporated in the future and reassessed according to the progress made during the first year. Sketches of the recommended modifications and estimates of costs and installation time schedules were provided as called for in the second task of the contract.

The third task called for the development of the scope of an R & D program to assess the waste-to-oil technology and an order-of-magnitude cost estimate and time schedule. In addition, this task called for an assessment of laboratory analyses that were likely to be required in the development program, including specification of each type of analysis needed, itemization of equipment required, and a preliminary estimate of sample-taking time ranges from one week to a month for the test runs anticipated.

Other tasks performed by Bechtel included identification and review of the biomass-to-synfuels processes under development or under consideration elsewhere, and of the potential environmental impacts associated with the Albany, Oregon, facility (including resultant operational constraints). The study also called for a list of equipment to be installed in the Albany facility, a spare-parts inventory for the equipment, and estimates of availability and delivery times.

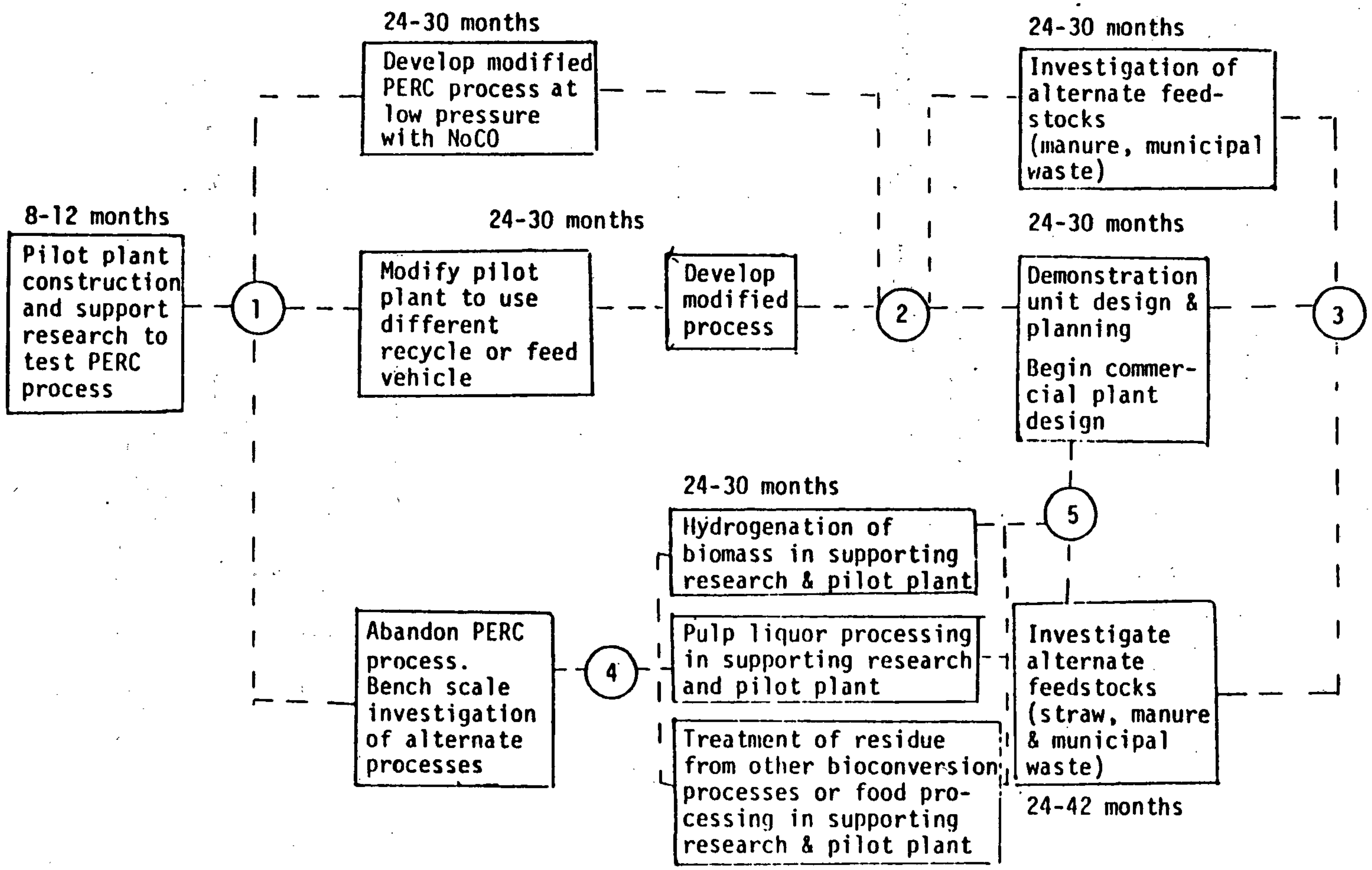
The cost estimate of the first-year operation of the facility (commissioning and shakedown) provided by Bechtel was slightly over $1 million, on the basis of a ready-to-run plant; i.e., both the office building and maintenance shop furnished and an initial set of spare equipment parts secured. The estimate did not include the cost of planned modifications nor of operating on a 7-day-weel schedule.

In the Bechtel proposal, assessment of task scheduling flexibility and partial plant utilization in case of failure of some process units received a great deal of attention. Because the importance of the various unit operations to the technical feasibility of the process was realized, special studies were formulated. Considering the biomass injection as a slurry, (cf. Figure 5 in Section 4), it was logical to ask what types of experiments were needed in order to accept or reject the method. Figure 9 shows the diagram of a study intended to evaluate the potential of biomass injection by blending the biomass flour with an oil, using a positive displacement pump to transfer the slurry into a high-pressure vessel, independently of the performance of the preheater or reactor.

In the studies indicated in Figure 9, it was anticipated that the rheological properties of the biomass could be a factor in thetechnical feasibility of the injection method. If Study A results were to indicate that injection of biomass flour blended with an oil at concentrations approaching 30% by weight was technically feasible, but the nature of the start-up oil and conditions of the operation required special attention -- then Study B, indicated by the logic diagram of Figure 10, would be recommended.

Figure 11 shows the logic diagram of the experimental program envisaged by Bechtel, as presented to ERDA in September of 1976. In retrospect we may state without reservation that adherence to the program schedule of priorities would have led to the dismissal of the PERC process, as early as April of 1978, as being not feasible chemically and technically.

The concern of the Bechtel team regarding the PERC process was not confined to the chemistry of the reactions taking place at the front end of the process (i.e., injection), start-up procedure, etc. Although not explicitly stated, a two-stage liquefaction process involving the treatment of a sludgy product was anticipated. The Bechtel proposal contained the conceptual design of oil recovery from a sludgy product shown in Figure 12.



Decision Points

1. Research completed on oil stability & CO-pressure requirements in the process or modification. Technically viable? Or should an alternate process be considered.
2. Research completed on wood or straw feedstock. Which alternate feeds should be considered? Begin demonstration plant development.
3. Decision to build demonstration plant and complete commercial plant design.
4. Decide which alternate should be investigated.
5. Decision to design and build demonstration plant.

Figure 8. Major Decision Points and Alternates - Thermochemical Conversion of Biomass to Oil or Fuel Products[17]

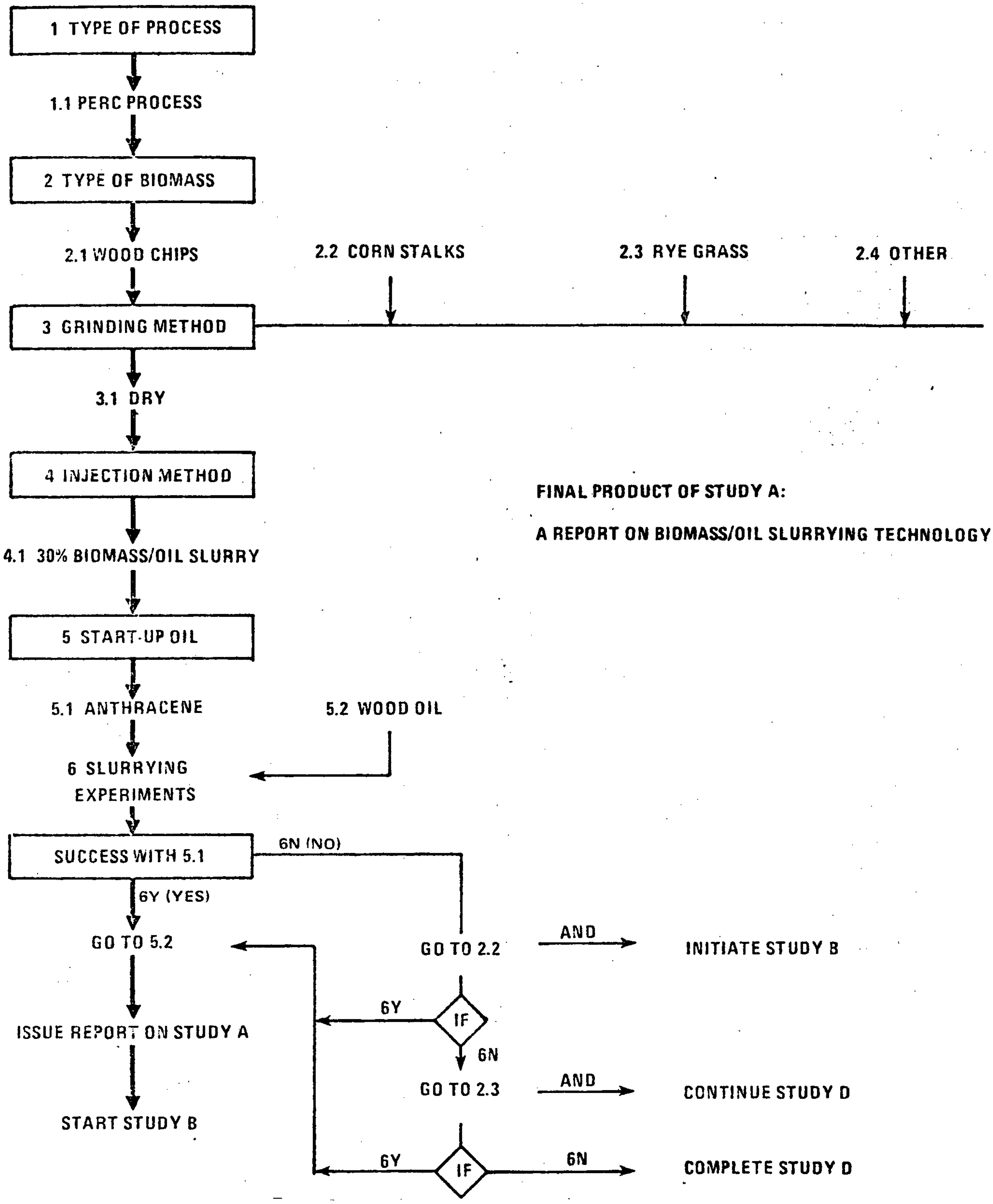
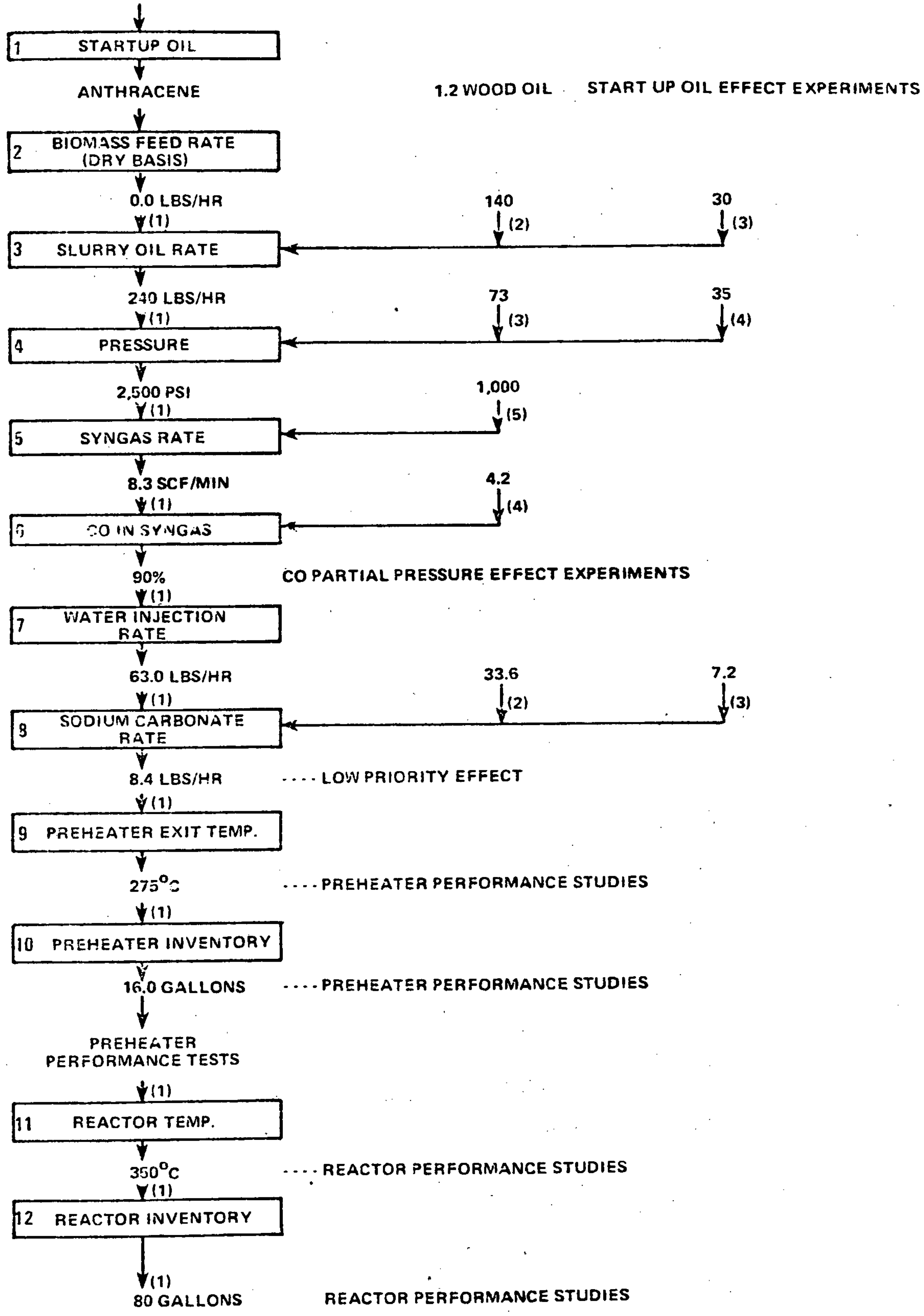
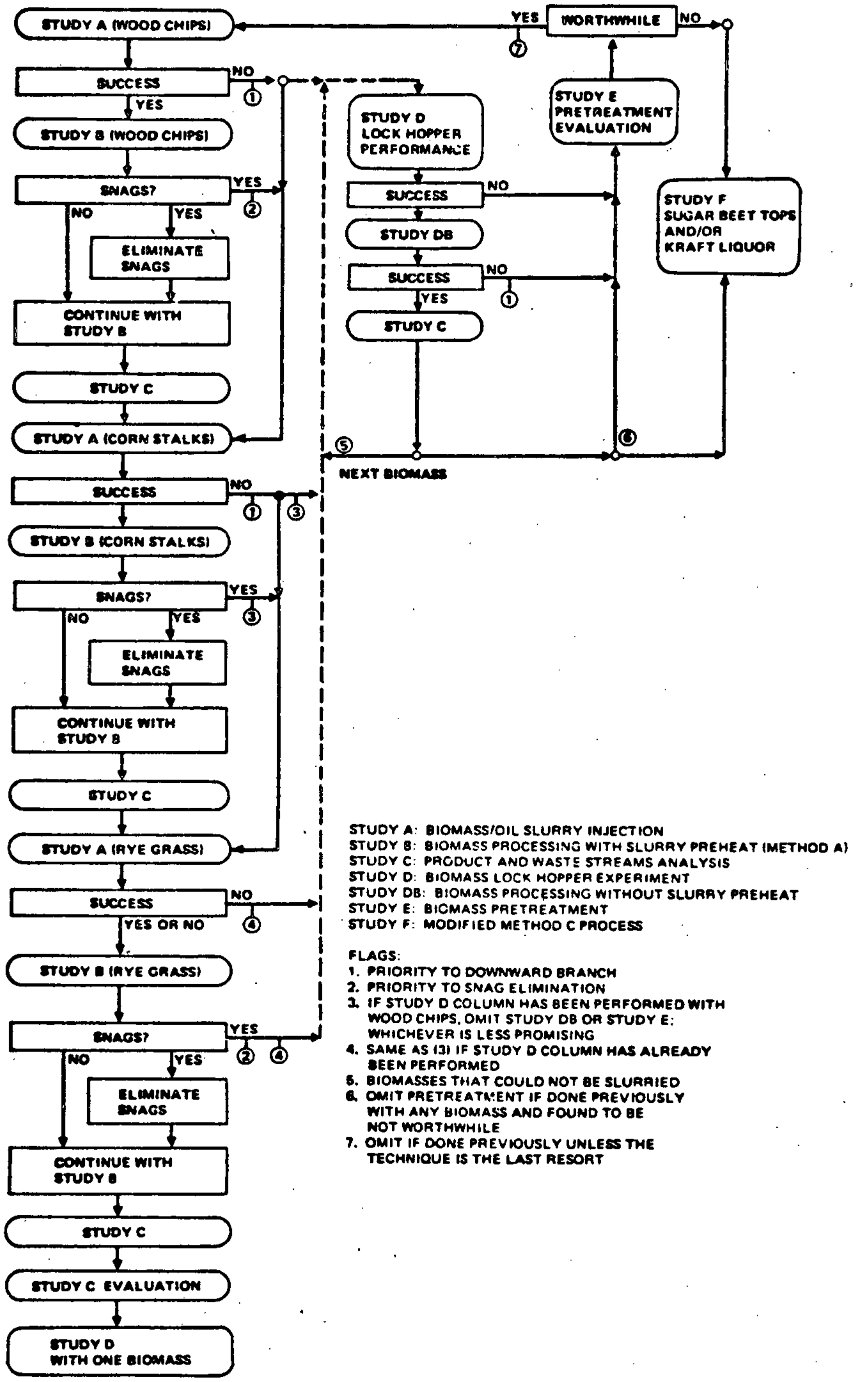


