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SOLVOLYTIC LIQUEFACTION OF WOOD UNDER MILD CONDITIONS

Suen-Man Yu
(Ph.D. thesis)

April 1982

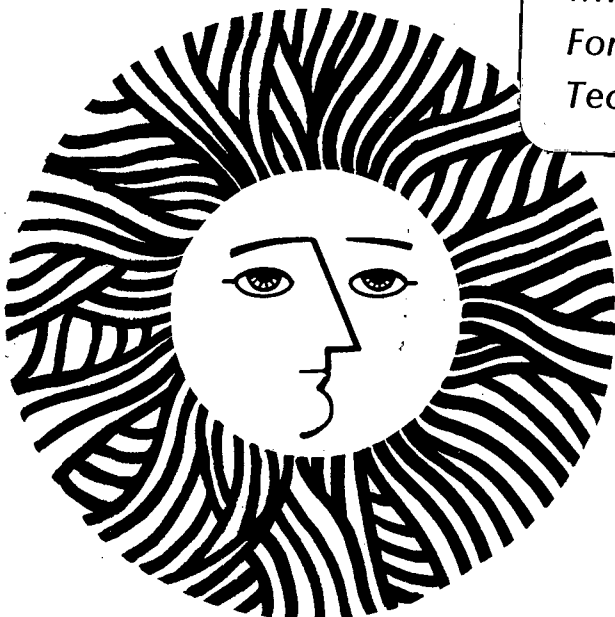
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SOLVOLYTIC LIQUEFACTION OF WOOD UNDER MILD CONDITIONS

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*Ph.D. Dissertation in Chemical Engineering

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ABSTRACT

Conversion of wood to liquid products requires cleavage of bonds which crosslink the wood structure. The current technology (PERC process) uses high temperature (360°C) to initiate thermolytic bond cleavage and several thousand psig of carbon monoxide in the presence of sodium carbonate to remove wood oxygen. At such high severity, energy and capital expenditure are understandably extensive.

This study examines a low-severity wood solubilization process utilizing a solvent medium consisting of a small amount of sulfuric acid and a potentially wood-derivable alcohol. In one half hour of reaction time at 250°C under 15 psia starting nitrogen pressure, over 95% of the wood (maf) was rendered acetone-soluble. The product is a soft, black, bitumen-like solid at room temperature but readily softens at 140°C. Between 25 and 50% of the original wood oxygen, depending on alcohol used, was removed as water. Approximately 2 to 17% of the alcohols were retained in the product. Gel permeation chromatography showed that the product's median molecular weight is around 300.

The solvolytic wood-liquefaction process was determined to be largely a kinetic-controlled process. Using computer-fitting technique, two kinetic models were evaluated. The reaction was determined

to be first order in wood and the rate was dependent on the amount of residual acid and/or wood-derived organic acids.

Based on experimental and literature results, a mechanism for wood solubilization is proposed. This involves protonation of the etheric oxygen atoms, leading to subsequent bond scission to form carbonium ions which are stabilized by solvent alkoxylation. At severe conditions, polymerization and condensation reactions result in acetone-insoluble materials.

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CHAPTER I

INTRODUCTIONA. The Energy Dilemma

Even those who questioned the reality of the energy shortage in our nation a few years ago have largely come to the same conclusion that we now live in an era of continuously dwindling fuel supply and continuously escalating fuel cost. Awareness of long gasoline lines in 1979, of buildings cold in winter and warm in summer, and of electricity bills now a major item, are all vivid evidences of the energy dilemma we are facing. The projection is that the situation will only get worse. It is thus generally agreed that additional energy supplies of all kinds will be needed, if our present standard of living is to increase at all or even hold constant.

A recent trend of energy consumption in the United States is illustrated in Table 1. Petroleum accounted for 45% of the total usage; of it, 51% was imported. As the present sole source of transportation fuel, petroleum has become a prime target for concern. Remedies range from strong conservation measures to total replacement from alternative sources. Among the alternatives, fossil and non-fossil, regenerable sources are generally regarded as the true long-term solution. This sentiment was echoed by a National Science Foundation Report (1), "Energy in Transition: 1985-2010," which stated that coal will provide one-third to one-half of U.S. energy by 2000, despite intervening problems. Soon afterward, however, "truly sustainable energy sources must begin to become available, to provide new

Table 1. U.S. Energy Consumption in 1980

Source	Oil or Oil Equivalent (MM Barrels per Day)	Percentage of Total	Quantity in Units Commonly Used for Each Source
Petroleum	17 ^{a,*}	45	17 million barrels per day
Natural Gas	9.2	24.5	19.2 trillion cubic feet per year
Coal	9.0 ^{b,*}	24	800 million tons per year
Nuclear	1.4*	3.5	251 billion kilowatt hours per year
Hydro	1.1	3	230 billion kilowatt hours per year
	<hr/> 37.7	<hr/> 100	

^aIncludes imports of 8.7 million barrels per day (mbd); also includes "natural gas liquid" (~ 2mbd), excludes 0.2 mbd of exports

^bExcludes exports of 0.6 mbd oil equivalent

*Updated information from:

(i) *Oil & Gas Journal*, Sept. 22, 1980

(ii) *Business Week*, Dec. 8, 1980

Source: Department of Energy, Energy Information Administration, Annual Report to Congress, Volume III, 1977 (Washington, D.C., Government Printing Office, 1978), pp. 5, 23, 51, 145

flexibility for energy policy and to relieve some of the pressure on coal and other energy sources."

B. Energy Alternatives

Alternative energy sources available to us are few and costly. The list includes shale oil, coal, tar sands, nuclear power, and solar energy. Although solar energy is the ultimate long-term solution, its extremely low concentration places in doubt its use as a major source of electric power. The high investment costs for solar cells or optical concentrators, added to the huge land needed, may always limit the amount of energy to be made available in this way. Nature, however, continuously concentrates solar energy in the form of biomass, and indirect utilization of solar energy through converting biomass to high-grade fuels is now technically feasible. The biomass feedstocks investigated include wood, energy crops like corn, and agricultural and municipal wastes. A recent assessment made for the Department of Energy (2) placed the total annual biomass resource availability at over 57×10^{15} Btu or 57 quads. For a thermal efficiency (3,4) of 72% in converting biomass to oil and a heating value of 6×10^5 Btu to a barrel of oil, the total biomass potential corresponds to 6.8×10^9 barrels of oil per year - this is more than the total annual crude oil consumption in the United States.

Using a more conservative estimate of recoverable or surplus biomass on a renewable basis of 8.6 Q per year (2,5), Ergun (6) pointed out that a modest 25% utilization amounts to, or is equivalent to, as much as 8% of the imported oil. At \$32 per barrel, this amounts to

8.32 billion dollars. This is sufficient incentive for intensive efforts to convert biomass to usable fuels.

As compared to other fuel sources, biomass offers many benefits: minimal environmental effects because of its low sulfur, nitrogen, and ash; renewability; and availability in easily recoverable quantities. Technologies for converting biomass to various types of fuels are currently available and benefits can be realized even in the near term. Above all, biomass is an indigenous resource that can reduce our dependent on imported oil.

C. Wood as a Source of Energy

Among the various sources of biomass, renewable plants rather than wastes may serve the ultimate objectives best. Wood, one of the renewable plant products, is the subject of this investigation. Cultivation of trees (silviculture), selecting species that give high energy yield per acre and a short growth cycle (4 - 7 years), is presently being explored (7-10). Energy farms utilizing such species, closely spaced, can be managed in the same way as present forest resources used for wood production. One obvious advantage of energy farms is that they minimize the exorbitant cost of biomass collection, handling, and transportation, recently estimated (11) at \$15 per ton of green wood (50% moisture) for a 40-50 mile collection radius.

Wood, like coal, was utilized extensively during the early twentieth century. In 1900, wood supplied roughly 25% of the total energy in the United States. Even as late as 1940, more than 20% of homes still used wood for space heating. Today wood contributes only

1.5% of all U.S. Energy consumption, equivalent to about one-half million barrels of oil per day. The wood fuel industry is small compared to the giant paper and lumber industries.

Apart from providing heat through direct burning, wood was also formerly used as a source of chemicals like charcoal, methanol, acetone, and acetic acid, and it remains a source of organic materials like turpentine, pine oil, resin acids, and tannins. It was not until the bountiful availability of "cheap" oil in the Middle East and of "cheap" natural gas in the U.S. that conventional wood usage started to decline. Now that oil and gas are no longer cheap and unlimited, interest has revived in wood as a dependable energy source.

Fuel energy from wood is now obtained almost entirely through direct combustion, providing the equivalent of 140,000 barrels of oil per day in the U.S.; this figure could double by the year 2000 (12). Although combustion is a simple process, the energy generated is difficult to store and transport, let alone its questionable ability to adapt to existing equipment. Converting wood to liquid and/or gaseous fuels can be viable alternative. Considerable research under way is aimed at identifying and establishing processes capable of converting wood to liquid fuel, either directly, or indirectly following initial gasification to synthesis gas.

Direct liquefaction processes include pyrolysis, reduction by synthesis gas (the PERC and LBL processes), and fermentation to ethanol from sugars formed by hydrolysis of the cellulose and hemicellulose constituents in wood. The product of pyrolysis or reduction is a heavy

oil which may substitute for no. 6 fuel oil. This product has 7 to 20% oxygen, depending on the degree of reduction; is rich in phenols; and has heating values up to 16,000 Btu per pound, depending on oxygen content; its storage stability and its possibilities for further refining remain in question. In the fermentation case, only the cellulosic fraction in wood is converted; lignin remains as a marketable solid by-product.

The indirect liquefaction routes can produce high-quality liquid fuels (methanol, Fischer-Tropsch liquids, Mobil-process gasoline) but require high capital investment and have fairly low overall thermal efficiencies.

D. Liquefaction Process Rationale

Wood is a complex heterogeneous material. Its conversion to a soluble product is inevitably a complex process. The conversion involves depolymerization of polymers of several types, and reduction of the high oxygen content. Since the majority of the oxygen exists as aliphatic hydroxyl in polysaccharides or phenolic hydroxyl in lignin, a wood liquefaction process must involve an attack on hydroxyl groups accompanied by a depolymerization. In terms of the structure of cellulose and lignin, the depolymerization process obviously involves breaking a number of carbon-oxygen bonds. This bond breaking can be effected through high temperature and pressure treatment (thermolysis) with or without catalysts, but less destructive reactions should be possible. The latter are preferred because of lower energy requirements. The problem is to identify the reactions and required catalysts.

