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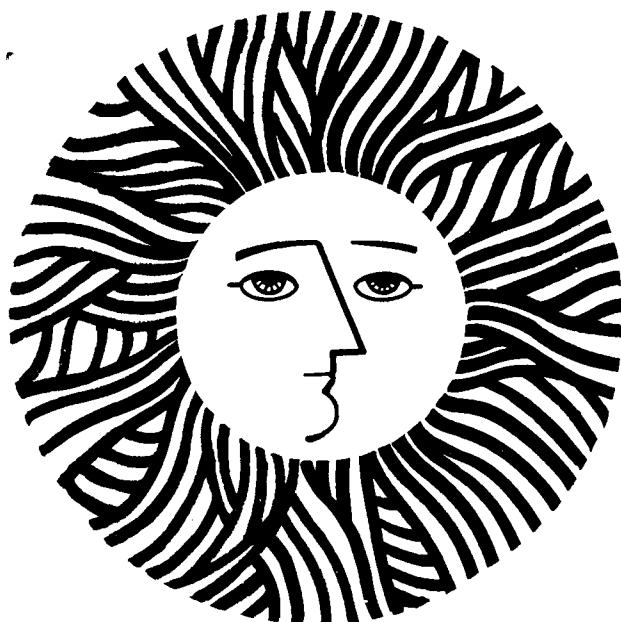
THE POTENTIAL FOR BIOMASS LIQUEFACTION

Manu Seth and Sabri Ergun

June 1979

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## THE POTENTIAL FOR BIOMASS LIQUEFACTION

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## ABSTRACT

A first, broad, overview of biomass liquefaction is presented. Four desirable chemical conversion routes that may be useful in the liquefaction of wood have been identified. Process conceptualization has been attempted based on an analysis of changes in physical structure, elemental composition and chemical transformation that may occur during liquefaction. Possible process streams have been characterized and likely separation procedures identified.

## INTRODUCTION

As technical monitors for the Thermochemical Conversion of Biomass, a major responsibility of the Coal and Biomass Group at LBL is to identify and define promising research and developmental areas related to the production of liquid fuels from biomass. As a first step a framework for techno-economic evaluation of developing liquefaction options is being formulated. This paper outlines the objectives, scope, approach and consequences of our first overview of biomass liquefaction. Subsequent papers will attempt to fill in the details and discuss experimental results and how these fit into or modify the evaluation framework.

## OVERVIEW

Several biomass feed-stocks are available for conversion to desirable fuels. These feedstocks in turn may be used to obtain a broad mix of products. Our objective, then, is to look for and develop a family of conversion processes. An integrated approach would enable us to apply experience gained with one feedstock or process-concept to other biomass feeds and conversion options. The developmental scheme is well represented by Figure 1, which outlines some of the feed-stocks and products of interest.

Each biomass liquefaction scheme can be characterized by the feed being processed, the products produced and the severity of the treatment. Apart from their ability to handle various feedstocks, the processes selected for development must also span a wide range of processing conditions. High severity processes, being capital intensive, could be used for large scale production whereas low severity processes could be used for dispersed, small-scale applications. As a first approximation, the severity of a process can be defined by the reaction temperature and residence time in the major conversion step. Figure 2 shows a hypothetical temperature-time region which future biomass conversion processes must attempt to span.