Figure 9. Biomass-Oil Slurry Injection[18]



NOTE:
FOR A RUN DESIGNATED BY A NUMBER IN PARENTHESIS, THE PREVAILING NUMBER IN ANY ROW IS THE LARGEST NUMBER WHICH IS EQUAL TO OR LESS THAN THE RUN NUMBER.

Figure 10. Biomass Logic Diagram[18]



STUDY A: BIOMASS/OIL SLURRY INJECTION
STUDY B: BIOMASS PROCESSING WITH SLURRY PREHEAT (METHOD A)
STUDY C: PRODUCT AND WASTE STREAMS ANALYSIS
STUDY D: BIOMASS LOCK HOPPER EXPERIMENT
STUDY DB: BIOMASS PROCESSING WITHOUT SLURRY PREHEAT
STUDY E: BIOMASS PRETREATMENT
STUDY F: MODIFIED METHOD C PROCESS

FLAGS:
1. PRIORITY TO DOWNWARD BRANCH
2. PRIORITY TO SNAG ELIMINATION
3. IF STUDY D COLUMN HAS BEEN PERFORMED WITH WOOD CHIPS, OMIT STUDY DB OR STUDY E: WHICHEVER IS LESS PROMISING
4. SAME AS (3) IF STUDY D COLUMN HAS ALREADY BEEN PERFORMED
5. BIOMASSES THAT COULD NOT BE SLURRIED
6. OMIT PRETREATMENT IF DONE PREVIOUSLY WITH ANY BIOMASS AND FOUND TO BE NOT WORTHWHILE
7. OMIT IF DONE PREVIOUSLY UNLESS THE TECHNIQUE IS THE LAST RESORT

Figure 11. Experimental Program Schedule of Priorities[19]

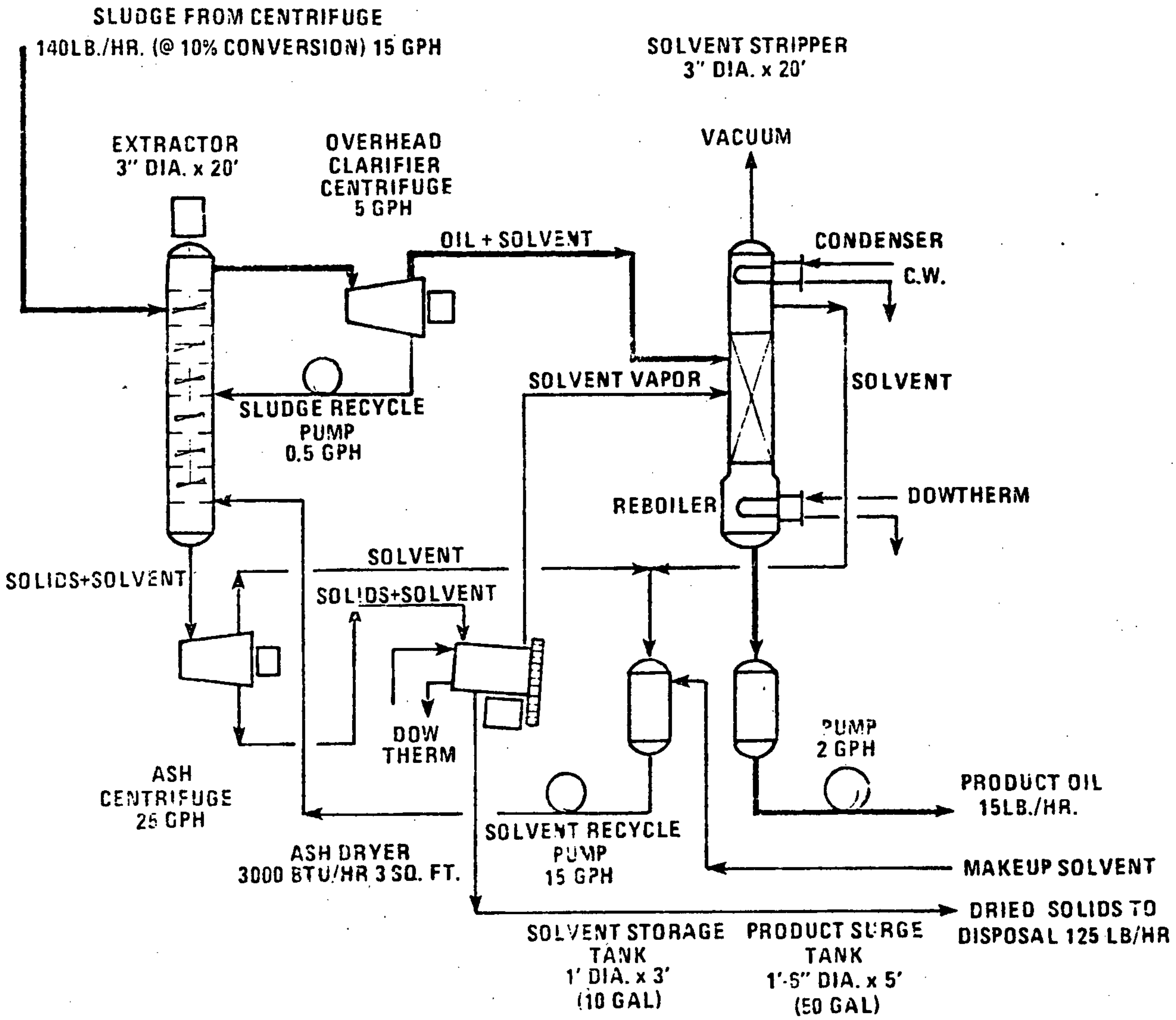


Figure 12. Oil Recovery from Sludge[19]

Section 6

CHECK-OUT, COMMISSIONING, AND OPERATION OF THE ALBANY BIOMASS LIQUEFACTION TEST FACILITY BY BECHTEL CORPORATION

Upon review of the studies made by PNL and Bechtel, and upon other information, ERDA negotiated a contract with Bechtel to check out the Albany PDU, commission it, and if possible, perform some test runs to produce oil. Bechtel was also given the responsibility to furnish the office building and the maintenance shop, secure an initial set of spare equipment parts, and to arrange for utility, janitorial, and security services.[20]

6.1 Concern by Bechtel over the Chemical and Technical Feasibility of the Process

In the Bechtel report to NSF, the reaction stoichiometry was singled out as a very important parameter, if not the most important, influencing the economic feasibility of the process. The validity of the stoichiometry deduced by PERC researchers was not in question, because it was based on the results of some rather straightforward experimental results. As an example, we may write the results of an experiment:

> A sample of 30 g Douglas Fir wood flour when impregnated with 1.8 g Na_2CO_3 in 7.2 g H_2O, blended with 70 g anthracene oil, and reacted with carbon monoxide under a total pressure of 4000 psig at 350 C for 45 min., resulted in 87.0 g organic material soluble in acetone. Since anthracene oil is soluble in acetone and was found to undergo no detectable reaction under the conditions imposed, it is reasonable to suppose that the reaction yielded an oil-like substance weighing 17 g.

Furthermore, assume now that we are given the stoichiometry shown in Section 4.3. It is very difficult to be skeptical about the results. What was found in the course of the Bethtel study for NSF is that the synthesis gas required in the stoichiometric relations deduced was extremely sensitive to the composition of the biomass, and to the yields and composition of the products. For this reason alone, it was concluded that the design basis of the process was not established.

Faced with the task of commissioning a pilot scale facility to establish the design bases of the process for which the facility was originally designed and built, Bechtel began to have second thoughts about the feasibility of the PERC process. There was, of course, no reason to doubt that a 17 g oil-like substance could be produced from 30 g of wood flour under the conditions described, provided of course, that 70 g vehicle oil was available to conduct the experiment. No researcher, however, had succeeded in separating the vehicle oil used in the first experiment and using it again in the subsequent experiments. It was reasoned that if the vehicle oil could not be physically or chemically separated from the oil produced, the process could not be regarded as technically feasible. On the other hand, it was argued that the concern over the fate of the startup oil was not justified, because the process would rely on recyle oil produced in the process, as its vehicle oil. This argument in defense of the PERC process focused the attention on the chemical feasibility of the process. The counter argument was that for the process to be chemically feasible, wood flour (30 g) when fixed with recycle oil (70 g) must result in a product oil (87 g) having a composition identical to the recycle oil. The Bechtel team included a few who were not convinced that the PERC process was chemically feasible, as revealed in the paragraph quoted below from the Bechtel proposal:

> For the PERC process to be self-sustaining, one of the following requirements must be fulfilled:
>
> o The vehicle oil must be separated from the product oil so that it can be recycled, or
> o The product oil must be identical to the vehicle oil
>
> Although various organic solvents have been used by PERC researhers, the problem of complete recovery of vehicl oil either did not receive adequate attention, or perhaps, proved to be impractical. The pilot plant design is therefore based on using the product oil for the vehicle oil. This premise is one of the ambiguous aspects of the present pilot plant design. For the premise to be valid, the recycled vehicle oil must go through the reactor unaltered and this does not appear to be likely. A logical solution appears to be separation of the oil emerging from the reactor into a recycled vehicle oil stream and a product oil stream by distillation, as is the case in the solvent refined coal process.

(Although the problem was stated awkwardly, the concern over availability of internally produced recycle oil was highly appropriate.)

6.2 Technical Approach Proposed by Bechtel

Bechtel's concern over the chemico-technical feasibility of the PERC process was genuine as indicated in the statement contained in their proposal which is quoted below:

> Since the process has not been developed beyond bench-scale experiments and much of the technology required for a commercial process is lacking, it is conceivable that the PERC process as presently designed may never become commercially feasible.

Accordingly, the broad outline of the Bechtel proposal included the following:

- o In-depth analyses of the performances of essential and unique equipment, individually and in tandem, available at Albany, with a view toward developing technology; i.e. not limited to the PERC process. The equipment singled out included blender, high-pressure pump, lock hoppers, pretreaters, recirculation pumps, pressure let-down system, and three-phase centrifuge.
- o Initial evaluation test runs on the PERC process, confined to conditions critical to the feasibility of the process.
- o Exploratory test runs on other process schemes that may be proposed.

6.3 Plant Check-out and Commissioning

Check-out and commissioning of the facility started in January 1977, and proved time-consuming. Because of reorganizations, neither the flowsheets of the facility design nor its construction received input from a team qualified to develop the process. The ground floor of the PDU was crowded (and still is) and had poor weather protection and limited access. Some rearrangement became necessary to meet State and OSHA regulations.

Difficulties with process equipment are not unusual in the development of a new process. However, the mechanical difficulties encountered at Albany were too numerous; they mostly resulted from improper material selection, equipment design, or faulty quality control. Moreover much of the equipment was not properly sized to permit flexibility in operation. For example, the grinder had only one-fourth the capacity specified in the design, and there were no specifications on the performance of the three-phase centrifuge.