Oxygen removed from wood would exit the process either in the form of water, carbon monoxide, or carbon dioxide. The sulfur and nitrogen content of wood is so low that their oxides are essentially negligible. From a product standpoint, oxygen removal raises the heating value and thus its value. However, a good fuel also demands high H/C ratio of the product. Therefore, a good liquefaction process might simultaneously aim for high feed solubilization and high carbon dioxide gas production. Carbon dioxide gas production results either from thermal decomposition (decarboxylation) or reduction by carbon monoxide, or by both as in the case of the PERC liquefaction process. Removal of oxygen in the form of water requires reduction by hydrogen, or an internal condensation reaction with water elimination.

In addition to effective wood depolymerization and oxygen removal, the ability of the process to prevent condensation of the depolymerized species is also very important. As in cases of coal liquefaction, the condensed or repolymerized product often turns out to be even more difficult to liquefy than the original materials. Thus, the success of any process also largely depends on this consideration. The probability of repolymerization reactions increases hand in hand with oxygen removal. The more oxygen is removed, the more bonds are broken, and the higher the chances of condensation. An ideal process, however, requires large amount of oxygen removal but little or no repolymerization reactions.

Various ways of lowering or eliminating condensation reactions were attempted; all of them have used the stabilizer technique:

depolymerized species are captured and made inert by stabilizers before they even have a chance to repolymerize. A common stabilizer is hydrogen which is supplied by hydrogen donor solvents. Techniques such as alkylation or alkoxylation (13,13a) were also tried and have achieved some success.

Because of its efficacy for preventing or reducing condensation reactions, hydrogenation has been one of the most popular routes. If molecular hydrogen is the agent, a catalyst is generally required. The catalyst may be heterogeneous (molybdenum, nickel, etc.) or homogeneous (zinc chloride (13b), metal carbonyls (13c), etc.). The use of hydrogen donor solvents is another approach to supply hydrogen for product stabilization. To name a few, tetralin, isopropanol and cyclohexanol are all proven H-donor solvents. Most of the possible processes when applied to wood suffer from two common drawbacks. Firstly, they operate at high temperature and pressure. Secondly, wood feed is in the form of a slurry; thus, limiting mass and heat transfer, not to mention product selectivity, during the defunctionalization or deoxygenation process. Therefore a process which uses a solvent or solvents that can solubilize wood before or during the reaction becomes of real interest. Preferably the solvent(s) will have the ability to stabilize, or to carry solutes which cap off depolymerized products. Finally, the economics of a process is greatly improved if the process operates under mild temperature and pressure.

In summary, an ideal liquefaction process would have all or most of the following qualities:

- o ability to depolymerize wood under relative mild conditions
- o little or no consumption of reducing gas
- o effect good overall oxygen removal
- o ability to prevent condensation reactions
- o produce a liquid product

E. Scope of this Investigation

Direct liquefaction of wood under an atmosphere of synthesis gas and steam has been demonstrated on a scale of about 50 lbs dry wood per hour in a nominal 3 ton/day DOE process demonstration unit (PDU) at Albany, Oregon, operating at 360°C and 4000 psig with residence time on the order of an hour. Slurry of wood flour (65 mesh) is fed in recycle oil (PERC process) or water (LBL process). To date, the system has been able to use only dilute-slurry feeds. Feed-handling problems and severe operating conditions have led to many mechanical difficulties with pumps, seals, phase separators, and check valves, and firm engineering data have not yet been obtained. While there is optimism that improvements in the LBL process will surmount the difficulties, a modified simple method of liquefying wood could be very attractive.

The objective of this investigation, therefore, was to search for such a process: one that is chemically sound; preferably using pre-solubilized wood rather than slurry; operating at low-severity conditions, i.e., moderately low temperature and low pressure; consuming a minimum of carbon monoxide and hydrogen; yielding quality liquid product; entailing simple product-separation steps; and adaptable to large-scale commercial applications.

The study was to include effects of process variables such as temperature, pressure and residence time, so as to establish the optimum conditions. Because of the availability of wood at various moisture levels, namely green wood (50% as logged), field-dried wood (10-15%), and dried wood (0-4%), the effect of treating these different grades of raw material would be of interest. As solubilization implies the use of a recycle solvent, solvent degradation and loss are always a primary concern relative to the process economics; thus, solvent recoverability would be a topic for study.

Experimental products would need to be characterized both physically and chemically by analytical techniques such as elemental analysis, melting point determination, structure examination by scanning electron microscopy and molecular-weight determination by permeation chromatography (GPC). From these measurements the liquefaction process chemistry with its mechanistic pathway was to be elucidated.

CHAPTER II

BACKGROUNDA. Structure and Reactions of Wood1. Structure

The principal components in wood are classified as cellulose, hemicellulose, lignin, and organic extractives, present in amounts of 40-50%, 20-35%, 15-35%, and 3-5%, respectively. For simplicity a softwood species, Douglas Fir, was chosen for use, because it is abundantly grown in the Pacific Northwest region where the Albany PDU is located.

As shown in Table 2, dried Douglas Fir is two-thirds carbohydrate: 41% cellulose and 26% hemicellulose. Lignin constitutes most of the rest. Minor components include 1% ether-soluble (organic materials), 3% organic acids such as glucuronic acid and about 0.5% inorganic ash. Table 3 gives the elemental analysis of moisture-free Douglas Fir: 53.0% carbon, 5.60% hydrogen and 40.54% oxygen. As with low-rank coals, this large oxygen content poses process economics problems in converting the raw material into fuels of high heating value. Unlike coal, the Douglas Fir contains such small amounts of sulfur, nitrogen, and inorganic ash that pretreatments to remove these components are probably not required.

The chemistry and structure of wood can only be described in terms of its constituents - cellulose, hemicellulose, and lignin - which are reviewed briefly in the following paragraphs.

Table 2. The composition of Douglas Fir

	Percent (moisture free basis)
Cellulose	41
Hemicellulose	26
Lignin	28
Uronic anhydride	3
Ether-soluble extractives	1.0
Acetyl	0.5
Ash	0.5
	<hr/> 100.0

Table 3. Typical Elemental Analysis of Douglas Fir

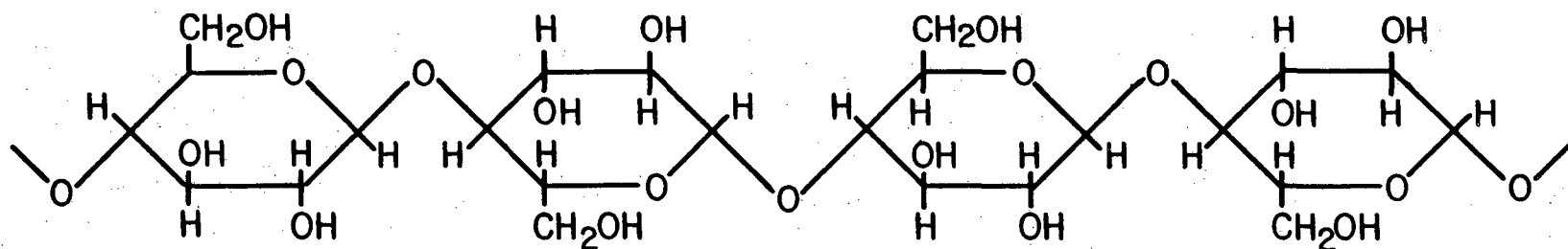
	Percent (moisture free basis)
Carbon	53.17
Hydrogen	5.61
Nitrogen	0.13
Sulfur	0.05
Ash	0.50
Oxygen (by difference)	40.54
	<u>100.00</u>

Cellulose, a major wood component, is a linear, highly crystalline polymer consisting of anhydrous glucose units linked together in "head to tail" fashion. In wood, its molecular weight ranges from 20,000 to 300,000. In the modular structure of cellulose (Fig. 1), the glucose units are connected by β -1,4 glycosidic oxygen bonds which break easily under hydrolysis. Because of the highly ordered molecular structure, most solvents (including water) are not capable of swelling cellulose.

Hemicelluloses in wood resemble cellulose in that they are both carbohydrates. Monomeric anhydrous sugar units such as mannose, galactose, xylose, arabinose, as well as glucose and sugar acids comprise the backbone of hemicellulose. Compared to cellulose, hemicellulose has a relatively unordered structure and a lower molecular weight (500 to 2000). Its structure is amorphous, thus making it an easier target for solvent attack and degradation.

It is generally believed that hemicellulose is not bonded covalently to cellulose. However, a high degree of hydrogen bonding and physical intermixing make it difficult, if not impossible, to separate the two without decomposing them.

Lignin probably comprises the most complex, least characterized, group of substances in nature. Lignins constitute 28% of the wood substance in Douglas Fir, and are defined as the total noncarbohydrate fraction of the extractive-free portion. Entirely different and separate from the carbohydrate polymers, lignin is essentially a highly branched three-dimensional amorphous polymer consisting of aromatic building units. Numerous wood chemists (14-16) have



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XBL 795-1647

Fig. 1. The Structure of Cellulose.