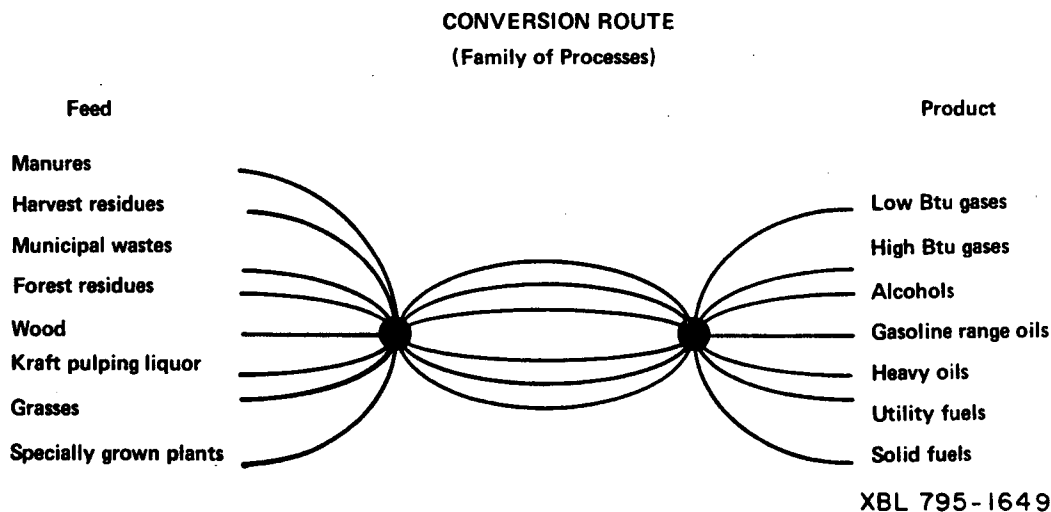
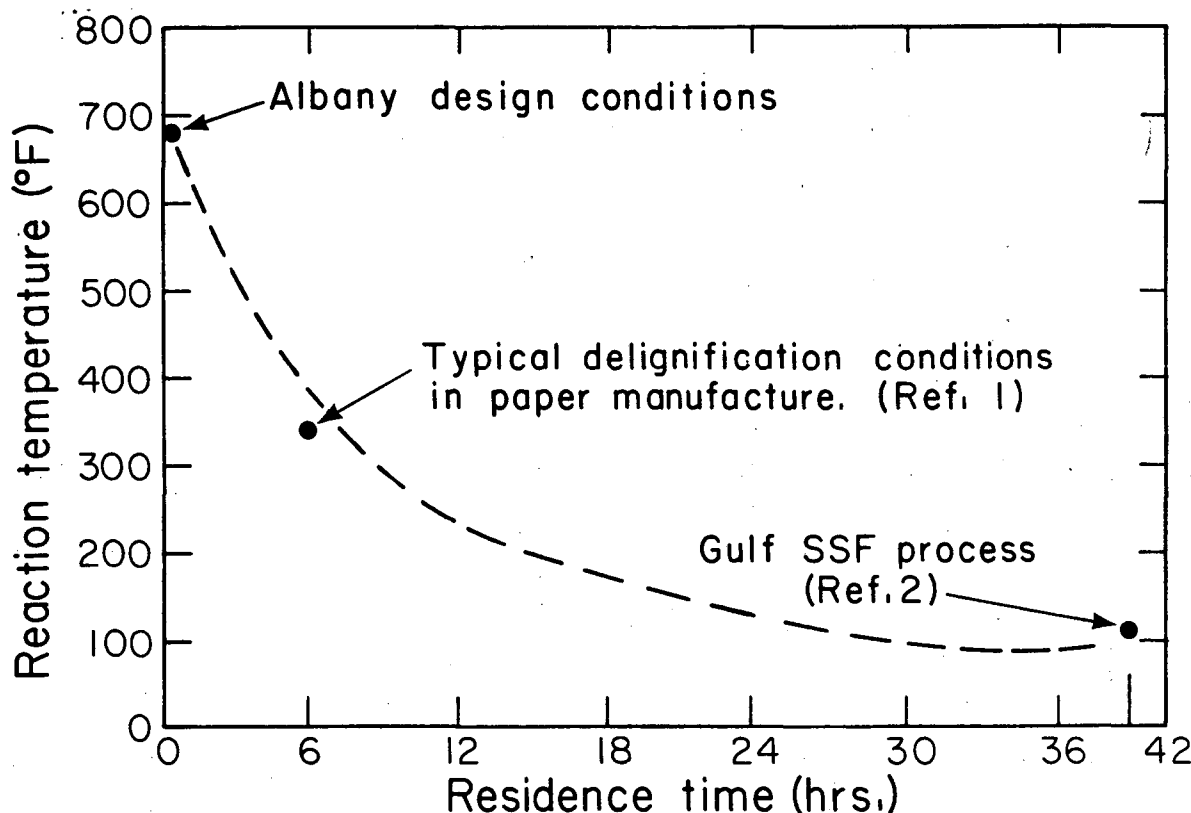


Fig. 1: Possible biomass feeds and products.