The schematic of the Albany PDU is shown in Figure 13. A detailed account of the mechanical difficulties and modifications made is given in the Bechtel report. Below are listed some of the check-out efforts and modifications made by Bechtel:

- o Added outlet nozzles to preheater
- o Made piping changes to feed synthesis gas through the preheater
- o Designed and constructed a high-pressure slurry sampling system between the preheater and reactor
- o Made piping changes to introduce sodium carbonate solution ahead of preheater
- o Added water heater for catalyst make-up
- o Added shed for catalyst storage
- o Added storage shed for wood chips
- o Added a 250 gallon product oil hold tank
- o Modified chip bin discharge device
- o Made piping changes to bypass reactor

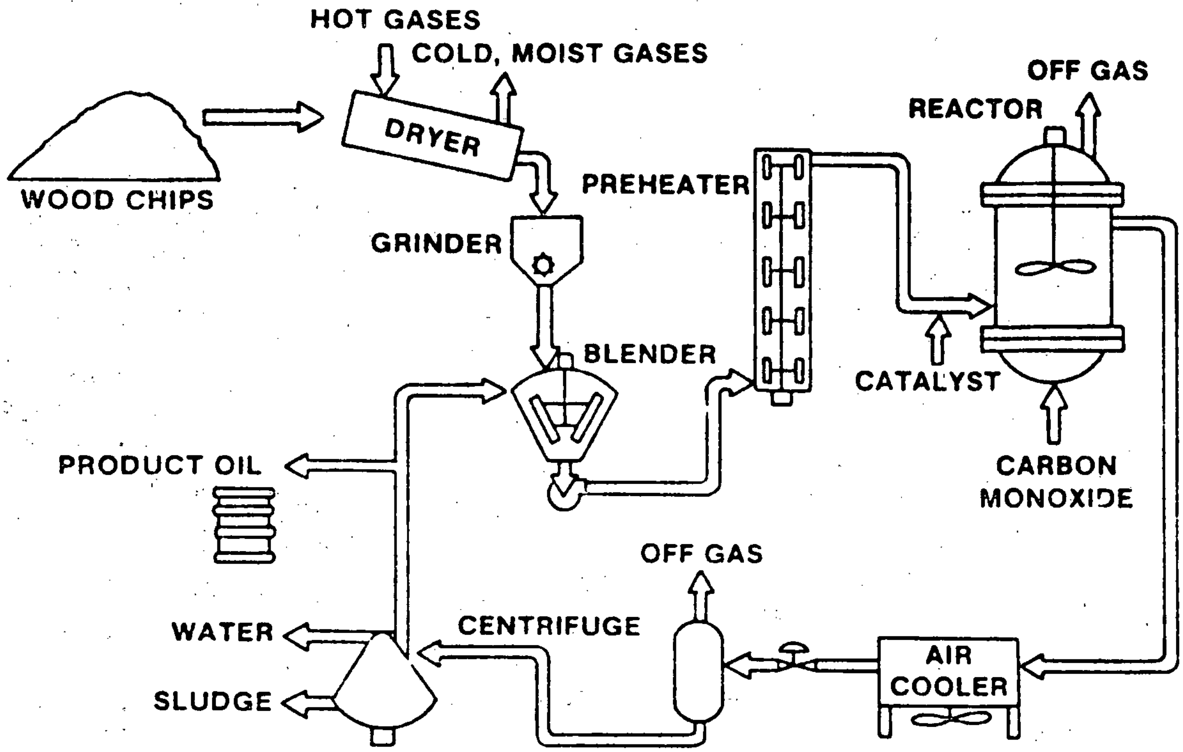


Figure 13. PERC Process Schematic[19]

- Made piping changes to permit upflow through the reactor
- Installed a blender to permit use of a hydrogen-carbon monoxide mixture in the system
- Replaced defective carbon monoxide compressor
- Replaced unsuitable gaskets and polymeric seals and pump starters
- Modified the reactor head closure to permit cycle operation
- Removed the reactor agitator because of inability of the agitator shaft seal to hold pressure

Before process testing began, th entire facility was checked out, and all equipment was proof-tested. The major process items requiring proof-testing were:

- seven pressure vessels
- fifteen pumps
- six heat exchangers
- six wood handling units
- forty electric motors
- sixty control loops

6.4 Operating Results

The difficulties encountered in the check-out and commissioning of the PDU upset the schedule of the activities anticipated. That the PDU was poorly designed and poorly constructed was not apparent until the facility was checked out. Consider now the following findings by Bechtel:

- The preheater of the PDU was not the prototype of a unit capable of being scaled-up. Its agitator shaft seal failed frequently, and the blades designed to scrape its wall broke down frequently.
- The heat input rate for the preheater was not adequate to provide heated slurries to the reactor at reasonable temperatures and rates.
- The seal of the agitator shaft was improperly designed or constructed; it would not hold pressure in excess of 750 psi, necessitating its removal. This prevented testing the lock-hopper system designed for 4,400 psi, the first system designed to exceed 1000 psi.
- The centrifuge installed for separation of sludge and aqueous phase from the oil did not function properly.

Bechtel originally had expected that the check-out of the facility and the evaluation of the performances of the various process units individually or in tandem would take about four months, and then the operation of the complete system to obtain "initial process" would start. After four months of plant check-out efforts, Bechtel realized that it was not going to be possible to achieve the original goals, so was faced with two options: 1) to improvise to obtain some oil, if possible; 2) to negotiate with ERDA to redesign, construct (or procure), and install or modify inoperative or flawed process units.

Bechtel chose the first option. It took two additional months to effect the improvisations and make test runs. In the test runs made, the centrifuge shown in Figure 13 was taken out of the system and the reactor was bypassed. Carbon monoxide and catalyst were injected into the slurry entering the preheater. The product was withdrawn at intervals of about eight hours.

Excluding the preliminary tests, Bechtel was able to conduct eighteen test runs lasting 24 hours or longer, totaling 850 hours, the longest test run lasting 90 hours. Bechtel processed about 19 tons (dry basis) of wood chips and produced about 48 barrels of oil derived from wood. The oil withdrawn from the system was mixed with the startup anthracene oil, and process-oil concentration in it did not exceed 50 percent. In general it took about 40 hours to reach the 50 percent level, and most of the runs had to be ended at that point. The average duration of twelve test runs was about 43 hours; in six more runs the test was lengthened by adding sufficient fresh anthracene oil to the blender to keep the wood-oil concentration at about 50 percent.

6.5 Summary, Conclusions, and Recommendations

Results and conclusions drawn in the Bechtel report are summarized as follows:

1. Process oil yield is about 50 percent.

2. Carbon, hydrogen, nitrogen, and oxygen contents of process oil are 83.5, 7.0, 0.4, and 9.1 percent, respectively, by weight on moisture and inorganics-free basis. The organics present in the product were estimated to be 7.5 percent, on a moisture- and solvent-free basis.

3. The estimated heat content of the process oil is 15,200 Btu/lb, and its vapor pressure at room temprature 13 Torr.

4. Temperature of the slurry leaving the reactor and carbon monoxide partial pressure in the exit gas have little effect on conversion, provided the former is above 550°F and the latter above 800 psi.

5. "Residence times of 16 to 18 minutes appear to provide technically acceptable conversion. Longer residence times provide small increases in conversion."

6. Partial water pressure in the preheater outlet gas phase is about 30 percent of the vapor pressure of water at the same temperature.

7. The failure to produce a pure process oil is the result of polymerization of the reaction product.

8. "Within the capabilities of the plant, much information was obtained that could be used for process evaluation, scale-up to large-sized equipment, and preliminary economic evaluation."

9. Process development activity at Albany should be continued.

Bechtel made a number of recommendations for continued studies at Albany in three general areas:

a. <u>PDU Reactor System Modifications (add the following units)</u>

- o Preheater coil
- o Reactor vessels (2)
- o Flash tube (2)
- o Gas scrubbers
- o Large capacity blender
- o Slurry feed pump
- o Slurry recirculation pump
- o Product incinerator
- o Steam boiler for decoking

b. <u>Increased Analytical Capacilities</u>

Laboratory facilities were proposed:

- o Elemental analyzer
- o Vacuum distillation
- o Gas and liquid chromatography
- o Infrared and UV spectrophotometers
- o Atomic absorption spectrometer
- o Differential thermal analyzer

c. <u>Process Development Studies</u>

- o Study of product separation techniques
- o Study of hydrogen/carbon monoxide mixtures (syngas) effects
- o Upgrading of product
- o Studies of alternate vehicle oils and biomass feeds
- o Studies on effluent treatability

6.6 Economic Evaluation

Bechtel conceptualized two integrated plants, one for liquefaction and one for gasification to provide synthesis gas for the liquefaction plant and for heat requirements. Each plant was sized to process 2,500 dry tons of wood daily. The schematic of the conceptualized facility is shown in Figure 14.

The reaction stoichiometry assumed in the design was:

$$CH_{1.517}O_{0.687} + 0.438\ CO \qquad CH_{1.517}O_{0.249} + 2.625\ CO_2,$$

which dictated that the amount of wood to be gasified to meet the synthesis gas requirements would be roughly equal to that liquefied. A breakdown of the cost analysis made by Bechtel revealed that the installed capital cost of the gasification plant processing 2,500 TPD wood would be 50 percent higher than that of the liquefaction plant processing the same amount of wood ($93 million vs. $62 million), and that the breakeven production cost of the oil produced would be just under $35/barrel. The Bechtel projection as to how this cost could be reduced with continuous development efforts is shown in Figure 15.

6.7 Overview of Bechtel Report

The Bechtel report[20] contains a detailed account of the experimental results, with extremely valuable information regarding equipment performance. The observations made below concern only the interpretation of the results and some of the conclusions.

- In the report the equipment breakdowns were well documented. The operational difficulties encountered, on the other hand, did not receive adequate emphasis in certain respects. The difficulties resulted in excessive fluctuations in temperature (625 ± 55°F in Run No. 19), wood flour feed rate (37 ± 11 lb/hr in Run No. 14), slurry feed rate (45 ± 10 gph in Run No. 16), etc., during the course of most of the test runs conducted. These difficulties were partly responsible for the lack of correlations between wood conversions and the operating conditions imposed (cf. items 4-6 in Section 6.5).

- Product oil polymerization was singled out in the report as the likely cause of failures to obtain a product containing more than 50 percent wood oil. Sudden jumps in the product viscosity suggest sludge accumulation in the preheater in which the slurry moves very slowly, less than 1 ft/min., with its contents not being mixed to any significant degree. A simple calculation shows that if the solid residue amounted to about 5 percent (based on wood flour) and initiated sludge settling in the preheater, a sludge composed of 50 percent solid residue would fill the preheater in about 40 hours, the average duration of most of the test runs conducted.

- The economic feasibility analysis made by Bechtel is flawed for two simple reasons:
  1. It assumes that it will be technically feasible to inject a slurry

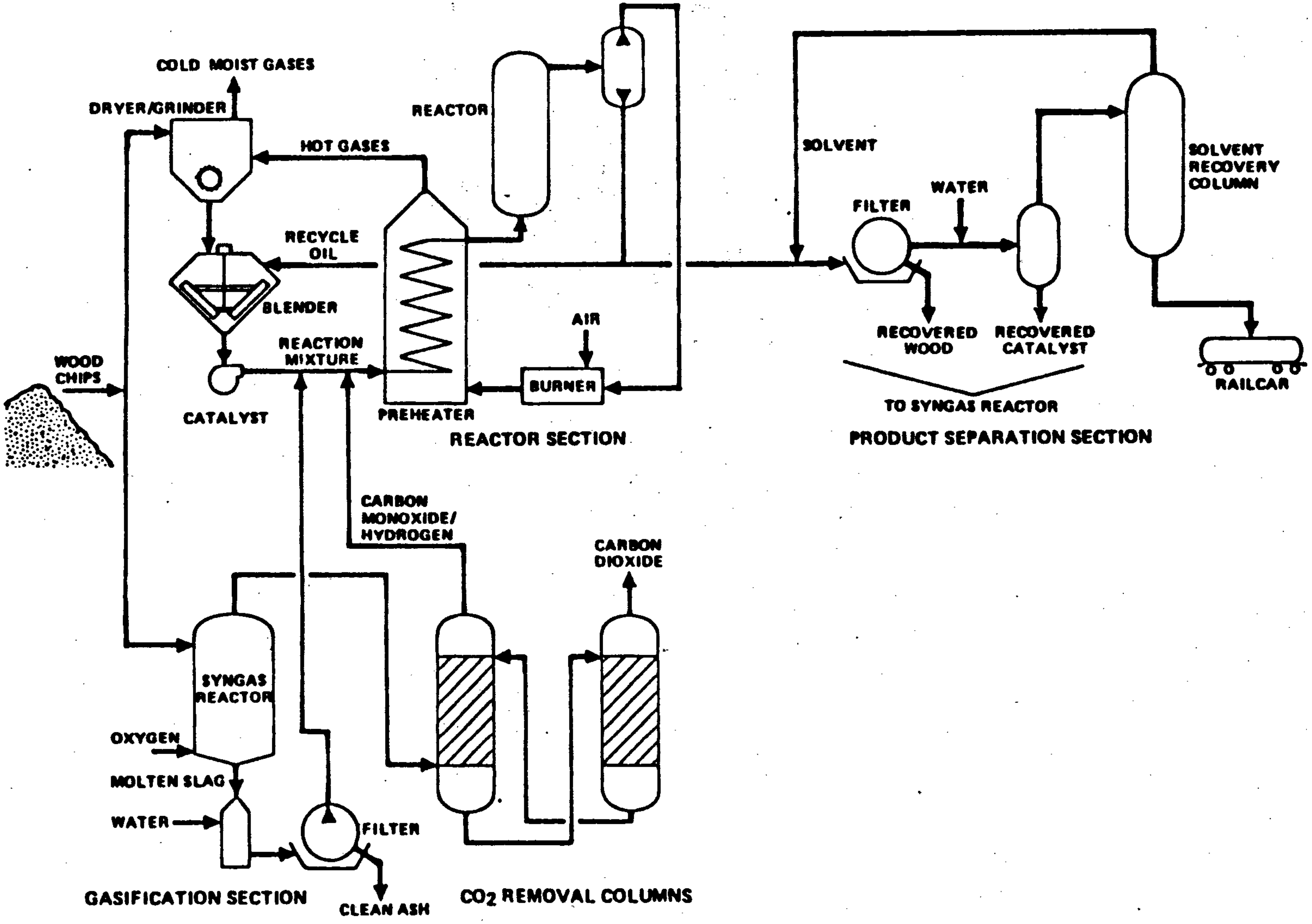


Figure 14. Commercial Biomass Liquefaction Pilot Schematic[20]