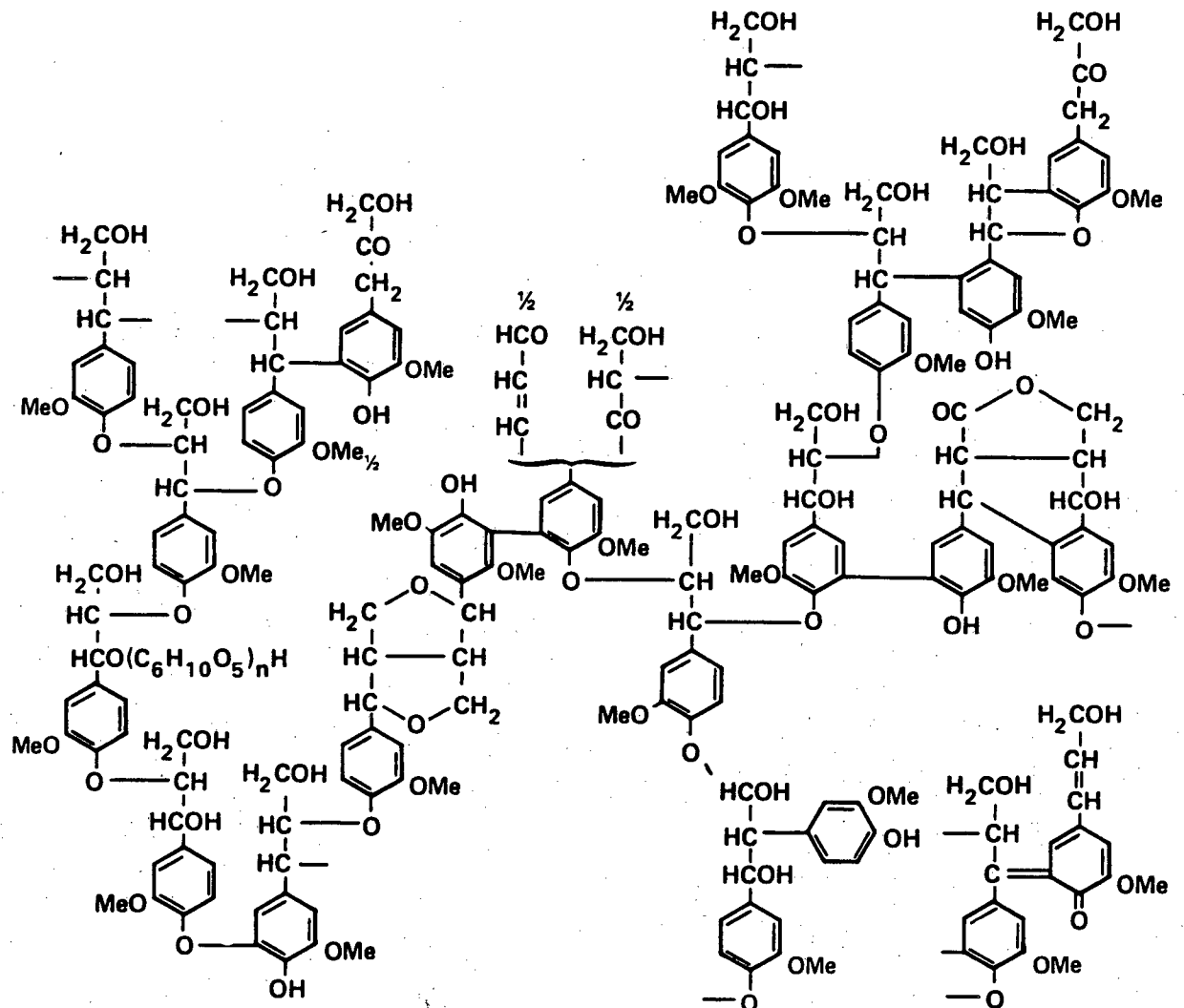
attempted to elucidate its structure; the lignin model devised by Freudenberg (17,18) (Fig. 2) is considered to be most nearly typical. Lignin consists primarily of methoxyphenyl-propane building units linked together by carbon-carbon and carbon-oxygen bonds, but many details remain in doubt. It is generally believed that lignin is bonded to hemicellulose via ether or glycosidic bonds; recent electron microscopy studies (19) seem to support this view.

A whole mature wood is made up of elongated cells (fibers) consisting of four major layers (Fig. 3a), the fibers being bonded together with intercellular substances. Lignin is present in high concentration (Fig. 3b) in the outer layers (P) and decreases rapidly towards the inner wall (S3). In contrast, cellulose content is low in P but comprises over 80% of S3. Hemicellulose is usually found in all layers, but its percentage increases in the inner layers.

Because lignin is concentrated in the outer layers of fibers, it is believed to provide structural rigidity, stiffening the fibers and holding them together. The aim of wood-pulping reaction is to remove this bonding layer so as to free wood fibers. In wood liquefaction the objective is complete solubilization, requiring reactive chemicals that can degrade both lignin and cellulose.

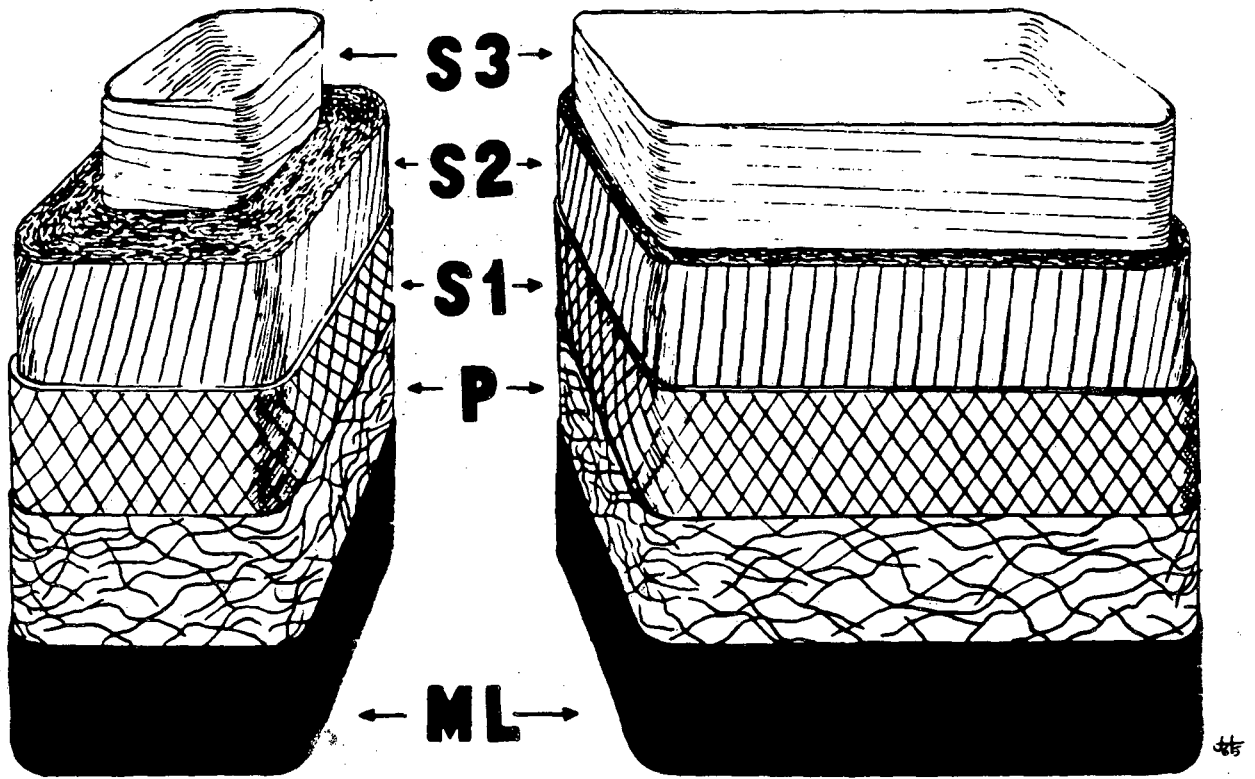
2. Chemical Reactions

At normal temperatures, wood has remarkable resistance to degradation by chemicals and solvents. Depending on the prevailing temperature and chemical environment, wood can be subjected to reaction but rarely undergoes total degradation. One noted example is the



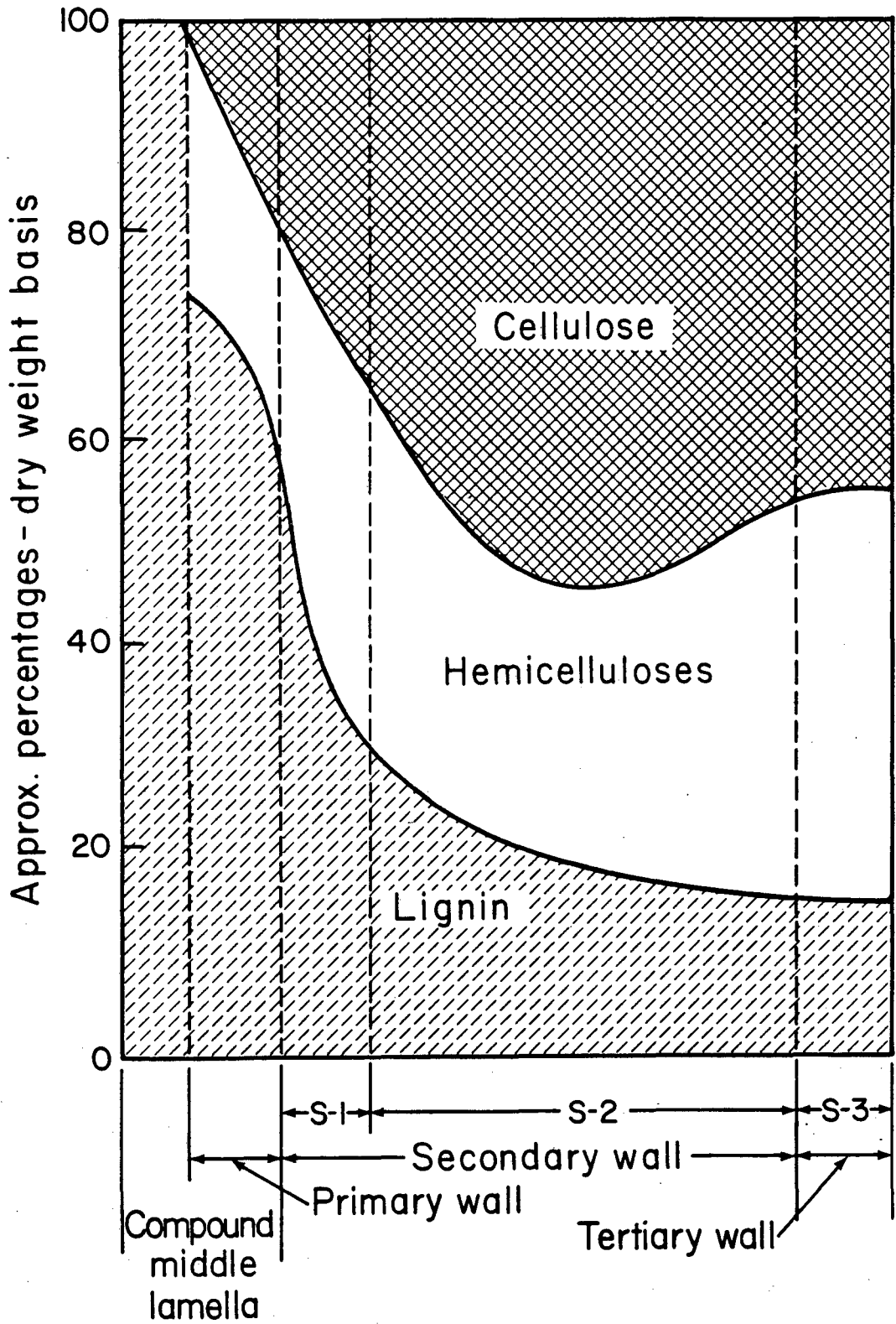
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Fig. 2. The Structure of Lignin.