XBL 795-1650

Fig. 2: Hypothetical temperature-time region for future biomass processes.

The conversion of solid biomass, especially wood, can be viewed on three levels. The physical state, elemental composition and chemical structure of the biomass feed all change simultaneously as the material moves through a process train. Analysis of each of these transformations and identification of desirable changes leads to an approximate definition of process boundaries and flow schemes. For the sake of simplicity and clarity their discussion is limited to a single biomass feed-stock --wood.

#### CHEMICAL STRUCTURE OF WOOD

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

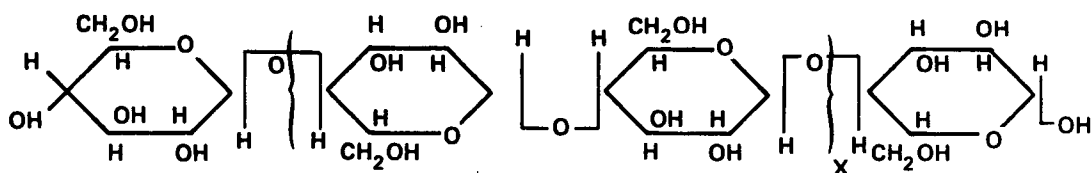
Cellulose is formed from D-glucose blocks joined by  $\beta$ -1,4-glucosidic bonds. Wood cellulose occurs as polymeric molecules with molecular weights generally in the range of 80,000 to 340,000. The structure of cellulose is shown in Figure 3.

Hemicelluloses are complex molecular chains of xylose or arabinose backbones. Xylans combined with substantial amounts of uronic acids are the most important hemicelluloses in wood.

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 [3] is shown in Figure 4. 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.