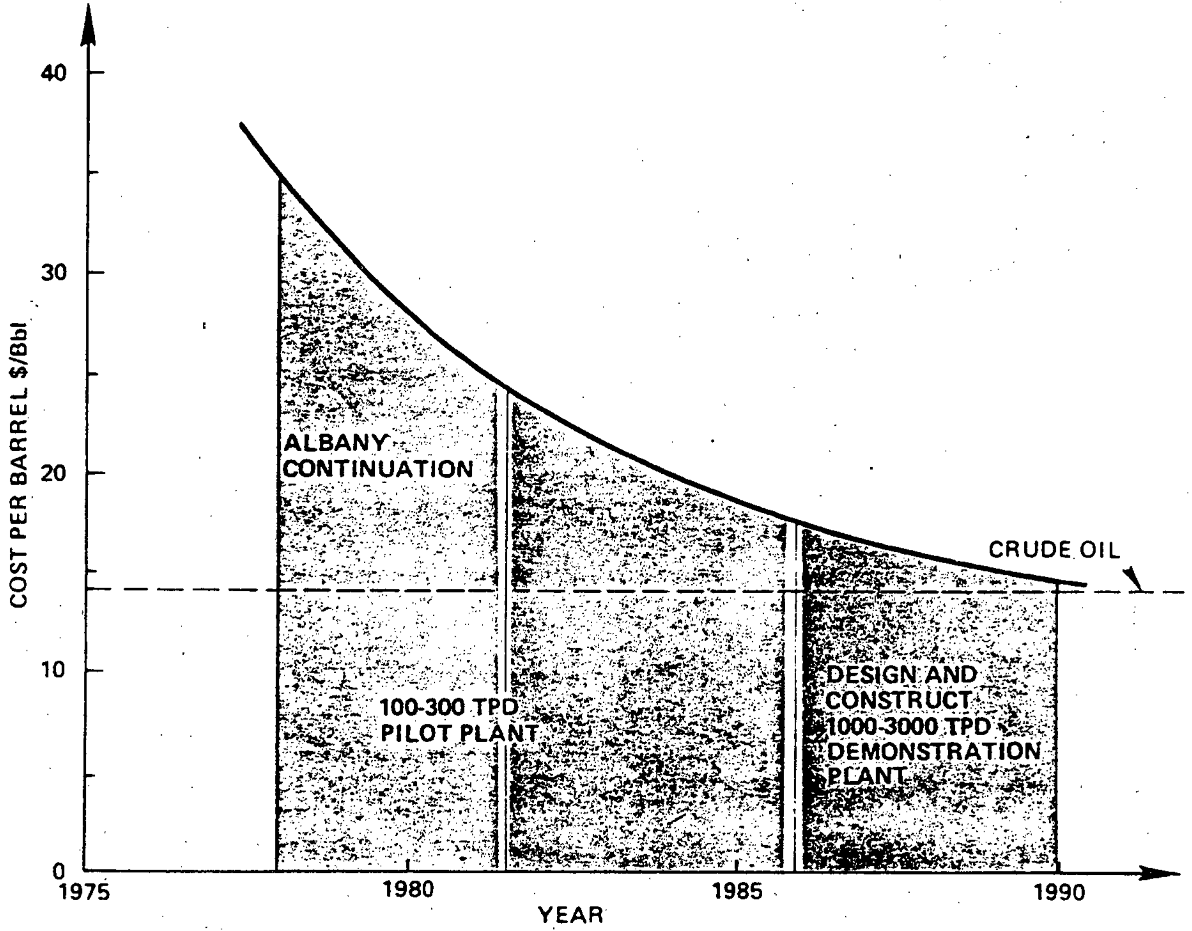


Figure 15. Future Activities[20]

containing 30 percent wood flour. This feat was not accomplished at Albany.

2. The reaction stoichiometry used (cf. Section 6.6) as a base for process economics is fictitious, for it calls for 100 percent carbon conversion, produces a product containing 22.8 percent oxygen, and yet consumes seven times the amount of carbon monoxide postulated in the Dravo study.[57] This assumed oxygen content is much higher than those shown in the analytical results contained in the Bechtel Report; cf. Table 3 of the review.

Table 3

Analytical Results on Reaction System Product[20]

	Wood Flour	Anthracene	System Product[a]
C, percent[b]	50.62	91.2	83.5
H. percent[b]	6.39	5.6	7.0
N, percent[b]	0.14	0.1	0.4
O, percent[c]	42.85	3.1	9.1
Inorganics	2.66	2.2	7.5
Heat content, Btu/lb	8,196	16,590	15,179

[a] Reported to be average

[b] On moisture and inorganics-free basis

[c] Indirect, i.e. by difference

The foregoing review critical of some interpretations contained in a report is not intended to suggest any shortcomings on the part of the Bechtel team assigned to the project. In fact the Bechtel team at Albany showed ingenuity and great skill in modifying the equipment and developing the know-how to permit operating the process under very trying conditions. Twenty-six runs in roughly the same number of weeks in a flawed pilot scale facility speak well for the Bechtel team.

Section 7

OPERATION OF THE ALBANY BIOMASS LIQUEFACTION TEST FACILITY BY RUST ENGINEERING COMPANY

The contract awarded the Bechtel Corporation was only for one year, i.e. January through December 1977. The contract was extended on a monthly basis to allow DOE to prepare a request for proposal. The Solar Energy Division of DOE was in a state of flux, as were many other divisions of DOE and reorganizations were frequent. Preparing the RFP and awarding the contract took nearly six months; the successful bidder was Wheelabrator Clean Fuel Corporation, through its subsidiary the Rust Engineering Company. Completion of a property inventory, transfer of property inventory, transfer of property accountability, and environmental, health, and safety assessments of the facility (at the request of the new contracting officer) took nearly four months; i.e. the development program was interrupted for about ten months.

7.1 Technical Approach Proposed by Rust

The scope of work described in the Rust proposal involved six phases:

Phase I	Preparatory work involving the orderly takeover of activities and facilities from the incumbent operating contractor.
Phase II	Operating adjustment period involving familiarization of the personnel with startup, operation, maintenance and shutdown procedures.
Phase III	Continuation of process investigation as permitted by the existing facility.
Phase IV	Modifications of plant configuration and/or process flowsheets as deemed necessary.
Phase V	Process development operations upon completion of the needed modifications.
Phase VI	Shutdown and phaseout.

The Phase I program concerned the orderly takeover of activities and material from the incumbent contractor, and involved such activities as staffing, organizing, and purchase or lease of essential equipment needed to operate the facility.

Phase II work involved familiarization with plant equipment; i.e. its operation, maintenance, cleaning, and repairs; conducting a test; test-run termination; and readying the plant for another run. The Rust proposal contained two additional tasks to be performed in the Phase II effort:

- o Design and construction of a recycle-solvent hydrogenation system
- o Design and construction of a product-oil vacuum distillation system to be used as an alternative to the centrifuge

Phase III effort involved continuation of process investigation pending the results of the Phase II activities in regard to modificaton of plant configuration and/or process flow. It was proposed that recycle-solvent hydrogenation and vacuum distillation systems be added to the plant during the Phase III effort.

Phase IV effort concerned modification of plant configuration and/or process flow, based on an analysis of performance of the various process units, and of test results. The Rust proposal was noncommittal regarding the Phase IV effort. They proposed that this effort effectively start concurrently with the Phase III program.

Phase V effort concerned process development operations that would provide data to determine the technical and economic feasibility of production of syncrude from biomass.

The proposal contained a conceptual commercial plant design illustrated in Figures 16 and 17. The salient features of the conceptual design are summarized thus:

- o The blending took place in a blender at atmospheric pressure and at a temperature of 500 to 600°F to make a slurry of about 30 to 50% solids by weight.
- o The hot biomass-oil slurry was pumped into the reactors through feed-slurry recirculation pumps and plunger-type high-pressure feed pumps. The feed was introduced into the reactor without further heating.
- o Further heating of the slurry to the desired exit temperature was accomplished in the baffle-type high-pressure vessel, by sparging hot synthesis gas at a temperature of 2500 to 3000°F through a dip-leg in the reactor.
- o The hot synthesis gas was produced in the partial oxidation reactor located atop the biomass reactor, by incomplete combustion of centrifuge sludge or vacuum-distillation bottoms with oxygen.
- o The off-gas from the reactor was cooled in two stages to condense most of the condensable organic materials and water, and sent to the partial oxidation reactor, a portion being bled for pressure control.
- o The reactor bottoms were flashed in a light-ends stripper to separate the light oils and to cool the slurry to 300-600°F.
- o The slurry leaving the light-ends stripper was sent to either a centrifuge or vacuum distillation system for solids separation, depending upon the results of test runs which were to be conducted at Albany.

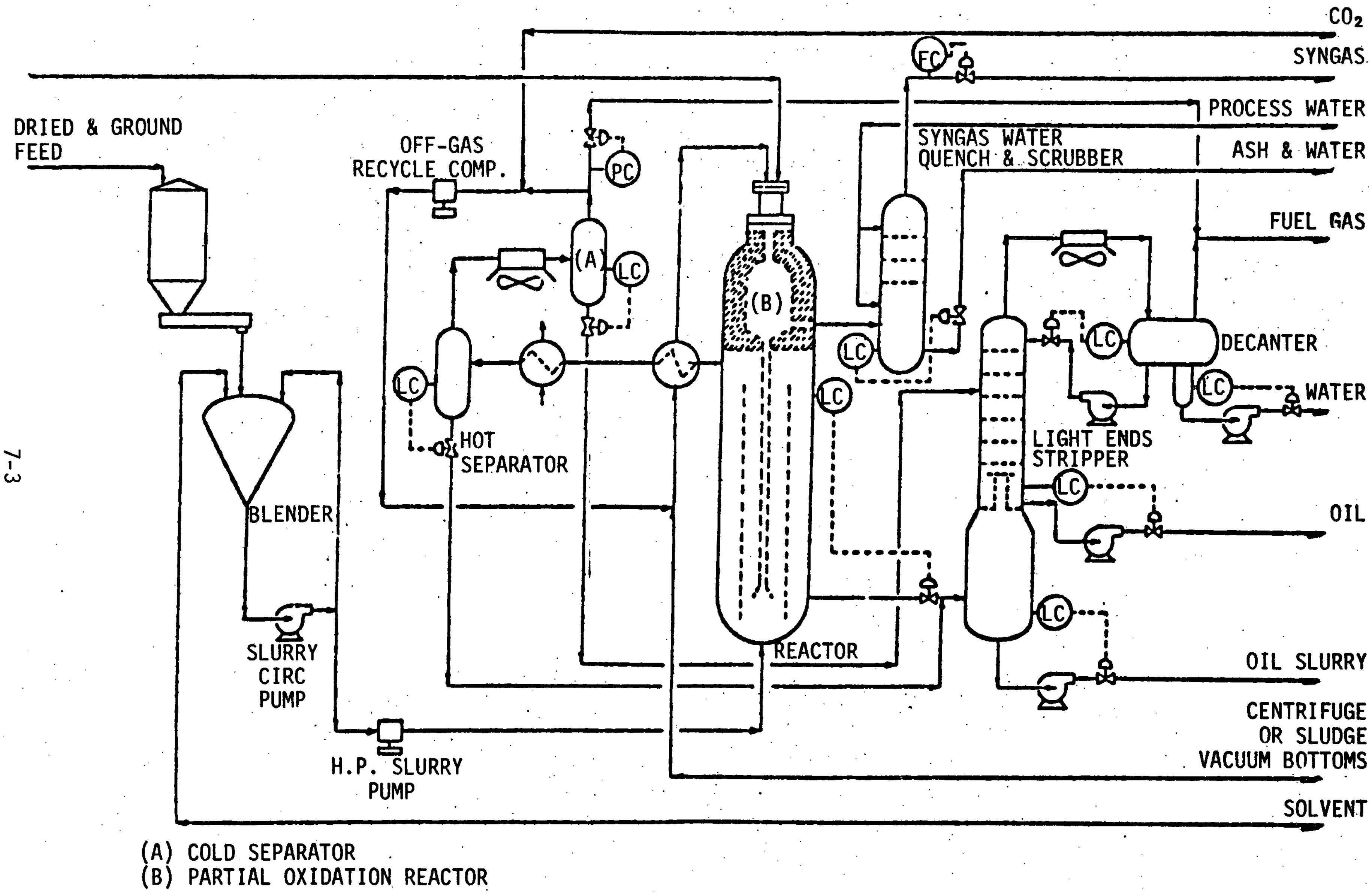


Figure 16. Biomass-to-Oil Conceptual Commercial Plant Design-Reaction Section (Ruse Engineering)[165]

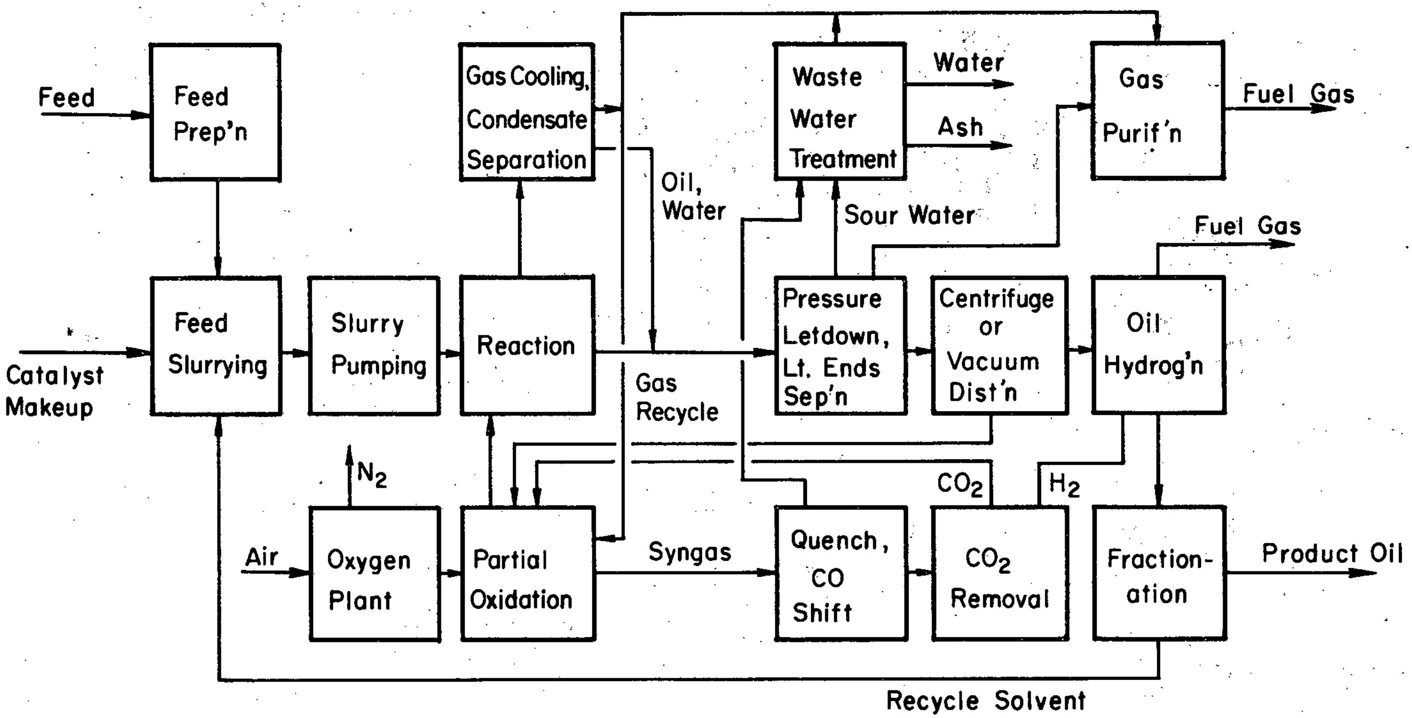


Figure 17. Biomass-to-Oil Commercial Plant Conceptual Design (Rust Engineering)[165]

XBL823-3686

- The oil leaving the centrifuge (or vacuum distillation system) was sent to a hydrogenation reactor, and the sludge (or vacuum distillation bottoms) was diverted to the partial oxidation reactor for synthesis gas production. Rust expressed the belief that a water-free slurry cooled to 300-600°F might be amenable to separation by centrifuging.
- The heavy oil from the centrifuge (or from the vacuum distillation system) was sent to a hydrogenation reactor for upgrading. Hydrogen needed was produced from a slip stream of the synthesis gas generated in the partial oxidation reactor, by diverting the quenched and scrubbed slip stream to a water-gas shift reactor.
- The hydrogenated oil was sent to a fractionation column to produce a heavy oil suitable for recycling to the blender as a vehicle oil and a light fraction as the product oil.