XBL 815-9720

Fig. 3a. The Structure of Wood Fiber.



XBL-813-397

Fig. 3b. Distribution of Chemical Constituents in the Cell Wall.

production of pulp, or delignified wood, for making paper. Some major wood reactions are summarized in the following paragraphs.

Water at room temperature has very little chemical effect on wood. This may be attributed to the highly complex interpenetrating network of wood fibers and high crystallinity of the carbohydrate system which effectively reduces the accessibility of chemical reagents. As temperature rises, reactions commence. Some weakly bonded hemicellulose fractions, notably the uronic acid (sugar acid) will be dissolved; the rate of dissolution goes up with temperature. As the dissolved acids make the system more and more acidic, hemicellulose and cellulose hydrolysis commences. At temperature above 140°C, removal of hemicellulose becomes rapid. Some lignin also dissolves to a lesser degree. Heating wood in slightly acidified water to 250°C produces a brownish liquid and a black charry residue.

Concentrated mineral acids at room temperature, for example 72% sulfuric or 42% hydrochloric acid, are capable of hydrolysing the carbohydrate fraction of the wood, leaving degraded but condensed lignin as a solid residue. This low-temperature high-acidity process constitutes a basis for lignin determination. Dilute acid, on the other hand, only reacts with wood at higher temperature (e.g., 180°C), to effect hydrolysis and recover reducing sugars (glucose) from wood. These sugars serve as a starting material to be fermented to a crude ethanol which, under current conditions, can be mixed with gasoline to make gasohol.

Wood is severely degraded in strong alkaline solution (10-25% NaOH) at room temperature. Hemicelluloses are most susceptible to dissolution. Extractives and lignin degradation products are also found in solution, especially when the temperature is raised. The Kraft pulping process is based on this principle for removing lignin from wood. However, alkaline pulping involves a penalty in reduced pulp yield, because cellulose is also subject to degradation.

Wood is moderately resistant to oxidation and reduction reactions except at relatively high temperature. Pyrolysis of wood, a process involving self-oxidation and reduction, is conducted at temperatures of 450-600°C. Catalytic wood hydrogenation (20) at above 300°C has been found promising in producing petroleum-like product.

(a) Reactions of Cellulose and Hemicellulose

Because of the similarity of structures of hemicelluloses and cellulose, known reactions of cellulose will often be applicable for hemicelluloses as well. Due to the lack of crystallinity and low molecular weight of the latter, their reaction will generally be faster and more complete.

Major reactions of cellulose will be summarized briefly. The reactivity (21-23) of cellulose is essentially attributable to the presence of one primary and two secondary hydroxyl groups on each anhydroglucose unit. On this basis cellulose should react like a polyalcohol, but there are two major differences between the reactions of cellulose and other alcohols. First, uniformity of cellulose reactions is sometimes very difficult to achieve. Because cellulose

is normally in a solid state during reaction, problems are encountered in making all hydroxyl groups fully available for reaction. Second, bond breaking of C-C and C-O links usually occurs in cellulose, giving faster degradation than for polyalcohols.

Cellulose degradation via hydrolysis in an acidic medium is a common reaction. The mechanism is well understood, in that β -glycosidic bonds between the glucose units are broken, and water is added to the depolymerized anhydroglucose units to make glucose monomers. Cellulose also degrades in alkaline medium as illustrated in the Kraft pulping process. The degradation starts at the reducing end of the chain and occurs through the formation of a carbonyl at carbon-2 position. The end product is a mixture of degraded cellulose and metasaccharinic acid which is formed via benzilic acid type rearrangement.

Cellulose reactivity for all reactions can be increased by swelling agents or complexing agents. The swelling agents expand the cellulose and weaken its crystallinity, so as to increase contact with the solvent. Complexing agents like strong sodium hydroxide, tetramine copper(II), ethylenediamine copper(II), or acid salts function similarly.

(b) Reactions of Lignin

Among the wide spectrum of reactions involving lignin, two pertinent to this study are pulping and alcoholysis reactions. The former involves dissolving lignin from wood in either alkaline solution as in the Kraft process, or acid solution as in Sulfite pulping. Mechanisms for both processes are well worked out.

In pulping, lignin is removed by carbon-oxygen bond scission, generating carbonium ions which are stabilized by nucleophilic additions of active pulping reagents. The active reagents in the Kraft and Sulfite processes are sodium hydrosulfide and sulfurous acid respectively.

Alcoholysis constitutes another important reaction of lignin in the context of liquefaction. As early as 1900 chemists working to extract and isolate lignin from plant material, with the aim of identifying its structure, used alcoholysis as a popular approach. Lignin for these experiments was obtained as the residue from acidic cellulose hydrolysis.

Harris and co-workers (24) used methanol with a small amount of HCl in dioxane to partially dissolve lignin at 120°C. MacGregor, Evans and Hibbert (25) isolated spruce lignin by cooking 10 grams of spruce wood flour in 350 cc ethanol containing 2% hydrogen chloride, at 70°C for 12 hours. The resultant light brownish solution was evaporated to recover the lignin. Structure determinations revealed that ethanol had alkylated to the β -carbon on the propyl side-chain of lignin. Hibbert and co-workers (26-28) attempted the ethanolysis of 1-(4-acetoxy-3-methoxy phenyl)-2-propane in a medium of ethanol and 2% hydrogen chloride at 50°C to model the reaction of spruce lignin obtained earlier.

Adler and Gierer (29) alkylated Brauns spruce lignin with methanol and 0.5% HCl at room temperature for 48 hours. As much as 0.5 methoxyl group per methoxyl group originally present was introduced, suggesting that methoxylation was an etherification type of reaction.

Hibbert et al. (30) and Sarkanen and Schuerch (31) have depolymerized spruce lignin by ethanolysis, using a mixture of ethanol and chloroform as solvent and a small amount of hydrogen chloride as catalyst. They discovered that extensive bond scissioning occurred if ethanolysis was carried out at high temperature (150°C). The extracted lignin has an α -carbonyl group in the propyl chain. The oxygen content of the product lignin was reduced, indicating a possibility of intramolecular dehydration reactions occurring concurrently.

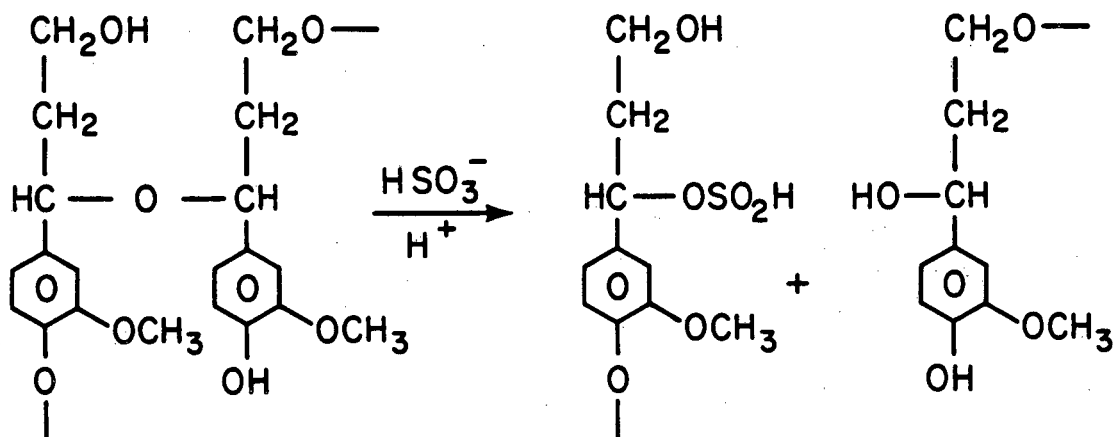
Kosilova and Polcin (32) found that methanolysis of spruce wood in a medium of 0.5% HCl in anhydrous methanol followed first-order rate behavior. Addition of 10% dioxane doubled the rate. Alcoholysis in general was discussed in terms of solvent acidity and solubility parameter. Again, product analysis turned up evidence of extensive β -carbon bond scission.

B. Wood Liquefaction Literature Review

1. Wood Pulping for Paper Making

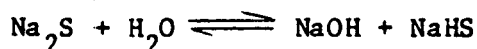
Mechanical pulping (33), the first pulping process to convert wood to low grade pulp, was developed in about 1800 and is still used. The wood blocks are held against a grindstone in the presence of water and the wood is reduced to a fibrous form. The product contains both cellulose and lignin, and makes poor paper.

Sulfite pulping (33) utilizes chemical reagents such as calcium sulfite and other sulfite salts. Wood chips are cooked in the weakly acidic pulping solution at 160 to 180°C for 5 to 10 hours. Delignification is believed to occur through attack by the HSO_3^- ions on carbon-oxygen bonds that link the lignin monomers:



XBL 815-3007

The other widely used pulping reaction, the Kraft process (33), involves cooking wood chips in aqueous sodium hydroxide containing sodium sulfide at 170 to 180°C for 5 to 10 hours. Here, the carbon-oxygen bonds are cleaved by sodium hydrosulfide, formed from hydrolysis of sodium sulfide:



The HS^- also "caps" the broken bonds and prevents their repolymerization. An undesirable side reaction of the Kraft process is a degradation of cellulose which reduces the overall yield.