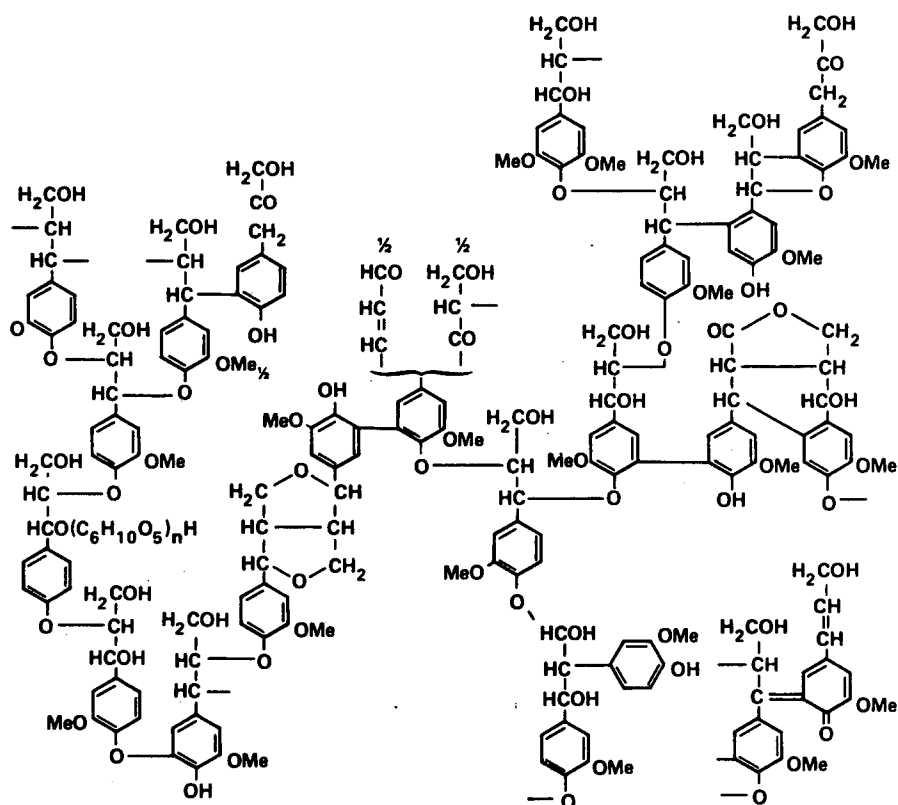
#### WOOD CHEMISTRY AND ITS APPLICATION TO LIQUEFACTION

Several areas of wood chemistry have been well explored. A variety of chemical conversions were tested with a view to elucidate the chemical structure of cellulose, lignin and hemicellulose [1,3,4,5]. Pulping of wood for the manufacture of paper is probably the most studied and best understood area of wood chemistry [1,6]. Hydrogenation of waste liquor from paper manufacturing processes has also been well investigated [4,7,8]. The hydrogenation and hydrogenolysis of wood and lignin were extensively studied by Lindblad [9], Harris [10], Lautsch [11] and Hachihama [12], among others. Substantial information also exists on the selective hydrogenation of carbohydrate materials such as cellulose, sugars and polyhydric alcohols [e.g., 13, 14].



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Fig. 3: Structure of cellulose.



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Fig. 4: Structure of lignin.

Review of the various methods of the degradation and hydrogenolysis of wood and its components lead to the selection of four major chemical routes for liquefaction. Criteria used for the selection included acceptable process conditions and the possibility for pilot-scale testing at the DOE Experimental Facility at Albany, Oregon.

The four selected chemical conversion routes are briefly discussed below, together with illustrative examples of processing conditions, reagents and possible applications to wood liquefaction.

#### TREATMENT WITH INORGANIC SALT SOLUTIONS

In both the Soda and Kraft processes for the production of cellulosic pulp for paper manufacture, the lignin in wood is degraded by the cooking chemicals and its fragments dissolve in the liquor. Typically cooking times of 4 to 6 hours at 170°C are used for delignification. Several complex reactions occur during the delignification process. It has been suggested [15,16] that aromatic ether links in lignin are hydrolyzed by the alkaline cooking liquors. Etherification of specific phenolic groups are postulated to result in rapid cleavage of some of the ether groups [15], resulting in the solubilization of about 1/3 of the lignin. The presence of sodium hydro-sulfide ions ( $-SH^-$ ) in Kraft cooking liquors are assumed to cause the increased extent of lignin solubilization in this process [15]. Model experiments indicate the initial step is addition of  $-SH^-$  ions to quinone methide lignin intermediates to form mercaptide ions ( $S^-$ ). The mercaptide ion is a strong nucleophile, and by a complex series of rearrangements leads to the depolymerization of virtually all the lignin [15].

Modifications of the chemistry of paper manufacture could lead to new process schemes for wood liquefaction. Research in this area must be geared to overcoming three drawbacks. Other inorganic nucleophiles should be screened to find salts that i) do not result in sulfur (or nitrogen) incorporation in the products; ii) substantially depolymerize cellulose; iii) result in products which either have no inorganic base incorporation or products from which incorporated inorganic materials can be easily removed.

Extensive screening of various catalysts by the LBL group has resulted in the identification of an acceptable catalyst. These results will be reported when testing is completed.

Mild oxidation of wood prior to treatment with alkali may also result in the simultaneous depolymerization of cellulose and lignin at 170-180°C [15]. This option is also being tested at LBL.

#### Hydrogen Transfer from Hydrocarbon Molecules

Hydrogenation of wood to distillable products can be achieved by treatment with hydrogen donor solvents at 320 to 400°C for 1 to 4 hrs [17]. Cyclo-

hexanol [18], tetralin [17] and decalin [19] have all been tested as sources of hydrogen. Liquefaction occurs by the donation of hydrogen from solvent molecules to thermally cleaved bonds in wood. An alternative approach for the transfer of hydrogen to wood is the acid catalyzed hydride transfer reaction. In this reaction, a hydrogen atom is transferred with its pair of electrons to a carbonium ion [20].  $\alpha$ -Pinene has been used as a hydride donor in the presence of a strong acid at 120-150°C [21].

Both thermal hydrogen donation and catalytic hydride transfer hold promise for wood liquefaction. In each case the spent solvent would have to be hydrogenated preferably in a separate hydrogenation reactor. Two possible problems may occur with either scheme. First, incorporation of solvent by condensation reactions with products or with wood residues could lead to unacceptably high solvent losses. Second, separation of solvent from reaction products by distillation may be difficult because of overlapping boiling ranges. To circumvent both problems wood-derived molecules should be tested as hydrogen donors or hydride transfer agents. Partially hydrogenated phenyl propane units (derived from lignin hydrogenation) and/or alcohols (from cellulose hydrogenation) may prove to be adequate hydrogen sources.