In the Rust proposal, design and construction of recycle-solvent hydrogenation and product-oil vacuum distillation systems were regarded as deviations from the Government Statement of Work. Estimated costs of these and other modifications proposed by Rust, shown in Table 4, were not included in the base cost of the proposal.

Table 4

Estimated Costs of Modifications Proposed by the Rust Engineering Company[68]

ITEM	COSTS Direct Construction	 Indirect Construction	 Total
Agitator replacement	9,090	7,490	16,580
Laboratory	80,300	19,250	99,550
Tubular preheater	42,250	37,240	79,490
Package boiler	59,420	54,110	113,530
Light ends stripper & vacuum distillation	165,559	127,441	293,000
Catalytic hydrogenation	198,592	152,408	341,000
Hot slurry feed system	37,800	33,730	71,530
Hot syngas feed system	140,540	122,450	262,990
TOTAL	653,251	524,869	1,277,670

7.2 Review of Rust Proposal

In October 1977, LBL was contracted with DOE to provide technical evaluation and monitoring services for its biomass liquefaction program. Soon after the Rust Engineering Company was awarded the contract to operate the DOE facility at Albany, LBL was requested to study and evaluate the Rust proposal. The review provided in Section 7.1 of this report regarding the approach proposed by Rust was in fact excerpted from the LBL report.[68] The basic LBL evaluation is summarized below:

- The Rust proposal is innovative in several respects:
  1. It proposes blending wood flour with a hot (500 to 600°F) recycle oil to produce a slurry containing 30 to 50 percent wood flour by weight and injecting the slurry using plunger-type high-pressure feed pumps.
  2. A partial oxidation reactor located atop the biomass reactor provides the synthesis gas required and, at the same time, caters to the reactor performance. Stated differently, Rust was proposing an integrated liquefaction and gasification plant (cf. Figure 17).
  3. A centrifuge or a vacuum distillation is required to separate the oil phase before it is catalytically upgraded.
  4. The product derived from biomass in the reactor needs further upgrading by hydrogenation, to produce a light fraction suitable as a product oil and a heavy fraction suitable as a recycle oil.
  5. A fractionation column is needed to separate the light oils from the recycle oil.
- Taken at its face value, the conclusion can be drawn from the Rust proposal that the original PERC process was not chemically and technically feasible.
- The proposal was vague regarding how much was committed to develop the Rust process at Albany (A total commitment would have increased the base cost of the contract as shown in Table 4). The schematics of the process development activities shown in Figure 18 indicated a strong commitment to the modified process. Yet, the retention of the blender and preheater in the schematic suggested adherence to the PERC scheme as far as the front-end of the process was concerned. The Rust scheme would have required a preheater for the recycle oil before it goes to the blender.
- A hot solvent with a boiling range of 500-900°F was to be used as a carrier oil, and heated to 500-600°F before blending. Blending wood flour with a boiling solvent in a blender with many openings at the top would be a very risky operation. Evidently Rust realized the hazards involved, because in the proposal the need of testing

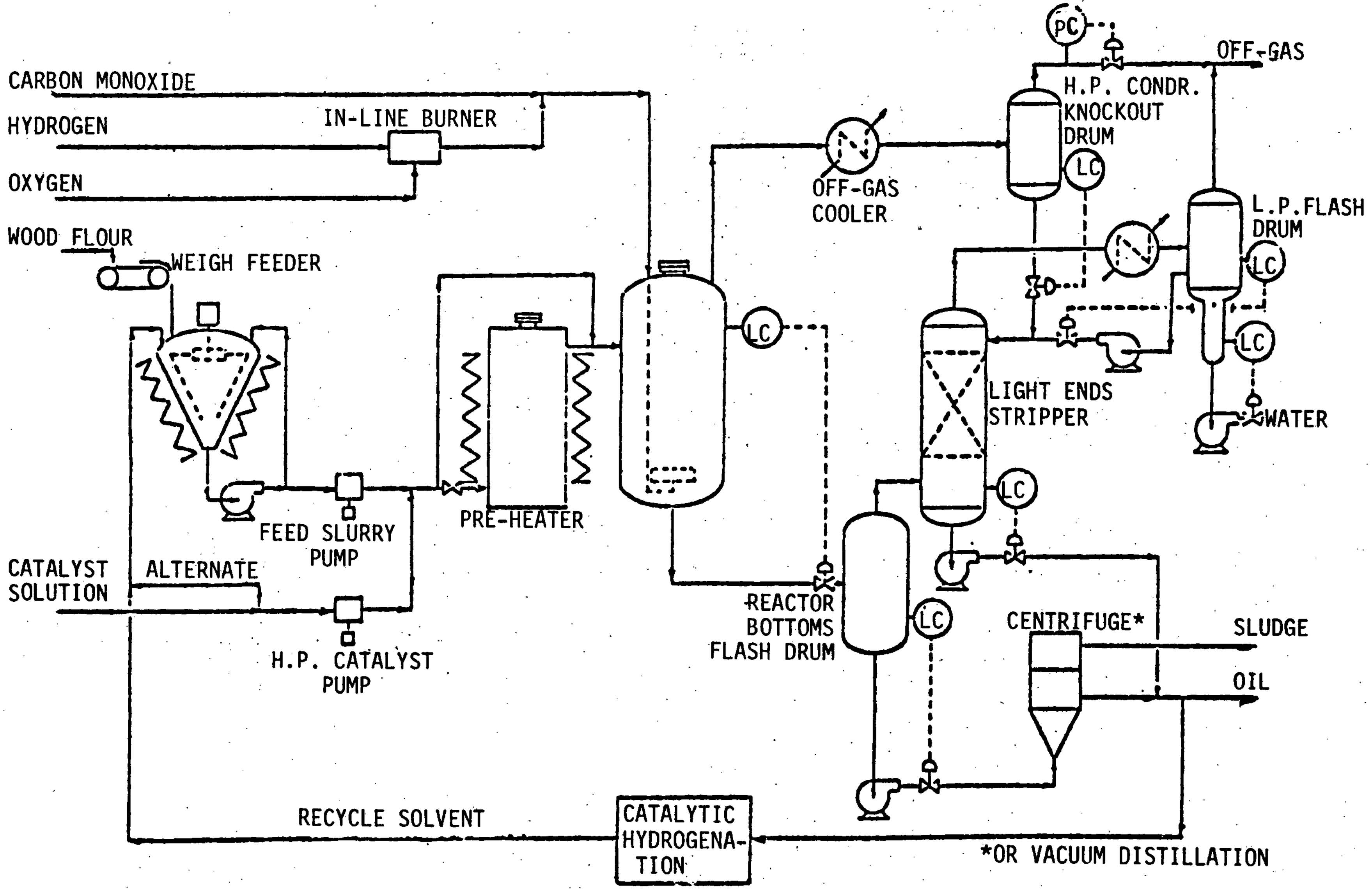


Figure 18. Process Development Operations (Rust Engineering)[68]

and developing a technique of preparing and pumping was recognized. LBL viewed this operation a formidable, costly task and recommended that developing a technique be made a separate task.

7.3 Takeover and Checkout Period

Upon being awarded the contract to take over the Albany facility, the Rust Engineering Company found themselves with many problems regarding the checkout of the facility: there were no supplies such as wood chips, start-up oil, chemical, carbon monoxide, or synthesis gas; the reactor was inoperative; the preheater was disassembled and effectively out of service because its shaft was broken and it needed new blades and seal; the centrifuge was not working. Moreover, preliminary tests revealed that many other modifications had to be made in order to conduct test runs and that the modifications would take time. Under these circumstances Rust had an opportunity to make a good case for the development of the process scheme they advanced instead of the PERC process, and to negotiate a change in their task schedules. The obstacle to the development of the new process was the cost of the additions to the facility (cf. Table 4) for which the DOE contract provided no funds. Rust could have proposed to eliminate Phase II and Phase III operatons and request that the savings to be realized be applied to the design and construction of the needed additions and modifications, i.e. jump to Phase IV. Unfortunately Rust chose not to forego Phase II and Phase III operations.

7.4 Operating Results -- July 1978 - February 1980

A special report entitled, "Proposed Modifications and Operations Plan for Biomass Liquefaction Facility, Albany, Oregon" issued by the Rust Engineering Company provides a concise account of the early Rust efforts. The report covers the results of Phase I through Phase III operations, a period of 20 months, and proposes to start Phase IV operations contingent upon the approval of funds for some modest modifications and additions to the facility.

The major additions involved an analytical laboratory, a magnetically driven agitator for the high pressure reactor, and a vacuum distillation and light ends stripper unit.

During the period, a total of seven experimental test runs was made by Rust. The results were described in the appendix of the Rust report and unfortunately were omitted from the text. In the report no comparison was made between the proposed program and the original Rust process concept. The operating results contained in the Appendix of the report may be summarized as follows:

- Three test runs were conducted in the PERC mode duplicating Bechtel's Reactor Run No. 6 with not much better success than Bechtel had.
- Performance tests were made of the Westphalia Separator belonging to the facility and a Bird Centrifuge rented for purposes of separating aqueous phase and residue from the reactor bottoms. The results obtained were not encouraging.
- Several tests were made to pretreat wood in 375 gallon pretreaters to obtain a pumpable slurry.
- Three test runs were conducted using hydrolyzed wood slurries. "Test Run 7 was carried out with the primary objective of producing five drums of wood-derived oil, operating in the LBL water slurry mode using acid-hydrolyzed wood as feed to the reactor. The objective was obtained in a highly successful run."

In the LBL slurry mode wood chips are prehydrolyzed in water containing 500-750 ppm sulfuric acid for 40 minutes at 360°F and about 130 psia. After pressure let-down, the slurry is sent through a refiner before it is sent to a stirred slurry hold tank. Sodium carbonate is added to the slurry (about 3 to 4 lb per 100 lb wood hydrolyzed) to bring its pH to about 7. The slurry then goes to a preheater followed by a reactor. After pressure let-down, the bottoms are sent to a gravity separator to cover the oil. Unlike the PERC process, this process involves once-through operation. In the test run conducted during this period (TR7), wood flour (instead of wood chips) were used and the concentration of the wood flour was only 16%. Concentrations approaching 33 percent wood chips (dry basis) were later successfully recirculated through the plunger type pump, but not through a preheater.

The discovery that pretreated wood chips could be injected into high pressure vessels at concentrations approaching 33% was good news, because pretreatment could be effected in commercially available equipment used by the paper and pump industry with little modifications. Obtaining nearly seven barrels of oil derived from wood (not contaminated with any start-up oil) was a big breakthrough. The drawback was, however, the low oil yield, 28 percent versus 37 percent anticipated from batch experiments. (As the overall material balance in the PDU runs was poor, losses may have occurred that could unfavorably distort the true yield.)

7.5 Operating Results -- March 1980 - July 1981

During this period the Rust Engineering Company conducted five test runs.[166] The results of four runs as tabulated in a report issued by the company (under Contract No. B-B2471-A-6) in July 1981 are reproduced in Table 5.

Specifically Test Run No. 12 was performed in the PERC mode with the objective of producing 30 barrels of wood-derived oil at a concentration of

Table 5

Some Properties of Oils Obtained in Test Runs 9-12[166]

	Run 9 PERC Mode Stirred Reactor Electric Heater	Run 10 LBL Mode Stirred Reactor Fired Heater	Run 11 LBL Mode Plug-Flow Reactor Fired Heater	Run 12 PERC Mode Plug-Flow Reactor Fired Heater
Wood-derived oil concentration	93.9%	100%	100%	99.9%
Heating value, Btu/lb	15,690	13,300	13,210	14,840
Viscosity at 210 F, cp	460	2700	782 to 137,200	135
Carbon content, percent	82.6	76.1	74.1	78.9
Hydrogen content, percent	7.98	7.03	7.00	8.51
Nitrogen content, percent	0.5	0.5	0.5	0.5
Oxygen content, percent	9.4	16.9	18.9	12.3
Solids, percent	9.6	0.4	1.7	1.8
Specific gravity	1.15	1.2	1.19	1.11
Yield, 100 lb oil/lb wood	33.7	26.3	28.5	53.3

over 90 percent. In the summary of the report was the statement: "This was the most successful operation of the liquefaction system that has yet been obtained. Wood totalling 21,970 pounds was fed for 572 hours at an average rate of 38.4 pounds per hour, resulting in the production of 11,027 pounds at an average concentration over 95 percent... The average yield of dry, solids-free, wood-derived oil was 53.3 percent of the dry wood fed... The run was terminated under control when the goal of 30 petroleum barrels of oil was reached."

In the fourth paragraph of page 10 of the Rust report was the statement: "Additionally, the technical feasibility of producing wood-derived oil continuously in commercially available equipment, i.e. fired tubular heater and plug-flow reactor without mechanical agitation was established." The statement is, in our opinion, overly optimistic. Some comments on this statement and on thelast sentence of the summary of the report are in order.

o Data given on pp. 14-19 indicate ten interruptions ranging from eight hours to 212 hours for the ten time spans (ranging from 16 to 112 hours) during which the system was operative. Interruptions are also indicated on p. 21. The system was down 53 percent of the period, suggesting that the test run in question was not under control at all times.