The waste liquors in both Sulphite and Kraft processes are evaporated to recover the pulping reagents and concentrate the dissolved lignin, which is then burned to provide process heat. Attempts (34,35) have been made to hydrogenate lignin-containing liquors with the aim of producing phenolic derivatives. The high sulfur content of the liquor and the non-uniformity of the products have led to unusually high costs of separation.

2. Wood Hydrolysis

Wood hydrolysis recently is becoming a more and more popular technique for obtaining sugars from wood by hydrolytic cleavage of β -glycosidic bonds, either in strong acid at low temperature or in dilute acid at high temperature (36-38). Glucose is the main product, with smaller quantities of mannose, galactose, xylose, and arabinose. In addition to sugars, decomposition products like hydroxymethylfurfural, other furfurals (42) and organic acids are also present in the high-temperature product.

Wood hydrolyzate is a good raw material for fermentation to ethanol (39-41) for blending with gasoline to be marketed as gasohol. Other fermentation products include butanol, acetone, butylene glycol, and organic acids, as well as yeast which is of value in animal feeds. Sugar degradation products like furfural and hydroxymethylfurfural (42) are at time intended products from wood hydrolysis. Levulinic acid, dervied from hydroxymethylfurfural, is being produced commercially for conversion to chemicals like diphenolic acid, chemical solvents, and plastisizers, etc.

3. The PERC Process

Appell and co-workers (43) at PERC discovered a way to dispose of urban waste, notably cellulosic matter, by converting it to oil. In 1921, Fischer and Schrader (44) demonstrated the effectiveness of solubilizing low-rank coals in a medium of carbon monoxide and water at elevated temperature (380°C) and pressure (4500 psgi). Conversion as high as 40% was reported. Later studies (45) were extended to process cotton, newsprint, and pine needles, using either 380°C or

250°C with 4500 psig of carbon monoxide for one hour. The low-severity experiment gave a soft bitumen-like product, solid at room temperature; it had high oxygen content (20%) and was sparingly soluble in benzene. The high-severity conditions gave a viscous dark brown liquid with an oxygen content of less than 10%, and was wholly soluble in acetone.

The investigation (46) was later extended to include wood waste and bovine manure as reactants. Using similar reaction conditions, batch autoclave experiments were used to evaluate the effects of temperature, carbon monoxide, water, and catalytic additives. Sodium carbonate was found to be the best catalyst, and presence of water was found to be essential (possibly for the generation of hydrogen by the water-gas shift reaction). Water also acted as a reactant for cellulose hydrolysis and as a solvent to receive water-soluble products, but its high vapor pressure tended to raise the operating pressure prohibitively.

At temperatures of 250 to 400°C (47) there was little effect on conversion and oil yield. Below 250°C reaction was too slow for any practical purposes, and above 400°C the product was carbonized. The 250°C product was tar-like at room temperature, and pumpable near 100°C or above. The 380°C product was a black free-flowing liquid with a viscosity of 150 centistoke at 50°C and 102 centistoke at 88°C. In processing wood waste, 325°C was reported to be an optimum temperature, at which a pourable product was produced.

Effects of carbon monoxide pressure on oil yield and conversion were studied. The results are summarized in Table 4. Using water as solvent, a 2000 psig operating pressure at 250°C corresponding to 600 psig of initial carbon monoxide was found to yield acceptable product quality and carbon monoxide consumption.

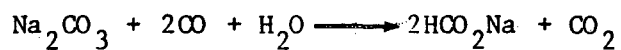
In an effort to increase oil yield and conversion by raising the process temperature, organic solvents were examined as reaction media. Anthracene oil, phenols, isoquinoline, and other high-boiling solvents were tested at 380°C and initial CO pressure of 600 psig for 15 minutes. It was found that the oil yield increased from 25% without the solvents to 50% or higher with the solvents. This improvement was believed due in part to the extraction of organic intermediates from the aqueous phase into the oil phase, where they are converted to oil. These high-boiling solvents also provided a polar liquid medium which assisted the breakdown of large carbohydrate molecules to soluble reactive species. Among the solvents tested, anthracene oil ranked best. Cresols were found to effect even a higher oil yield but incorporated into the product resulting in solvent loss. From the process standpoint a wood-derived carrier oil would be ideal, because its incorporation would be economically acceptable.

Process mechanistic studies (45) were carried out through the use of methyl ethyl ketone, n-butyraldehyde, benzaldehyde, acetophenone, and other model compounds at 250°C with sodium carbonate as catalyst. Based on these studies and certain earlier work, a reaction mechanism consisting of the following steps was proposed:

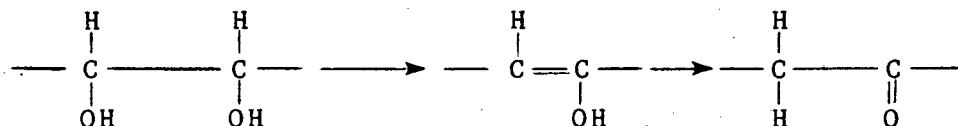
Table 4. Effects of Carbon Monoxide Pressure on Cellulose Conversion.

Initial CO(psig)	Oil yield (%)	Conversion (%)	Operating Pressure (psig)
0	24	78	960
100	24	76	1,150
200	32	83	1,380
300	32	82	1,480
400	34	84	1,500
500	35	87	1,640
600	40	90	1,840

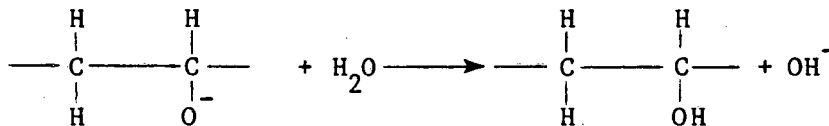
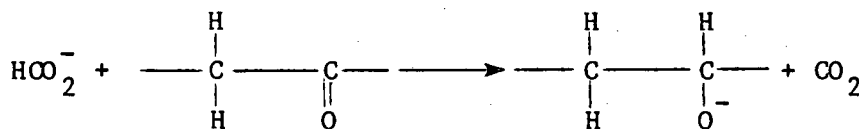
(i) Sodium carbonate in water reacts with carbon monoxide to yield sodium formate.



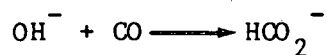
(ii) Adjacent hydroxy groups in carbohydrate dehydrate to form enol which isomerizes to ketone.



(iii) Formate ions and water reduce this carbonyl group to make alcohol.



(iv) Hydroxyl ions react with CO to regenerate formate ions.

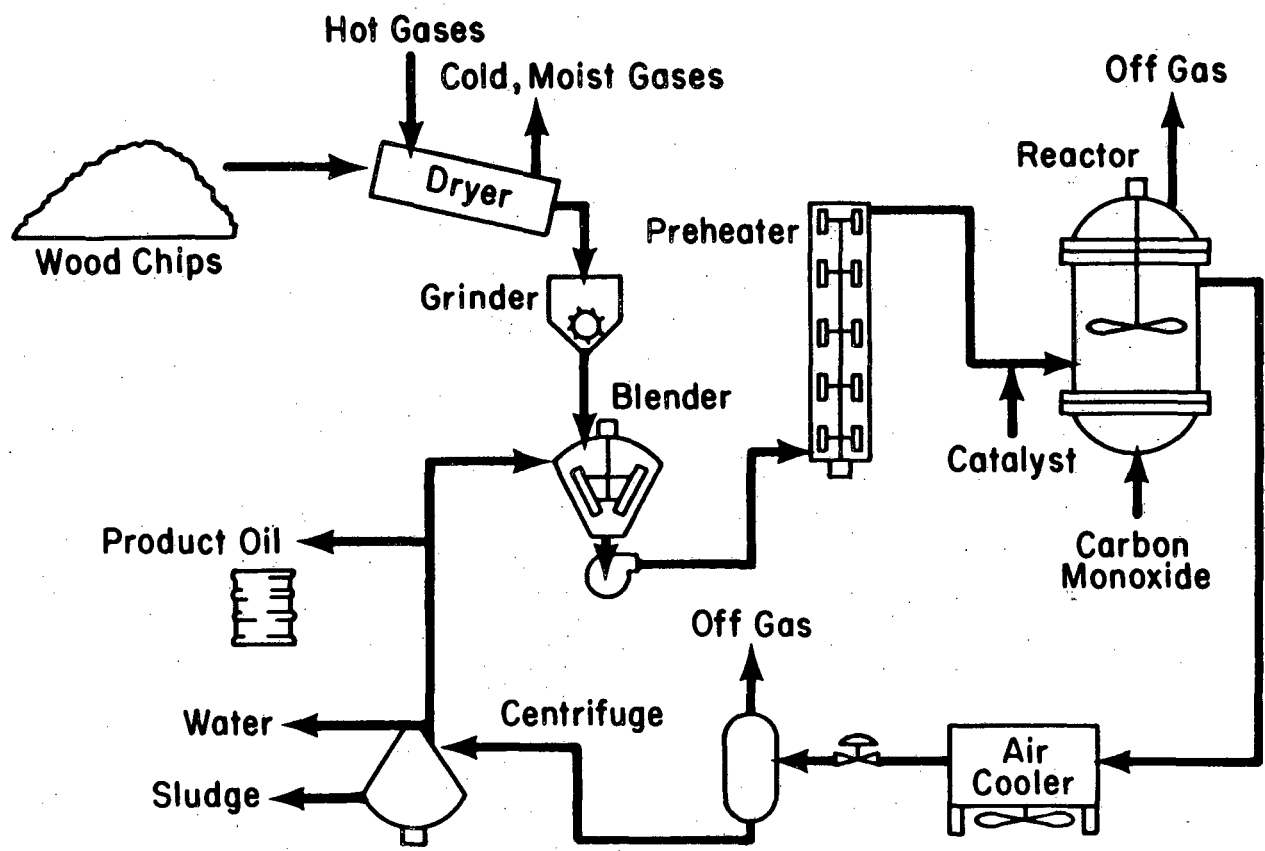


Two major side reactions were believed to have taken place. A desirable one involved benzylic-acid rearrangement of two adjacent

carboxyl groups, yielding hydroxy acid which then decarboxylated (lowering the oxygen content without consuming CO or formate). An undesirable side reaction involved condensation with formation of char, a step which appears to be inhibited by higher pressure and carbon monoxide. The mechanistic pathway for converting lignin to oil (45) was said to involve reduction of carboxyl groups by carbon monoxide (eqn. iii) via formate ions (eqn. iv). This thus eliminated much of the cross-linking and charring that normally accompanied the heat treatment of lignin. Eliminating condensation and cross-linking of depolymerized material seems to be the key for obtaining good quality product at high temperature and pressure.