#### Solvolysis

Solvolytic degradation of cellulose and of lignin have both been well studied [7,22]. Solvolysis in an acidic medium can occur under a variety of conditions ranging from 0.8 wt-% acid at 170°C to 40% acid at 40-60°C, with solvents such as water (hydrolysis), methanol, ethanol and even phenol [8].

Solvolysis of cellulose is an acid catalyzed reaction involving the rapid formation of an intermediate complex between the glycosidic oxygen and a proton; this is followed by the slow, rate-determining scission of the glycosidic bond adjacent to C<sub>(1)</sub> [22]. When lignin is treated with alcohols in an acidic medium new alkoxy groups are introduced at ambient conditions [7] without significant lignin depolymerization. At higher temperatures (e.g., 79°C with ethanol) this rapid hydroxyl displacement reaction is followed by degradation of lignin to monomers and soluble oligomers.

By carefully controlling reaction temperature and acid concentrations it may be possible to liquefy wood by simultaneous solvolysis of lignin and cellulose, using acceptably small levels of solvent consumption. If low boiling alcohols are used for solvolysis the overall process must also include an alcohol recovery or production unit.

#### Organometallic Complexes as Liquefaction Catalysts

The application of homogeneous organometallic complexes for hydrogenation and hydroformulation reactions are well known. Such catalysts appear



Separation and recovery of products from reactor effluents could be an important (and expensive) part of biomass liquefaction processes. Typical intermediates and products obtained from the depolymerization of cellulose and lignin in reduc-

ing atmospheres were examined so as to obtain some understanding of the unit operations that could be used for product separation and recovery. A partial list of cellulose and lignin decomposition products is shown in Figures 5 and 6, together with their estimated boiling points and solubilities in water.

The depolymerization of wood in reducing atmospheres results in the formation of products of progressively lower oxygen content and polarity. In general the lignin in wood 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

the formation of polymeric materials from condensation and degradation reactions. It does, however, enable us to begin estimation of the physical properties of process streams and selection of possible separation processes.

A two-phase liquid effluent can be expected from the liquefaction reactor(s). The light, aqueous, phase would contain any added process water (and water from wood dehydration) together with dissolved low-molecular-weight phenols and alcohols. Higher molecular weight wood-derived oils and any non-polar organic slurring 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.

Where the aqueous phase is a large fraction of the product stream, decantation or centrifugal separation may be considered so as to avoid high evaporation costs. Such phase separation would also permit the recirculation of water soluble catalysts.

Of the organic phase only materials lower boiling than dilignols (from lignin) and sugars (from cellulose) can be distilled. Reactor conditions should therefore be optimized for the production of substituted phenyl propanes (monolignols) and polyhydric alcohols. The non-distillable fraction of the organic phase could be used for the production of reducing gases and/or process heat generation.

#### CONCLUSION

A two-step wood liquefaction process has been envisioned using wood chips as the feed. The first low-pressure step would be used to obtain

	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			

Fig. 5: Cellulose depolymerization products in reducing atmospheres.

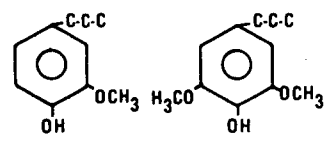
	Example	Boiling point (°C)	Solubility in water
Lignin			Insoluble
↓			
Oligomers			
↓			
Phenylpropanes		265-400	
↓			
	4-methoxy-2 methyl phenol	252	Insoluble
↓			
Substituted phenols and cresols	Cresolol Ethyl phenol	249 207	
↓			
Phenols	Phenol	182	Soluble
↓			
Cyclohexanols	Methyl cyclohexanol	155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

Fig. 6: Lignin depolymerization products in reducing atmospheres.

a pumpable slurry. The second step, which could occur at higher pressures, would convert the biomass to distillable oil. Four possible chemical routes that could prove useful for wood liquefaction have been identified. An analysis of likely changes in elemental and physical composition during liquefaction resulted in a broad definition of process characteristics and the identification of desirable changes. Probable components of reactor effluent streams have also been identified and appropriate separation procedures suggested.

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