- The amounts of the crude wood oil collected (shown on pages indicated) including samples and spills, etc., 78 percent (by weight) of the wood fed. The crude collected is stated to contain catalyst, water, and solids. In Balance No. 1 the contaminants amount to 32 percent by weight of the crude collected, and Balance No. 8, the longest operating period, to about 15 percent.
- Evidently Rust tried to refine the product without success, for we note the statement contained on page 19 of the Rust report:

  > One run to distill the crude wood-derived oil by vacuum flash distillation was begun. The run was soon terminated when it became impossible to pump the high melting point column bottoms material that resulted after moisture and some volatile components had been removed.

  The statement is ominous in that product purification may require additional process steps.
- The heating value of oils contaminated with water, catalyst, etc. to the extent of 16 to 32 percent would of course be less than indicated in column 4 of Table 5. Evidently if water is removed, the crude becomes exceedingly viscous. The low viscosity reported by Rust for the oil obtained in Run 12, 135 cp, is not consonant with the plot shown in A-2 of the Rust report.
- Finally we note that in Run 12, the wood flour concentration was kept below 11 percent. Unless the wood flour concentration can be raised to levels approaching 30 percent, the process will not economically be feasible; therefore the claim "...tehcnical feasibility... was established," in the report cited should be qualified by adding "under conditions not considered to be economically feasible."

The conclusion of the author is that an overly optimistic view regarding the chemico-technical feasibility of the PERC has been presented in the Rust report. Nevertheless, the excellent closure of Rust's later material balances attests their ability to operate this process or future variations of it effectively in the Albany PDU.

Section 8

RECENT ASSESSMENTS OF LIQUEFACTION PROGRAM

Early in 1980, DOE authorized four studies concerning the operation of the Albany facility, feasibilities of the processes investigated at Albany, assessment of the facility, and of the supporting research activities.

8.1 Assessment by Econergy Associates

The study by Len Seglin of Econergy Associates contained the following stated objectives:[59]

- Compare the economical and technical merit of the PERC and LBL Processes for the liquefaction of wood chips (biomass)
- Then compare the better of these two processes with other alternate liquid fuel options, and if this comparison indicates potential commerical interest
- Recommend a development program for bringing the better technology to commercial readiness

Evaluation of available data by EA led them to conclude that the necessity of using either the catalyst (sodium carbonate) or the synthesis gas in the two processes studied was suspect. Based on this conclusion, they conceived an optimistic case in which neither synthesis gas or catalyst was used in these processes, and compared it with the pessimistic case in making cost estimates. The conclusions reached by EA were as follows:

"1. The PERC process appears to be superior to the LBL process.
2. The PERC process at a 1000 TPD (dry) wood scale appears to be competitive with large-scale coal liquefaction plants to produce a heavy oil for industrial or utility use.
3. The PERC process product oil is probably not suitable in a conventional petroleum refinery. Upgrading this oil to transportation fuels would best be done in a large special, central plant, serving many small PERC plants.
4. The above is based on an independent assessment from these available data that CO - H_2 is not required and catalyst may not be required."

The assumptions by EA concerning the elimination of synthesis gas and catalyst are not based on any firm data. Additional assumptions involved in the EA analysis are that, 1) it will be possible to inject (in the PERC mode) a slurry containing 30 percent wood flour by weight, and 2) a vacuum still will suffice to obtain a pure product. Additional effort at Albany on the PERC process, after issuance of the EP report, did not substantiate the validity of any of the assumptions made in the EA analysis.

8.2 Assessment by SRI International

The assessment of the liquefaction program of DOE by Don Wilhelm and Jeffrey Stallings of SRI[196] was in part based on an earlier SRI "Solar Data Bank" project. The major conclusions drawn in this SRI study were:

- There is no significant cost advantage between PERC and LBL process.
- Direct liquefaction does not offer any significant advantage over indirect liquefaction.
- Properties of oil derived from wood by these processes are not comparable to any known commercial fuel oils.
- Upgrading the oils obtained would render their cost twice as much as those of conventional fuel oils.
- Industrial steam generation by burning wood-derived oil is about twice as expensive as direct wood diring.

The basic recommendations made by SRI were:

- Terminate Albany wood-liquefaction PDU operations.
- Concentrate on bench-scale continuous studies to quantify the role of process variables; also use continuous bench-scale experiments to characterize the product, and to develop techniques for product recovery, separation, and upgrading.
- Batch studies should be confined only to some special catalyst research.

8.3 Assessment by D. H. Bond

Desmond H. Bond[32] focused his attention on the assessment of the objectives of the Albany project itself. He found that the PDU at Albany "...is neither satisfactorily prepared nor adequately equipped to be considering process commercialization." He concluded that process knowledge and hardware are yet lacking; and that considerable basic research and development are essential for precise process definition, before process commercialization, product characterization, and market assessment can realistically be contemplated. He therefore recommended a redefinition of the objectives of DOE's Albany facility, with emphasis on process technology R&D rather than on commercialization of the not-yet-formulated processes. Specifically he concluded that contracts with LBL, Rust, and PNL should be continued.

8.4 Assessment by Mitre Corporation

Abu Talib and Martin Neuworth of the Mitre Corporation[191] reviewed the past and ongoing (1980) studies of biomass liquefaction, and prepared an assessment paper which contains very useful information. The paper provides a historical perspective, elaborate discussions of the PERC and LBL processes, an analysis of the assessments made by Econergy, SRI, and S. H. Bond, and an account of a review meeting on direct wood liquefaction, July 10, 1980, sponsored by DOE. Based on the observations regarding the quality of the oil obtained in the PERC process (about 15 percent contaminants), its poor distillation characteristics, and most importantly the low wood feed concentration (below 10 percent), Mitre recommended discontinuation of work on the PERC process and mothballing the Albany facility. The LBL modification was found to be "...more attractive and overcomes many of the limitations of the PERC process." However, the low oil yield was found to be discouraging, and the need to recover the soluble organics was stressed.

Section 9

PROSPECTS OF OIL FROM WOOD: OBSERVATIONS AND RECOMMENDATIONS

Oil from wood can be obtained via gasification to produce a synthesis gas and Fischer-Tropsch synthesis. Another method, proposed by Mobil Oil about eight years ago (for coal) is to convert the synthesis gas to methanol and convert methanol to gasoline using zeolite catalysts. The economic feasibility analyses of these two approaches for oil from coal did not lead to the abandonment of efforts on direct liquefaction of coal. Wood has been found to be amenable to direct liquefaction under much milder conditions (650°F) than coal (850°F), and the effort spent on wood liquefaction has been insignificant when compared to that on coal. This fact alone compels us to consider direct liquefaction of wood seriously.

9.1 Chemical Considerations

The PERC Process

In Section 3 of this report, it has been pointed out that hydrogenation or hydrogenolysis of wood or of its components neither has been studied exhaustively nor has been neglected entirely. The "Energy Crisis" and other considerations led the Bureau of Mines to decide on a process (PERC) and build a PDU to develop the process and other processes that could evolve from the supporting research they had planned. One of the reasons put forth in favor of building a PDU was the failure, in a bench-scale continuous process-evaluation unit constructed at the Bureau of Mines, to inject slurries containing more than 10 percent wood flour in recycle oil. The system simply plugged. The use of small diameter tubing (1/4 inch ID), small bore elbows, fittings, valves, etc., in bench-scale experiments was explained as the likely cause of pluggage. It was believed that a system using 1.5 inch ID piping, i.e. a PDU, would be needed to demonstrate the technical feasibility of injecting concentrated slurries containing 30 percent wood flour.

In the test runs conducted by Bechtel, it became necessary to reduce the wood flour concentrations to below 10 percent as soon as the concentration of startup anthracene oil was reduced to 50 percent by the make-oil. Thus the chemical and/or technical feasibility of the PERC process became questionable.

As pointed out in Section 7.2, the modified process scheme proposed by Rust Engineering Company implied a recognition by Rust that the PERC process was perhaps not technically and/or chemically feasible. Nevertheless, they pursued the development of the PERC process with great determination. They succeeded in replacing the startup oil almost totally, and running the PDU for 112 hours, but the wood flour concentration in the feed remained at a level of 10 percent. Assume now that the operational period can be extended to 5000 hours, and that contaminants in the oil (15 percent or more including sodium), can be somehow removed economically. The moot question is "Would a commercial-scale pump permit increasing the flour concentration from 10 to 30 percent?" If we further assume that the quality of the product oil would not be altered when the wood feed concentration is increased from 10 to 30 percent, a "maybe" answer could be credible. The last assumption, however, is questionable if we consider that an increase in the wood flour concentration from 10 to 30 percent would decrease the residence time of the recycle oil in the reactor by a factor of about four, i.e. from 8.5 to 2.2 hours, assuming a wood residence time of 30 min. The decrease in recycle residence time as a result of increase in wood flour concentration might well result in production of a more viscous product that could eventually plug the system.

The conclusion drawn by this writer is that the PERC process is, as originally conceived, not chemically feasible under the operating conditions imposed by the economics of the process. It requires radical modifications.

The LBL Process

The second process tried at Albany involved prehydrolysis of wood chips and refining the hydrolyzed pulp to render it pumpable. Moist wood chips (30 part dry basis) and water (70 parts including the moisture in the chips) containing 0.1% sulfuric acid are injected into a digester operating at about 180°C and 150 psi. The digested pulp is neutralized with sodium carbonate and passed through a refiner to a slurry hold tank. The middle portion of the process is similar to that of the process described. After cooling and pressure let-down, the stream is diverted to a gravity separator (API type). This process is now under evaluation in a flow mode in bench scale as illustrated in Figure 19.

The advantages of the water-slurry process include: 1) high concentrations in the feed can be achieved, up to 30% or more of wood plus wood-derived organics; 2) separation between oil and water phases is relatively easy; 3) expensive drying and grinding wood-preparation steps are replaced by a light prehydrolysis plus refining, which can be accomplished in commercial equipment; and 4) no oil recycle is necessary. At the present level of development, the disadvantages include: 1) the oil-phase yield is lower than in the PERC process; maximum achievable is estimated at about 40%, and the highest yields to date are about 35%;[54c,72a] and 2) there are large amounts of water-soluble products (carboxylic acids and other organics) on the order of 25 wt-% of the original wood.

Under LBL process conditions it has been shown recently[54a,54c,72a] that little or no synthesis gas is consumed, and that hydrogen can be substituted for carbon monoxide as reducing gas without substantial effect on the product. This substitution would provide considerable economic advantage over the PERC

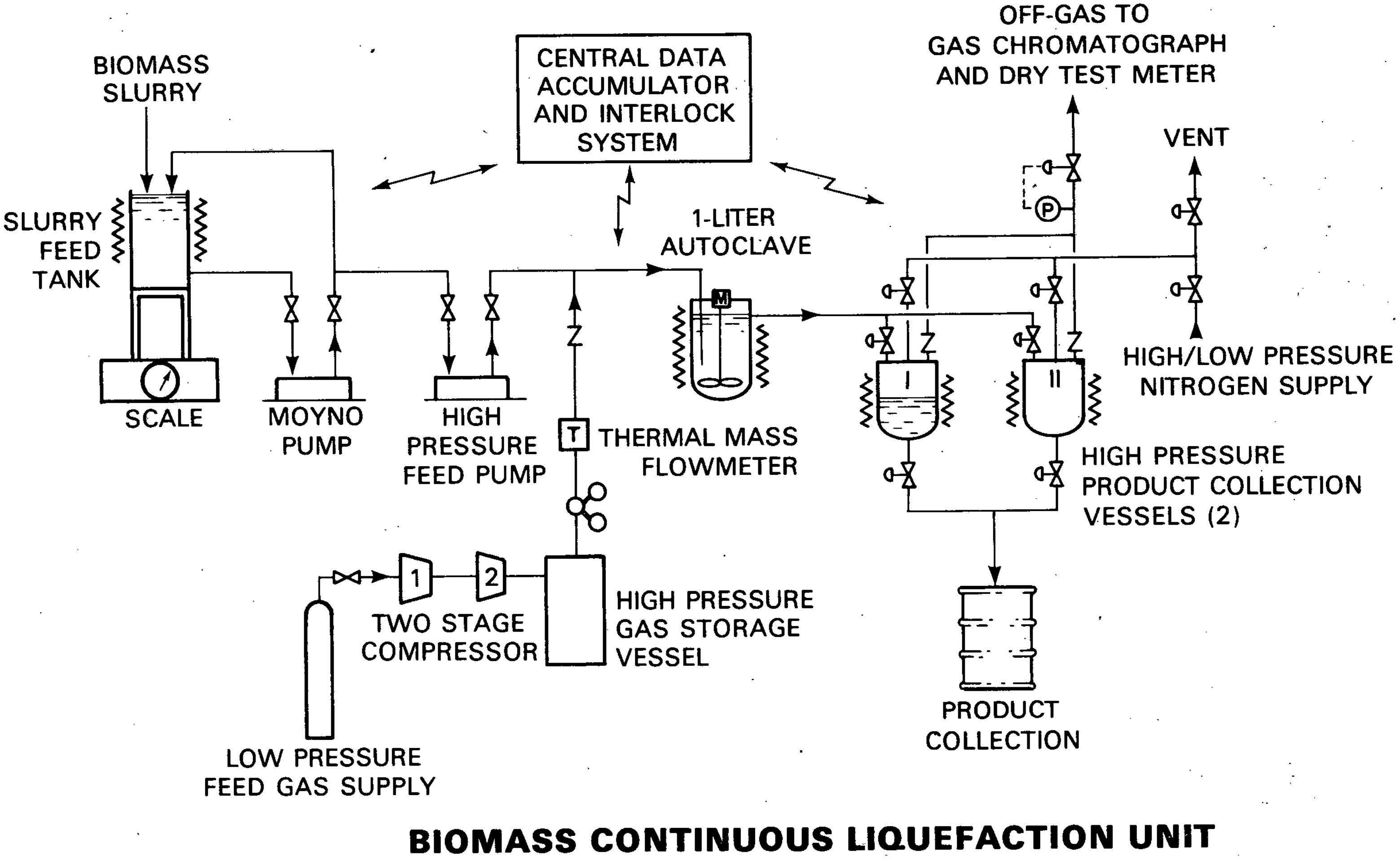


Figure 19. Biomass Continuous Liquefaction Unit
(Lawrence Berkeley Laboratory)

XBL 817-1023

process, which has high CO consumption.[54a] The lack of consumption of reducing gas makes it more difficult to reduce the oxygen content of the oil below 16-18%, and may also relate to the high yields of water-solubles. The personnel conducting the bench-scale research, who have supplied these two paragraphs, believe that an optimized process requiring little or no reducing gas could be relatively inexpensive to operate, and could have broad application to water-laden types of biomass or even to peat.