To pursue this development, a process demonstration unit (Fig. 4) was built at the Bureau of Mines facility in Albany, Oregon, in 1977 to handle 3 tons of wood feed per day. After the unit was commissioned, it was plagued with operational problems which raised serious doubts regarding process feasibility of the carrier (anthracene oil) to slurry more than 10% wood flour, compared with 30% in the original design. Even at below 10% slurry, serious equipment and check-valves failures occurred.

Lawrence Berkeley Laboratory contracted with DOE to monitor the PDU development in mid-1978. An immediate task was to help to overcome the equipment plugging. Research indicated the benefit of adding a front-end acidic hydrolysis reactor which broke down both wood chips and wood flour and rendered the mixture pumpable by conventional pumps. With this approach, a first barrel of wood-derived oil was produced in



XBL 815-3006

Fig. 4. The PERC Process Schematic.

1979, establishing the "LBL Process" feasibility. However, acid used in the hydrolysis reaction needs to be neutralized before the liquefaction step.

The oil from Albany PDU using the LBL modified approach is a black viscous liquid at room temperature. It is soluble in acetone, and has a specific gravity and 210°F viscosity of 1.10 and 52 centipoise, respectively. Elemental analysis showed that it contains roughly 13% oxygen and an H/C ratio of 1.17. The heating value for the product was estimated to be around 15,000 BTU per pound.

Schaleger (48) and Battelle Pacific Northwest Laboratory (49) conducted some extensive chemical characterization tests and found that the product contains 30-35% phenolic materials, 45% neutral oil, and the rest heavy residuals. Roughly 65% of the product is distillable at 210°F and 10 torr. GCMS result revealed the presence of guaiacol and propyl-guaiacol (apparently derived from lignin) and furfurals, cyclopentanone, and cyclohexanone (apparently from cellulose degradation).

More recently, equipment modification in the PDU has resulted in a successful run without prior hydrolysis. A product oil relatively free of start-up anthracene oil (50) was found to be quite similar to the "LBL" oil, but lower (<7%) in oxygen content.

4. Miscellaneous Wood Related Hydro-Liquefaction Process

Fierz-David (51) and Bowen et al. (52) showed in early 1900's that cellulose could be converted to liquid materials by means of high-temperature (420-440°C) hydrogenation. They also demonstrated the

feasibility of turning cellulosic plant materials into a bitumen-like material under elevated temperature in caustic medium. Their work thus set the course for converting biomass material to hydrocarbon.

Fierz-David's work was followed up by Berl et al. (53-56), who reacted cotton with sodium hydroxide at 310 to 330°C and obtained gases and tars. The tars were subsequently hydrogenated at 420°C to yield more gases and hydrocarbon oils. Heinemann (57-59) confirmed the earlier result by transforming cellulosic matters, notably sugar cane, cotton wood, bamboo sticks, etc. to a bitumen-like material under alkaline conditions at elevated temperature. By-products include carbon dioxide, methane, water, phenols, and phenolic carboxylic acids. The process conditions used were quite severe: five hours digestion at 250°F, followed by another five hours at 800°F in a 7.5 to 1 ratio of 1 N. aqueous NaOH to biomass. The yield of bitumen solid was low, and varied proportionally with the alkali charged. Hydrotreating the bitumen materials with catalysts like molybdenum oxide or sulfide at 750°F under 1000 psig hydrogen yielded gasoline, middle distillate, and lubricating oil.

Lignin was also tested as a substrate for hydroliquefaction. Lautsch and others (60,61) used 1-4% sodium hydroxide media at 250 to 350°C for 8 to 12 hours with various nickel, cobalt, and copper salts as catalysts. Products obtained were soluble in ether (10-30%) and were about one-third distillable; they were primarily phenolic materials with less active catalysts, or cyclohexanol and cyclohexanol derivatives with more active catalysts.

In other work, Harris and Adkins (62,63) used copper chromite to hydrogenate lignin at 250 to 300°C for 12 to 15 hours in dioxane, yielding 30 wt% of distillable product. Hachihama (64) and Ritchie (65) used Raney nickel at 250°C for 5 hours at 300 psig of hydrogen to hydrogenate lignin, and obtained a product of which 24 wt% was distillable. Hibbert and co-workers (66) used both copper chromate and Raney nickel under similar conditions, and obtained 70 wt% distillable. Ruthenium and its salts were found by Vasyermica (67,68) and Sergeeva (69) to be effective catalysts in treating alkali lignin.

A mixed solvent containing sodium hydroxide, ethanol, and water was used by Lutch and Prayolo (70,71) to hydrogenate lignin with Raney nickel as catalyst, at 350°C for 9 to 11 hours, up to 80% of lignin was converted, and the resultant product was up to 50% distillable. Other solvents investigated included phenol (72,73) and cresol (74) with catalysts such as molybdenum oxide, molybdenum sulfide, and bog iron ore. Oil and tar from lignin as high as 75% were obtained; addition of small amounts of sulfur, in some cases, enhanced the hydrogenation and increased the oil yield.

Acid media for catalytic hydrogenation of lignin were also investigated. Hachihama and Jyodai (75-77) hydrogenated lignin isolated with hydrochloric acid treatment from sources like wood, beech and bagasse. With a nickel oxide catalyst at 300°C, conversion was high (>70%) and the products were determined to be phenolic derivatives. Sakakibosa et al. (78-80) used copper chromite and also cobalt, molybdenum, and nickel carbonyls to hydrotreat lignin obtained

from acid hydrolysis of wood. Catalysts were found to be effective in the temperature range of 400 to 450°C, but phenol yields were lower than those obtained from alkali lignin under the same conditions.

Whole-wood hydrogenation to make distillable product has also been looked into. Lindbold (81) impregnated sawdust with nickel hydroxide and tested it at 250°C in an atmosphere of hydrogen. Approximately 5% hydrogen (based on wood) was absorbed, and 30% of the product was distillable. When cobaltous sulfide was used to impregnate wood, 7% of hydrogen was absorbed giving 40% of oil product of which 67% distilled below 180°C. Higher temperature (400°C) produced excessive gaseous products unless nickel hydroxide, zinc chloride, or molybdic acid was present to suppress gas formation. Hallonquist (82) carried out numerous hydrogenation reactions of Douglas Fir in acidic (pH=4) aqueous solution. The experiments were run at 250°C and 2500 psig of hydrogen using Raney nickel as catalyst. Up to 10% of hydrogen was adsorbed to yield approximately 50% distillable liquids. Rantala (83) reported that copper and cobalt hydroxides, nickel formate, ammonium molybdate and chromate each catalyzed the liquefaction of sawdust at high temperature yielding oil yield as high as 35%. Snajberk and Savarin (84) used wood flour impregnated with nickel acetate under hydrogen atmosphere at 165-230°C, and obtained more than 70% of liquid products with very little gas formation. More recently, Boocock (20,85) of the University of Toronto treated a fast growing hardwood, hybrid poplar, suspended in water at temperatures around 350°C and hydrogen pressure of approximately 1500 psig. Raney nickel was used

as a hydrogenation catalyst. Complete conversion of wood to oil and gas was reported. The oil was low in oxygen (~10%) and had a heating value of 17,500 Btu per pound.

H-donor liquefaction approaches reminiscent of German technology for liquefying coal were also tried, Boomer and Edwards (86) heated Douglas Fir sawdust in tetralin at 300 to 350°C with an initial hydrogen pressure of 1000 psig, with complete conversion of wood and partial conversion of tetralin to naphthalene. Bobrov and Kolotova (87) hydrogenated spent sulfite liquor in hydrogenated oil at 350°C, observing substantial hydrogen consumption at 350°C with a high yield of heavy oil; a lighter oil boiling below 150°C was obtained by treatment above 400°C. Suida and Drey (88,89) hydrogenated spruce lignin using decalin at 450°C and 12 hours; product consisting of 40% liquid, 15% tar, 30% residue and 15% gases and water was obtained. Similar results were obtained by Kleinert (90,91) who treated spruce liquor with cyclohexanol at 300°C for three hours. Other solvents, cyclohexadiene, cyclohexene, and α -pinene, were also investigated as possible hydrogen donors.

CHAPTER III

PROCESS FUNDAMENTALSA. Concept

Wood liquefaction involves a lot of bond breaking which can either be achieved thermally, with and without catalysts, or via chemical reactions. Catalytic and non-catalytic thermolysis processes have been shown to be feasible. The Albany PDU's PERC process is a classical example of the application of high-temperature catalytic process in wood liquefaction. In this case, high temperature is needed because of the inability of the solvent to solubilize wood at low-severity conditions. It was predicted that if wood can be dissolved, better mass and heat transfer will result in a liquefaction process feasible under milder process conditions. Therefore, the key is to solubilize wood.

Generally speaking, solubilization usually requires high temperature. However, a chemical reaction if effected properly will allow the dissolution process to take place under milder conditions. Hence an immediate objective was to identify this "chemical reaction." Since chemistry of wood is described via chemistry of its constituents, chemical reactions of lignin and cellulose therefore would be the sources of ideas for wood solubilization processes. After an extensive literature survey and an indepth look at wood chemistry, such "chemical reaction" was identified.

The liquefaction process concept developed is based on two well known reactions, they are:

- o cellulose hydrolysis
- o lignin alcoholysis

1. Cellulose Hydrolysis

Cellulose has always been relatively easier to solubilize than lignin. Cellulose hydrolysis involves depolymerizing cellulose in an acidic medium at relatively low temperature (<200°C) for an hour or less. For this step, no gas is needed (other than water vapor).

With respect to oxygen removal, hydrolysis acts in the wrong direction. The β -glycosidic carbon-oxygen bonds are opened and capped, usually by water in the solvent; this in effect increases the oxygen content in the product. However, if process conditions can be found to promote dehydration without condensation, oxygen can again be removed in the form of water. Cellulose can be transformed via glucose into hydroxymethylfurfural or related compounds as an intermediate at low-severity atmospheric-pressure conditions, thus largely eliminating the need for reducing gas.