The conclusion drawn by the writer is that the LBL process is economically unfeasible unless methods can be found to convert the soluble organic matter into fuel or salable chemicals. It is recommended that the emphasis should be shifted from quantifying the roles of process variables to finding economically feasible treatments of the aqueous phase to recover oil or salable chemicals.

New Process Concepts

Recently LBL researchers[69] have discovered new catalysts which improve direct liquefaction in three ways. First, the catalysts act to allow wood to be dissolved in wood oils. Second, the catalysts enable hydrogenation of the wood oil product which improves the handling and end-use characteristics. Third, the catalysts eliminate the formation of water soluble organics because of the absence of an aqueous phase. A modest effort has been funded to explore the potential of this discovery.

Wood starts to decompose when heated to temperatures above 500°F. The decomposition products are a pyrolytic oil (containing 33 percent oxygen), char, and gases; certainly not a product oil that has been the aim of the direct liquefaction program. Catalytic depolymerization and hydrogenation to produce a product oil having the desired quality must therefore proceed at rates much faster than thermal decomposition and recombination reactions, in order to minimize the amounts of the unwanted products. Evidently sodium carbonate as a catalyst is not satisfactory. A 30 min. residence time for wood flour translates into 8.5 hr. recycle oil residence time when wood concentration is 10 percent. The same quality oil has to be produced within 2.2 hr. residence time to permit injection of 30 percent slurry. It is clear that catalysts much more effective than sodium carbonate must be found for wood liquefaction to be economically feasible.

The conclusion of the writer is that there is ample data indicating the existence of powerful catalysts for this purpose, and efforts in this direction should be pursued. The efforts would be more rewarding if the research program is carried out within the framework of a process concept.

9.2 Technological Considerations

The failure to demonstrate the viability of many liquefaction processes in pilot-scale development efforts is attributed in general to the technical difficulties encountered. The importance of injection of a slurry containing more than 30 percent wood flour has been dictated by the economics of the process conceived solely on the basis of batchwise experiments. The diversity of the efforts to meet this goal (i.e. plunger type pumps, lockhoppers, pretreaters, extruders, etc.) has largely stemmed from the concern over the availability of technologies to permit injection of wood flour at rates one-half or larger than the rate of recycle oil which is essential as a vehicle. The conclusion reached by the writer in this regard is that the concern proved pointless because the chemistry of the process was flawed.

The observation made above and, as a matter of fact, many other statements contained in the various sections of this report may imply that the concerns over the technical difficulties were unwarranted because of the flaws in the chemistry of the processes investigated. In reality, however, technical difficulties encountered at Albany were numerous and formidable. The experience gained in overcoming them is extremely valuable; unfortunately, however, it has received little recognition. Innovations or additions made at Albany concerned many process units, e.g. wood matering, pretreatment, preheating, slurry recirculation and injection, pressure letdown and flashing, centrifuging, vacuum distillation, gravity separation, etc. The writer is of the opinion that, from the point of view of design, the state of the art is far advanced compared to what existed about eight years ago.

Unfortunately, experience gained regarding equipment suitability, operating characteristics, etc., will be lost with time. The engineers who were actively involved in performance evaluations and design modification will probably recollect less and be hard to locate as time passes. The writer recommends that an in-depth study be made of the performance of the critical process units at Albany to design and specify a new PDU, as if it were intended to build a new biomass liquefaction test facility or to modify extensively the existing facility to accommodate a process involving solvolysis and heterogeneous catalysis. Only through such an attempt can missing information or links be identified and basic research can be properly channeled.

Finally the author recommends maintaining the Albany facility as a test and development center in a state ready to operate, and operate it on an as-needed basis. Although conceived at LBL, th prehydrolysis and liquefaction scheme took its wings at Albany. In retrospect it appears that it would have been advisable to install the bench-scale process evaluation unit at Albany and share operators and engineers with the development program.

9.3 Economic Considerations

Economic feasibility analyses of the processes (conceived on the basis of bench-scale experimental results) are needed for deciding whether to develop the processes, because development efforts are costly. A genuine feasibility analysis can be extremely useful in identifying critical design bases, and relative costs of the various unit operations. As such it should guide not only the course of the development activity but also the course of the supporting research. At the least it should provide an idea about when to quit.

In the case of biomass liquefaction, design bases have not been firm, and reliance has had to be made upon "engineering judgment." Under such circumstances it is advisable to obtain a parametric cost analysis or a second independent evaluation. Moreover, updating of the cost estimate may become necessary if either breakthroughs or major obstacles are encountered, or if the process is modified.

After an initial cost analysis by Blaw-Knox in 1973 for the Bureau of Mines, numerous cost analyses of the PERC process have been made: Bechtel for NSF (1975), PNL for ERDA (1976), Bechtel for DOE (1978), SRI for DOE (1979), Rust for DOE (1979), Econergy for DOE (1980), SRI for DOE (1980). Unfortunately most of these analyses were authorized to decide whether or not to end the program, rather than to provide guidance to the process development activity and/or redefine the objectives of the program. Late in 1979, it became evident that process knowledge and hardware were lacking to define a process precisely, and thus emphasis on process commercialization, product characterization, and market assessment were unwarranted.

Section 10

REFERENCES

1. Adkins, H., Frank, R. L. and Bloom, E. S., J. Am. Chem. Soc., 63, 549 (1941).

2. Adler, E. and Gierer, J., Acta Chem. Scand., 9, 84 (1955).

3. Adler, E., Lingren, B. D. and Salden, E., Suensk Paperstidn, 55, 245 (1952).

4. Adler, E., Pepper, J. M. and Erikson, E., Ind. Eng. Chem., 49, 245 (1957).

5. Alich, J. A. and Inman, R. E., "Effective Utilization of Solar Energy to Produce Clean Fuels," Final Report, SRI Project 2643, Menlo Park, CA., June 1974.

6. Alich, J. A., et al., Symp. on Fuels and Energy from Renewable Resources, 174th ACS Meeting, Chicago, Ill., August 1977.

7. Anderson, L. L., Bu Mines IC 8549, 1972.

8. Appell, H. R., "Fuels from Waste," Academic Press, 1977.

9. Appell, H. R., et al., Bu Mines RI 7560 (1971).

10. Appell, H. R., et al., Bu Mines RI 8013 (1975).

11. Appell, H. R. and Tosh, J. A., U. S. Patent 3,733,255, May 1973.

12. Appell, H. R., Wender, I. and Miller, R. D., Ind. Eng. Chem., 61, 1703 (1969).

13. Appell, H. R., Wender, I. and Miller, R. D., Bu Mines TPR 25 (1970).

14. April, G. C., et al., Tappi, 62, 83 (1979).

15. Aronovsky, S. I. and Gartner, R. A., Ind. Eng. Chem., 28, 1270 (1936).

16. Ball, D. H. and Jones, J. K. N., J. Chem. Soc., 33, 1958.

17. Battelle - Pacific Northwest Laboratories, "Study to Determine Optimal Use of Albany, Oregon, Pilot Plant for Advancement of Processess for Conversion of Cellulosic Materials to Liquids," prepared for ERDA, March 1976.

18. Bechtel Corporation, "The Technical and Economic Desirability of Waste-to-Oil Liquefaction Processes," prepared for NSF, June 6, 1975.

19. Bechtel Corporation, "Technical Evaluation of the Waste-to-Oil Pilot Plant at Albany, Oregon," prepared for ERDA, E-04-3-1194, October 1976.

20. Bechtel National, Inc., "Operation of the Albany, Oregon Biomass Liquefaction Facility," Final Report, May 1979.

21. Bergius, F., Naturwiss, 16, 1 (1928).

22. Bergstrom, H. and Cenderquist, K., Produkter ur tra VI, 1930.

23. Berl, E., Proc. 34th Int. Conf. on Bituminous Coal, 2, 820 (1932).

24. Berl, E., Naturwiss., 20, 652 (1933).

25. Berl, E., Science, 99, 309 (1944).

26. Berl, E. and Biebascheimer, H. Annalen der Chemie, 504, 38 (1933).

27. Berl, E. and Schmidt, Ibid., 496, 283 (1932).

28. Bernardin, L. J., Tappi, 41, 491 (1958).

29. Bikales, N. M. and Segal, L., "Cellulose and Cellulose Derivatives, Part V, Chapter XVIII, Wiley-Interscience, New York, 1960.

30. Blaw-Knox Chemical Plants, Inc., Pittsburgh, PA, "Economic Feasibility Study for Conversion of Solid Wastes to Oil," BKC-2475, prepared for BuMines DOI, October 31, 1972, BKC-2515, June 22, 1973.

31. Bovrov, P. A. and Kolova, L. I., Compt. Rend., Acad. Sci., USSR, 24, 46 (1939).

32. Bond, D. H., "The Role of the Albany, Oregon Facility in Development of Commercial Biomass Liquefaction Process(es)," prepared for PNL (Contract DE-AC06-76 RLD 1830) July 1980.

33. Bognar, A., Chem. Abst., 30, 3967 (1936).

34. Boocock, D. G. B., Can. J. Chem. Eng., 57, 98 (1979).

35. Boocock, D. G. B., et al., Ibid, 58, 466 (1980).

36. Boomer, E. H., Argue, G. H. and Edwards, J. Can. J. Research, 138, 337 (1935).

37. Bowen, A. R. and Nash, A. W., Fuel in Science & Practice, 5, 138 (1926).

38. Bowen, A. R., Shatwell, H. G. and Nash, A. W., J. Soc. Chem. (London) 44, 507 (1935).

39. Bower, J. R., McCarthy, J. L., and Hibbert, H., J. Am. Chem. Soc., 65, 1192 (1963).

40. Bowers, G. H. and April, G. C., Tappi, 60, 102 (1977).

41. Brauns, G. E., "The Chemistry of Lignin," Academic Press, 1959.

42. Brauns, F. E., and Brauns, D. A., "The Chemistry of Lignin," Supp. volume, Academic Press, 1960.

43. Brauns, F. E. and Hibbert, H., Can. J. Research, 138, 78 (1935).

44. Brewer, C. P., Cooke, L. M. and Hilbert, H., J. Am. Chem. Soc., 70, 3052 (1968).

45. Brieger, G. and Nestrick, T. J., Chem. Rev., 74, 367 (1974).

46. Broido, A. C., et al., J. Appl. Polymer Sci., 17, 3627 (1973).

47. Bronovitskii, V. E. and Kalinskaya, L., "Uzbek. Khim. Zh., 11, 31 (1968).

48. Brown, S. A. and Nuesh, A. C., J. Am. Chem. Soc.,81, 2419 (1959).

49. Browning, B. L., "The Chemistry of Wood," Interscience, New York, 1963.

50. Casey, J. P., "Paper and Pulp," Interscience, New York, 1960.

51. Chemical Engineering News, 58, 11 (1980, also Feb. 12, 1980.

52. Clark, I. T., Ind. and Engineering Chemistry, 50, 1125 (1958).

53. Cooke, L. M., McCarthy, J. L., and Hibbert, H., J. Am. Chem. Soc., 63, 2056, 3052 (1941).

54. Coscia, C. J., Schubert, W. J. and Nord, F. F., Tappi, 44, 360 (1961); J. Organic Chem., 26, 5085 (1961).

54a. Davis, H. G., Kloden, D. J., and Schaleger, L. L., "Chemistry and Stoichiometry of Wood Liquefaction," 3rd Symposium on Biotechnology in Energy Production and Conservation, Gatlinburg, Tenn., May 1981. Biotechnology and Bioengineering Symp. Series, in process. Also included in Report LBL-13449, Lawrence Berkeley Laboratory, Oct. 1981.

54b. Davis, H., Figueroa, C., Karatas, C., Kloden, D., Schaleger, L., and Yaghoubzadeh, N., "Research and Development Activities on Direct Liquefaction Technology - Quarterly Report," LBID-426, Lawrence Berkeley Laboratory, July 1981.

54c. Davis, H. G., Figueros, C., and Schalarger, L. Ibid. LBID-470, Dec. 1981.

55. Deno, N. C., Petersen, H. J. and Saines, G. S., Chem. Rev., 60, 1,7 (1960).

56. Derenesenyi, T., Lawrence Berkeley Laboratory Report 9777 (1979).

57. Dravo Corp. "Economic Feasibility Study for Conversion of Wood Wastes to Oil," prepared for BuMines, DOI, June 22, 1973.

58. Dunning, J. W. and Lathrop, E. C., Ind. Eng. Chem., 37, 24 (1945).

59. Econergy Associates, "A Technical and Economic Assessment of PERC and LBL Wood-to-Oil Conversion Processes," prepared for LASL (Contract 4-L40-0742M-1), March 1980.

60. Ekman, K. H. and Lindberg, J. J., Suomen Komistilethi, 39B, 89 (1966).

61. Electric Power Research Institute, EPRI 261-1, 1978, EPRI ER-746, 1978, EPRI AF-974, 1979.

62. Elliott, D. C., "Process Development for Biomass Liquefaction," Reprints Division Fuel Chemistry, ACS, August 1980.

63. Engler, C. R., Report No. 61, Inst. for Systems Design and Optimization, Kansas State University, Manhattan, Kansas, 1974.

64. Ergun, S., "Biomass Liquefaction Program, Albany, Oregon," Interim Report No. 1, LBL, University of California, April 1978.

65. Ergun, S., Proc. 3rd Annual Biomass Energy Systems Conference, June 1979, SERI, 103, LBL 9188.

66. Ergun, S. and Figueroa, C., Proc. Eng. Found. Conference on Resource Recovery, New Hampshire, 1979, Chapter 13, LBL 9845.

67. Ergun, S., et al., "Oil from Biomass -- A Progress Report," AIChE Meeting, Seattle, Washington, August 1980, LBL 9846.

68. Ergun, S., "Biomass Liquefaction Program, Albany, Oregon," Interim Report No. 2, LBL, University of California, June 1978.

69. Ergun, S. and Yu, S. M. G., "Biomass Liquefaction with Compounds of Transition Metals," Patent disclosure, July 1981.

70. Fierz-David, H. E., Chem. Ind. (London), 44, 942 (1925).

71. Fierz-David, H. E. and Hannig, M., Helv. Chim. Acta, 8, 900 (1925).

72. Figueroa, C. and Ergun, S., Proc. 3rd Annual Biomass Energy Conference, June 1978, SERI, p. 109.

72a. Figueroa, C., Schaleger, L. L. and Davis, H. G., "LBL Continuous Bench-Scale Liquefaction Unit - Operation and Results," Report LBL-13709, Lawrence Berkeley Laboratory, December 1981.