Hydroxymethylfurfural monomer is a liquid at room temperature. It has an O/C ratio of 0.5, compared to 1.0 for glucose and 0.83 for cellulose. Further oxygen reduction can be achieved by hydrogenation. Decarboxylation offers another viable option, but carbon monoxide input is needed for this method.

2. Lignin Alcoholysis

Lignin alcoholysis is less thoroughly understood. It involves solubilizing lignin in a solvent or mixture of solvents. This concept of solubilizing lignin was utilized quite extensively in the early

1900's by wood chemists such as Brauns (14,15), Hibbert (26,27), and Freudenberg (17) in their isolation of lignin from plant materials. Their reaction conditions were rather mild: 40° to 120°C, at from 5 to 48 hours, with very low yields (5%). Nevertheless, the method of dissolving lignin into solvents was firmly established.

Research using combinations of alcohols as delignification agents has continued actively over the last fifty years (92-96). Process severity was mild (160 - 250°C), but residence times were long (5 - 10 hours). Yields as high as 90% lignin removal were reported, but unacceptably high solvent or alcohols losses occurred through incorporation. Recent work (97) indicates that adding a catalyst could conceivably catalyze lignin solubilization without adversely incorporating excessive amounts of solvents. The catalysts used were mainly acid salts such as zinc chloride, ferric chloride, and aluminum bromide.

With processes for separately liquefying or solubilizing cellulose and lignin potentially available, the aim has been to identify a system such that both cellulose hydrolysis and lignin solvolysis could occur simultaneously. This translated into the problem of finding a solvent or mixture of solvents capable of solubilizing lignin and cellulose.

B. Approach

Once the liquefaction concept was decided, a trial process had to be conceived. With the aim to utilize lignin alcoholysis and cellulose acid hydrolysis, acidified alcohol in solvents were the

obvious choice - but which acids and which alcohols? Process conditions were another issue yet to be solved.

1. Solvent Selection

Dissolution of cellulose and hemicellulose in acidic medium has been much investigated (98-102). It is only a matter of choosing the process conditions such as acid concentration, temperature, and residence time. On the other hand, solvents that can dissolve lignin are not so well established. The situation is further complicated by the fact that the solvent or solvents which are capable of dissolving lignin must simultaneously solubilize cellulose. For this reason, a careful literature study was initiated to screen solvents.

One frequently studied method to dissolve or extract lignin is ethanolysis. Other alcohols like phenol (103), butanol (103), and ethylene glycol (104) and also non-alcoholic solvents such as DMSO and DMF (104) have been used; but since the objective was structure determination, little consideration was given to their capacities and extraction rates. The process temperatures used were mild (from 40° and 120°C), rates slow, and the yields of lignin removed very low. Thus, the procedures had little relation to industrial application.

Other solvents were tested with better results. Kachi and Terashina (105) treated dry pine meal with benzyl ethyl ether in anhydrous dioxane at 90°C for 8 hours obtaining 25% solubilization of lignin, or more if small amounts of catalysts like hydrogen chloride and boron trifluoride were added. Scherch (106,107) discovered that solvent effectiveness increases as the hydrogen-bonding capacity of

the solvent increases, attributable to the carbonyl and hydroxyl groups in lignin. He suggested that the best lignin solvents have a Hildebrand solubility parameter of about 11. His data are shown in Table 5 and Figure 5. Ekman and Linberg (108) found that binary organic solvent mixtures dissolve lignin better than the individual solvents. Using milled wood lignin from Scotch pine, they correlated lignin solubility empirically as a function of solvent composition, solubility parameter, dielectric constant, and molecular weight using the data shown in Table 6.

2. Solvents Derivable from Wood

From an overall point of view, a process self-sufficient in supplying its own process solvents would be highly desirable. The overall process economics would be more favorable and could potentially shorten the lead time for process commercialization.

(a) Lignin

Acid degradation with 0.2 M hydrochloric acid in dioxane-water (9:1) for 4 hours was used by Lundquist (109,110) on milled wood lignin from birch. He obtained considerable amounts of phenols with one or two aromatic rings. Most of the phenols identified were related to derivatives of arylglycerol β -aryl ether, 1,2-diaryl-1,3-propanediol, or syringaresinol structures.

Pepper and co-workers (111), in hydrogenation of spruce lignin using Raney nickel and palladium-charcoal as catalysts, obtained phenols, phenolic derivatives (catechol, cresol, and methoxy phenols), and a small amount of straight-chain alcohols. Dioxane-extracted

Table 5. The Solubility of Isolated Lignin in Single Solvent.
(Refs. 106, 107)

Solvent	Cohesive Energy Density (cal/cc) ^{1/2}	"Indulin" Kraft Pine	"Meadol" Soda Hardwood
Hexane	7.4	Ins	Ins
Ether	7.5	Ins	Ins
Carbon tetrachloride	8.6	Ins	Ins
Xylene	8.78	Ins	Ins
Diethylene glycol	9.1	Sol	Sol
Ethyl acetate	9.1	Sli	Sli
Benzene	9.15	Ins	Ins
Methyl ethyl ketone	9.3	Par	Par
Chloroform	9.3	Ins	Sli
Chlorobenzene	9.5	Ins	Ins
Carbon disulfide	10.0	Ins	Ins
Dioxane	10.0	Sol	Sol
Nitrobenzene	10.0	Ins	Sli
Acetone	10.0	Par	Par
Methyl formate	10.16	Par	Par
Acrylonitrile	10.5	Sli	Sli
1-Nitropropane	10.7	Ins	Ins
Pyridine	10.7	Sol	Sol
Nitroethane	11.1	Ins	Ins
Butanol	11.4	Ins	Ins
Propanol	11.5	Sli	Ins
Acetonitrile	11.89	Sli	Sli
Nitromethane	12.6	Sli	Sli
Ethanol	12.7	Sli	Sli
Ethylene glycol	14.2	Sol	Sol
Methanol	14.3	Par	Par
Glycerol	16.5	Ins	Ins
Water	23.4	Ins	Ins

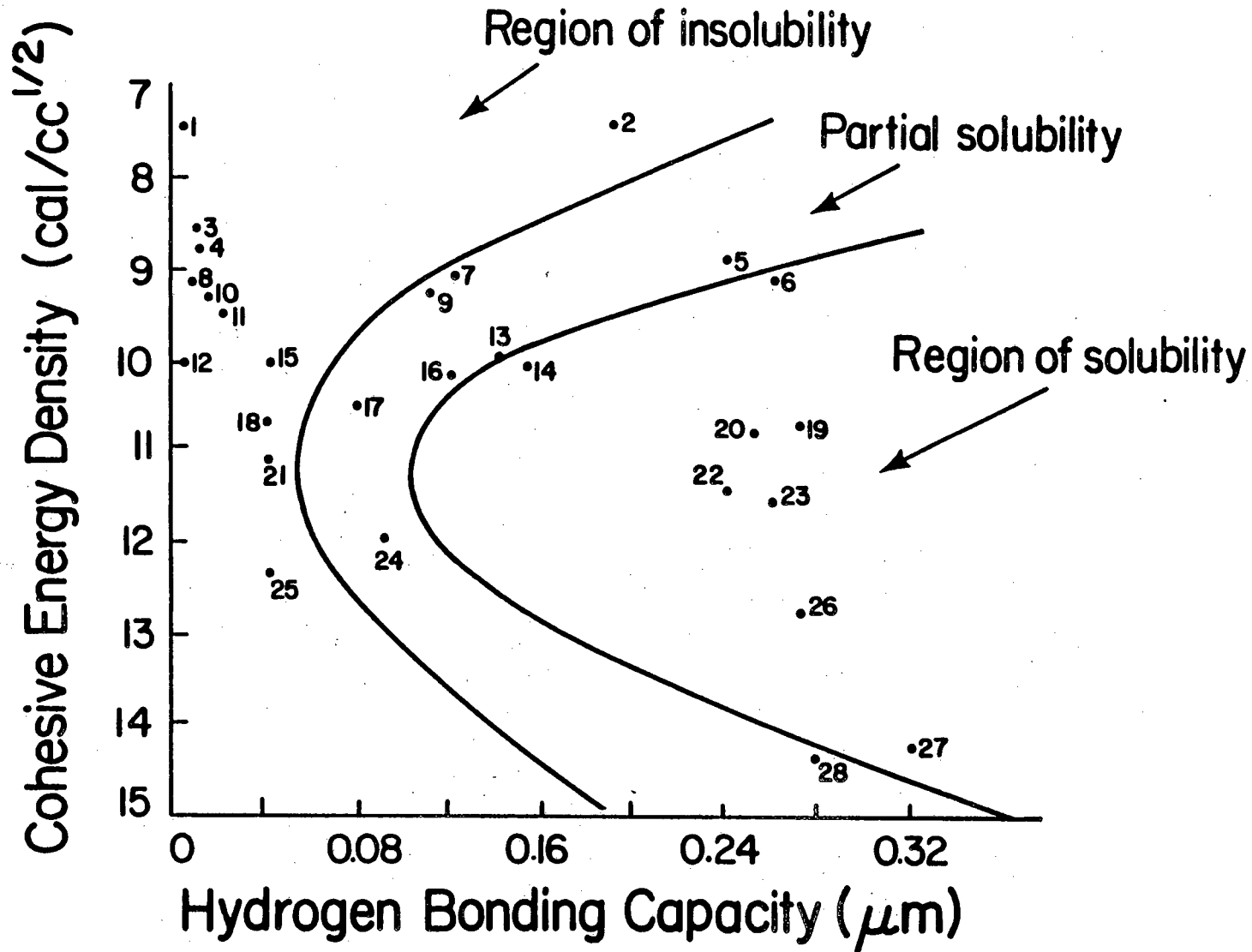
Notes:

Ins : insoluble

Sli : slightly soluble

Par : partially soluble

Sol : soluble



XBL 815-906

Fig. 5. Relation of Kraft Lignin Solubility to Solvent Properties.
(Refs. 106, 107)

Table 6. Solubilities of Pine Lignin at Room Temperature. (Ref. 106)