73. Fischer, F. and Schrader, H., Brennst. Chem., 2, 257 (1921).

74. Fisher, E. H., Kulka, M. and Hibbert, H., J. Am. Chem. Soc., 66, 598 (1944).

75. Freudenberg, K. and Neusch, A. C., "Constitution and Biosynthesis of Lignin," Springer-Verlag, Inc., New York, 1968.

76. Friedman, S., et al., Proc. 3rd Mineral Waste Util. Symposium, Chicago, Ill., May 14, 1972.

77. Fuchs, W., Ber., 61B, 948 (1928).

78. Fu, Y. C., Illig, E. G. and Metlin, S. J., Evir. Sci. & Tech., 8, 737 (1974).

79. Fu, Y. C., et al., Preprints Div. Fuel Chem., ACS Meeting, New York, August 1972.

80. Gardiner, D., J. Chem. Soc., 1968C, 1473-6.

81. Gardner, J. A. F. and Hibbert, H., J. Am. Chem. Soc., 66, 607 (1944).

82. Gaslini, F., U. S. Patent 2,947,739, August 1960.

83. Geerards, J. J., Van Krevelen, D. W. and Waterman, H. I., Ber. Chem., 39, Sil (1938).

84. Gillet, A. and Colson, P., Ind. Chim. (Brussels), 22, 696 (1959), Ibid., Suppl. 1, 402 (1959).

85. Goddard, H. P., McCarthy, J. L. and Hibbert, H., J. Am. Chem., 62, 988 (1940); 63, 3061 (1941).

86. Goheen, D. W., "Lignin Symposium," Div. of Fiber, ACS Meeting, Atlantic City, N. J., September 1965.

87. Grion, G. and Freudenberg, K., Ber., 92, 1355 (1959).

88. Gupta, D. V., Kranich, W. L. and Weiss, A. H., Ind. Eng. Chem., Process Des. Dev., Vol. 15, No. 2, 1976.

89. Hachihama, Y. and Jyodai, S., J. Soc. Chem. Ind., (Japan) 44, 773 (1941); 45, 302 (1942); 46, 132, 304 (1943); 47, 763, 781 (1944).

90. Hachihama, Y., et al., Ibid. 47, 218 (1944).

91. Hachihama, Y., Jyodai, S. and Takeda, M., Ibid., 47, 215 (1944).

92. Hachihama, Y., Jyodai, S., and Umezu, M., Ibid., 43, 144 (1943).

93. Halloquist, E. G., Ind. Eng. Chem., 43, 1427 (1941).

94. Hamilton, J. K. and Mitchell, R. L., "Encyclopedia of Chemical Technology," R. E. Kirk and D. T. Othmer, eds. John Wiley & Sons, New York, Vol. 4, 1963.

95. Hansen, S. M. and April, G. C., Division of Fuel Chemistry, ACS, preprints, p. 319 (1980).

96. Harris, E. E., "Wood Chemistry," L. E. Wise and E. C. Jans, eds., Reinhold, New York, Chapter "Wood Hydrolysis," 1952.

97. Harris, E. E. and Adkins, H., Paper Trade Journal, 107, 20, 38 (1938).

98. Harris, E. E., D'Ianni, J. and Adkins, H., J. Am. Chem. Soc., 60, 1497 (1938).

99. Harris, E. E., et al., Ind. Eng. Chem., 37, 12 (1945).

100. Harris, E. E., Saeman, J. F. and Bergstrom, C. B., Ind. Eng. Chem., 41, 2063 (1949).

101. Harris, E. E., Saeman, J. F. and Locke, E. G., presentation at 10th Natl. Mtg. of FPRS, Ashville, N. C., June 1956.

102. Harris, E. E., Saeman, J. F. and Sherrard, E. C., Ind. Eng. Chem., 32, 440 (1940).

103. Harris, J. F., Appl. Polymer Symp., 28, 131-144 (1975).

104. Heinemann, H., Pat. Refiner, 29(2), 111 (1950).

105. Heinemann, H., Ibid., 33(8), 135 (1954).

107. Henge, H. R., Wyatt, B. W. and Allen, B. B., J. Org. Chem., 7, 48 (1942).

108. Hibbert, H., Ann. Rev. Biochem., 11, 183 (1942).

109. Hibbert, H., Cooke, L. M. and McCarthy, J. C., J. Am. Chem. Soc., 63, 3052 (1941).

110. Hoope-Seyler, F., Berichte, 4, 15 (1971).

111. Horn, O., Berichte, 61B, 2542 (1928).

112. MacDonald, R., "Pulping of Wood," Vol. 1, McGraw-Hill, 1969.

113. Inman, R. E., "Silviculture Biomass Farms," Technical Report 7347; Mitre Corporation, May 1977.

114. Intertechnology Solar Corp., "The Photosynthesis Energy Factory," June 1977, Warrantown, Va.

115. Kachi, S. and Terashima, N., J. Japan Wood Res. Soc., 9, 453 (1974).

116. Kashima, K., Ann. Dept. Noguchi Inst., No. 9, 23 (1960).

117. Kashima, K. and Osada, T., ABIPC 32, 567 (1962).

118. Kashima, K., et al., Ibid., 34, 817 (1964).

119. Kashima, K., Takata, H. and Watunabe, H., Ibid., 33, 1026 (1963).

120. Kashima, K., et al., Ibid., 34, 817 (1964).

121. Keppeler, G. and Edler, E., Brennstoff Chem., 21, 109 (1940).

122. Katzen, R., Aries, R. S., Othmer, D. F., Ind. Eng. Chem., 37, 442 (1945).

123. Klab, L. and Strup, E., British Patent No. 425,889; March, 1935.

124. Kleinert, T., Monatsh. Chem., 83, 623, 1009 (1952).

125. Kleinert, T., Tappi, 57, 99 (1974).

126. Kleinert, T., Ibid., 58, 170 (1975).

127. Kosikova, B. and Polein, J., Chem. Zvesti, 16, 562 (1972).

128. Kratzl, K., et al., Monatsh. Chem., 90, 771 (1959).

129. Larson, S. and Lindberg, B., Acta Chem. Scand., 16, 1757 (1962).

130. Lautsch, W., Cellulose Chem., 19, 69 (1941).

131. Lautsch, W., Brennstaff. Chem., 23, 265 (1941).

132. Lautsch, W. and Piazolo, G., Ber., 76, 486 (1943).

133. Leuth, C. W. and DuPuis, R. N., Ind. Eng. Chem., 37, 152 (1945).

134. Lindblad, A., Ing. Veternskaps Anad. Hendl., No. 107, 7 (1931).

135. Lundquist, K., Acta Chem. Scand., 27(7), 2597 (1973).

136. McCartney, J. T., Pub. 350 Lawrence Berkeley Laboratory, 1980.

137. MacGregor, W. J., Evans, T. A. and Hibbert, H., J. Am. Chem. Soc., 66, 41 (1944).

138. Mariani, E. O., "The Eucalyptus Fuel Plantation as a New Source of Energy," Marelio, Inc., Beverly Hills, CA, 1978.

139. Mitchell, L. and Hibbert, H., J. Am. Chem. Soc., 66, 602 (1944).

140. Moldavskii, B. L. and Vainshtein, S. M., Khim. Tuerdogo Topliva, 6, 656 (1935).

141. Nahun, L., Ind. Eng. Chem., 4, 71 (1965).

142. National Research Council, "Energy in Transition: 1985-2010," National Acad. Sci., Washington, D. C., 1979.

143. Nekrasov, V. V., Sokolov, O. M. and Bokhovkin, I. M., Lesnoi Zh., 10, 114 (1975).

144. Nelson, R. and Schuerch, C., J. Polymer Sci., 22, 635 (1956).

145. Nikitin, V. M., Lesnoi Zh., 2, 148 (1967).

146. Nikitin, V. M., Khim Drev., 2, 61 (1968).

147. Office of Technology Assessment, "Energy from Biological Processes," OTA-E-123, 1980.

148. Oshima, M., Kashima, K., Tappi Lignin Symposium, Chicago, Ill., August 1961.

149. Oshima, M., Maede, Y. and Kashima, H., U. S. Patent 3,105,095, Sept. 1963; Can. Patent 700,209, December 1964.

150. Oshima, M., Maeda, Y. and Kashima, H., Japan Patent 13,864, August 1963; 17,018, September 1963.

151. Oshima, M., Maeda, Y. and Kashima, H., ABIPC, 34, 1067 (1964).

152. Panshin, A. J. and Zeeun, C., "Textbook of Wood Technology," McGraw-Hill, New York, 1964.

153. Parker, P. E., Diss. Abstr., 27, 9, 3044B (1967).

154. Pearl, I. A., "The Chemistry of Lignin," M. Dekker, Inc., New York (1967).

155. Pepper, J. M. and Hibbert, H., J. Am. Chem. Soc., 70, 67 (1948).

156. Pepper, J. M. and Steck, W. F., Can. J. Chem., 41, 2867 (1963).

157. Pepper, J. M., et al., Adv. Chem. Ser., 59, 238 (1966).

158. Probluda, H. J. and William, R., Symp. on Biomass as a Non-Fossil Fuel Source, ACS Meeting, Honolulu, April 1979.

159. Rieche, A., Redinger, L., and Linderheyn, K., Brenstoff Chem., 11, 326 (1966).

160. Ritchie, P. F. and Purves, C. B., Pulp & Paper Mag. Can., 48, 12, 74 (1947).

161. Root, D. F., Saeman, J. F. and Harris, J. F., Forest Prod. J., p. 158, May 1959.

162. Roseveare, W. F., Ind. Eng. Chem., 44, 168 (1952).

163. Routale, O., Acad. Sci. Fenn., A2(3), 115 (1930).

164. The Rust Engineering Company, "U.S. Bureau of Mines Wood-to-Oil Pilot Plant - Final Design Report," prepared for BuMines, February 1974.

165. The Rust Engineering Company, "Proposal Modifications and Operations Plan for Biomass Liquefaction Facility, Albany, Oregon," prepared for DOE Contract No. ET-78-C-06-1092), February 1980.

166. The Rust Engineering Company, "An Investigation of Liquefaction of Douglas Fir by a Process Developed at the Pittsburgh Energy Research Center as Modified by the Rust Engineering Company at the Biomass Liquefaction Facility, Albany, Oregon," prepared for PNL (Contract B-B2471-A-G), July 1981.

167. Saeman, J. F., Ind. Eng. Chem., 37, 43 (1945).

168. Sakakibasa, A., ABIPC, 34, 1868 (1964).

169. Sakakibasa, A., Abe, I. and Araki, T., Ibid., 33, 360 (1963).

170. Sakakibasa, A., Araki, T., Wood Res. Soc., 7(1), 19 (1961).

171. Sakakibasa, A., et al., Makugai Gakkaishi, 15, 84 (1969); Chem. Abs. 71, 82805 u (1969).

172. Sen John, L. and Dobrev, S. T., Tseluloza Khartiya, 4, 22 (1973).

173. Sarkanen, K. V., "Lignin -- Occurrence, Formation, Structure and Reactions," Wiley-Interscience, New York, 1971.

174. Sarkanen, K. V., et al., J. Am. Chem. Soc., 79, 4203 (1957).

175. Schaleger, L. L. and Brink, D. L., Tappi, 6, 65 (1978).

175a. Schaleger, L. L., Yaghoubzadeh, N., and Ergun, S., "Pretreatment of Biomass Prior to Liquefaction," Report LBL-10093, Lawrence Berkeley Laboratory, November 1979.

176. Schuerch, C., J. Am. Chem. Soc., 72, 3838 (1950); 74, 5061 (1952).

177. Schuerch, C., "The Chemistry of Wood," B. L. Browning, ed., Interscience, New York, 1963.

178. Schuerch, C., Ind. Eng. Chem., 2, 71 (1965).

179. Sergeva, V. N. and Surna, A. Y., ABIPC, 32, 905 (1962).

180. Seth, M., Ph.D. Theris; University of California, Berkeley, CA, 1980.

181. Seth, M. and Ergun, S., Proc. 3rd Annual Biomass Energy Systems Conference, June 1979, p. 131.

182. Seth, M., et al., LBL-10091, UC-61, Lawrence Berkeley Laboratory, Berkeley, CA, 1979.

183. Seth, M., et al., LBL-9789, UC-61, Lawrence Berkeley Laboratory, Berkeley, CA, 1980.

184. Shinn, J. M., Ibid., LBL-9372, 1979.

185. Snajberk, K. and Zavarin, E., Tappi, 53, 1507 (1970).

186. Snider, H. and Prey, Y., Ber., 74, 1916 (1941).

187. Storch, H. H., et al., BuMines, TP 622, 1941.

188. Suida, H. and Prey, Y., Ber., 74, 1916 (1941).

189. Suida, H. and Prey, Y., Ber., 74, 1580 (1942).

190. Taran, R. D., et al., Environ. Sci. & Tech., 5, 545 (1971).

191. Talib, A. and Neuworth, M. B., "Assessment Paper on Albany, Oregon Wood Liquefaction Plant," The Mitre Corp., November 1980.

192. Vasyunina, N. A., et al., ABIPC, 31, 350, 732 (1961).

193. Wada, I., Chta, M. and Sakakibasa, A., Mokuzai Gakkaishi, 15, 218 (1969); Chem. Abs., 72, 112991 s (1970).

194. Wallin, J. H., U. S. Patent 608,075, November 1967.

195. Weiss, A. H., Textile Research J., p. 525, September 1972.

196. Wilhelm, D. J. and Stallings, J. W., "Assessment of the Biomass Liquefaction Facility in Albany, Oregon, and Related Programs," prepared for DOE (Contract DE-AC03-80CS83008), June 1980.

197. Winfrey, J. C., "A Laboratory Evaluation of Biomass Oil (TR7-136)," prepared for the Rust Engineering Company by Southern Petroleum Laboratories, Inc., Lab Report #77782, December 1979.

198. Willstatter, R. and Kalf, L., Chem. Ber., 55B, 2637 (1928).

198a. Wrathall, J., and Ergun, S., "Hydrolyzed Wood Slurry Flow Modeling," Report LBL-10090, Lawrence Berkeley Laboratory, November 1979.

199. Yu, G., Ph.D. Thesis, University of California, Berkeley, CA, 1982.

199a. Yu, G., et al., "Solvolysis of Douglas Fir Wood in Acidified Organic Solvent," in Report LBL-11983, pp. 3-18 to 3-20, Lawrence Berkeley Laboratory, March 1981.

200. Yu, J. and Miller, S., Ind. Eng. Chem., 19, 237 (1980).

201. Zartman, W. H. and Adkins, H. J., J. Am. Chem. Soc., 55, 4559 (1933).

202. Zoldner, Y. A. and Surna, Y. A., Khim Drevesiny, 5, 67 (1970).

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720