Solvent System	w% ⁽²⁾	Solubility, mg/ml		
		Milled Wood Lignan	Dioxan Lignin	Soda Lignin
Ether - 1,2-Dichloroethane	0	0.0	0.165	0.050
	20		0.300	0.070
	40	(1)	0.715	0.122
	60		0.340	0.310
	80		0.330	0.174
	100		0.575	0.220
- Dioxan	0	0.0	0.075	0.0
	20	0.055	0.130	0.0
	40	0.085	0.255	0.090
	60	0.185	0.310	0.202
	80	0.255	1.335	0.845
	100	6.25	55.75	2.78
- Acetone	0	0.0	0.112	0.042
	20	0.030	0.285	0.220
	40	0.095	0.460	0.194
	60	0.105	0.580	0.386
	80	0.315	0.615	0.428
	100	1.200	2.405	0.840
- Ethanol	0	0.0	0.0	0.0
	20	0.040	0.195	0.020
	40	0.060	0.395	0.130
	60	0.065	0.615	0.234
	80	0.070	0.715	0.230
	100	0.140	0.805	0.330
1,2-Dichloroethane - Ethanol	0	0.0	0.175	0.336
	20	(1)	1.200	0.690
	40		14.90	1.440
	60		71.50	35.40
	80		58.00	3.780
	100		1.035	0.226
t-Butanol - Acetone	0	0.0	0.090	0.026
	20	0.005	0.315	0.266
	40	0.050	0.738	0.410
	60	0.930	0.910	0.430
	80	1.970	1.280	0.872
	100	1.200	2.405	0.907
- Ethanol	0	0.005	0.090	0.026
	20	0.030	0.160	0.046
	40	0.085	0.150	0.074
	60	0.050	0.245	0.162
	80	0.070	0.400	0.202
	100	0.140	0.865	0.410
- Methanol	0	0.005	0.080	0.026
	20	0.015	0.295	0.080
	40	0.030	0.540	0.130
	60	0.055	0.470	0.186
	80	0.060	0.740	0.382
	100	0.385	1.100	0.338
Dioxan - Water	0	6.26	56.50	0.740
	40	6.45	37.5	-
	85	0.585	0.262	0.106
	90	0.500	0.135	0.094
	95	0.130	0.115	0.154
	100	0.030	0.085	0.046

Notes:

(1) Very soluble.

(2) Percentage of second component.

lignin dissolved in diesel oil was hydrogenated by Rieche and Lindenhayn (112) under high hydrogen pressure (300 atm.) and high temperature (400°C), using oxides and sulfides of iron, copper, molybdenum, or tungsten as catalysts. The yield of monohydroxy phenols ranged from 1 to 38%, along with other products such as guaiacol, anisole, and p-tolymethyl ether. Similar results were obtained by Parker (113) by hydrogenating maple lignin over Raney nickel in 5% sodium hydroxide solution.

Bronovitskii and co-workers (114) hydrogenated lignin in a mixture of recycled phenols over sulfides of cobalt, copper, nickel, and iron. An 80% conversion gave products varying from monomeric hydroxyphenyl propane, cyclohexanol, ethylene glycol, and glycerol, to ethanol and methanol. Dimers, trimers, and polymers of phenyl propane structures were also observed.

San John and Dobrev (115) reported infrared and gas chromatographic data for mixed alkyl phenols and neutral substances obtained by hydrogenation of corncob lignin in anthracene oil with limonite catalyst at 330°C, under hydrogen pressure of 240 atm. for 2 hours. p-Cresol accounted for 54% of the total phenols. Figure 6 depicts solvents derivable from lignin.

(b) Cellulose

Liquid solvents from cellulose, as studied by Harris and co-workers (102), contain hexoses and pentoses, some carboxylic acid, and decomposition products such as hydroxymethylfurfural and other furfurals. Clark (116) discovered that hexose sugars readily hydrogenated to their

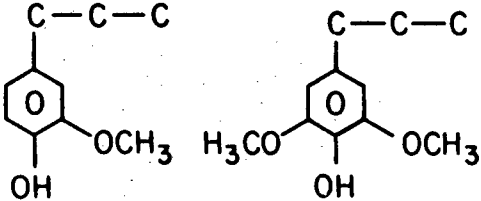
	Example	Boiling Point (°C)	Solubility in Water
Lignin			Insoluble
↓			
Oligomers			
↓			
Phenylpropanes		265-400	
↓			
Substituted phenols and cresols	4-methoxy-2 methyl phenol Cresol, catechol, guaiacol Ethyl phenol	252 210-230	Insoluble
↓			
Phenols	Phenol	182	Soluble
↓			
Cyclohexanols	Methyl cyclohexanol	155	Insoluble
↓			
Cyclohexanes	Cyclohexane	81	Insoluble

Fig. 6. Lignin Depolymerization Products in Reducing Atmosphere.

corresponding sugar alcohols; higher temperature was required for cleavage of the sugar molecules resulting in products like sorbitol, 1,2-propanediol, glycerol, ethylene glycol, and aliphatic alcohols like hexanol, butanol, ethanol, and methanol. Figure 7 depicts the possible products from depolymerization of cellulose.

All of these solvents are quite polar, with large hydrogen-bonding capacities. The solubility parameters of the wood-derived solvents just mentioned vary from a high of 15.7* (ethylene glycol) and 14.5* (phenol) to a low of 10.4* (butanol) making them possibly good solvents for lignin.

3. Selection of Process Conditions

After identifying the solvents potentially feasible to solubilize wood, it was decided to devise liquefaction process conditions under which to examine the solvents' capability to liquefy wood.

(a) Solvent Medium

A mixture of two solvents was envisioned: alcohol to solubilize lignin, and aqueous acid to hydrolyze cellulose. Preferably these two solvents should be completely miscible. Immiscibility of the organic and aqueous solvents would tend to retard the solubilization of both lignin and cellulose, even though it might facilitate recovery of the alcohols for process recycle.

* King, C. J., "Separation Processes," p. 738, Table 14-7, McGraw-Hill, New York, 1970.

	Example	Boiling Point (°C)	Solubility In Water
Cellulose			
↓			
Oligomers			Insoluble
↓			
Sugars	Glucose	—	Soluble
↓			
Polyalcohols	Sorbitol	295 (@ 3.5 mm Hg)	Soluble
↓			
	Glycerol	290	v. Soluble
↓			
Alcohols	Propanol	98	v. Soluble
↓			
	Ethanol	79	v. Soluble
↓			
Alkanes			

Fig. 7. Cellulose Depolymerization Products in Reducing Atmosphere.

These considerations suggested the use of a half-and-half mixture (by volume) of alcohol and water at a fairly low pH. Possible acidifiers were sulfuric acid, and carboxylic acids such as acetic, formic, or glucuronic acid. Emphasis was given to using organic acids because they are, like alcohols used, derivable from wood.

(b) Process Temperature

Typical Kraft process or Sulphite process (33,117) delignification ("pulping") is carried out at temperatures from 160°C to 200°C for times of 2 to 5 hours. Alcoholic delignifications (95-97) reactions investigated entail similar process conditions. Pepper and Steck (118), in hydrogenation of aspen lignin, found that 195°C for 5 hours resulted in the best yield (~50%) of phenols and phenolic derivatives. In addition, cellulose hydrolysis takes place at 120°C to 200°C. Thus, a median temperature of 180°C could serve conveniently as a base temperature to be studied. The Albany PDU (PERC Process) uses 325°C to 360°C, and other hydrogenation researchers (20,85,119) have often used temperature over 300°C, because high temperature serves to break carbon-oxygen and carbon-carbon bonds. However, in this investigation, bond scission should be greatly enhanced by alcoholysis and hydrolysis. Hence, a temperature of 300°C or higher was not believed necessary, and 250°C was picked as the highest temperature to be investigated.

(c) Reaction Time

Delignification typically requires 2 to 5 hours, depending on temperature. Cellulose hydrolysis is much faster, needing less than 30 minutes above 180°C and about an hour below 120°C. Hydrogenation

and hydrogenolysis have residence times varying from 1 to 24 hours. For an economical process, long residence times appear prohibitive, and it was concluded that a reaction time of 1 hour would be sufficient to establish solvent suitability and system performance.

(d) Reducing Gas and Catalyst

Reducing gas in the form of carbon monoxide and hydrogen has been utilized in the high-temperature PERC process and in lignin hydrogenation, where these gases are believed to act as capping agents to stabilize depolymerized species. On the other hand, reducing gas was never used in alcoholysis or other solvent delignification, or in cellulose hydrolysis. To be able to compare our results with those at the PDU or in LBL's bench-scale development unit, it was decided to use 400 psig of synthesis gas (1:1 carbon monoxide and hydrogen) in the present study. Since no reducing gas usage was anticipated, most of our runs would be made without added catalysts.

CHAPTER IV

EXPERIMENTSA. Raw Materials1. Wood Procurement and Analysis

The raw feed used in this investigation was wood flour of a soft-wood species, Douglas Fir, shipped to this laboratory from DOE's Albany PDU. The Albany PDU procures wood chips from a nearby paper mill, dries them, and grinds them to approximately 65 mesh. They are then further dried to a moisture of 4%, stored, and shipped in barrels. Upon arrival at this Laboratory, the wood flour was allowed to equilibrate with room temperature air, which raised its moisture content to about 10%, and was used as-is.

Douglas Fir has roughly 40% cellulose and 30% each of hemicellulose and lignin (Table 2). It contains about 1% of organic extractives and 0.5% inorganic ash. Sulfur and nitrogen are approximately 0.05% and 0.13%, respectively.

2. Other Reagents

In addition to wood flour, the other reactants used were butanol, ethylene glycol, cyclohexanol, and phenol, as well as methanol, ethanol, glycerols, catechols, etc., all of reagent-grade quality.

Along with alcohols, small amounts of acids were used to catalyze the solubilization. They were sulfuric, hydrochloric, acetic, and formic acids. Among inorganic acids, sulfuric acid was utilized extensively and was generally preferred because of its relative low hazard.

Other reagents such as zinc chloride, ferric chloride, α -phallendrene, and cyclohexadiene were also used in some of the experimental runs in conjunction with either an aqueous system or an alcoholic system.

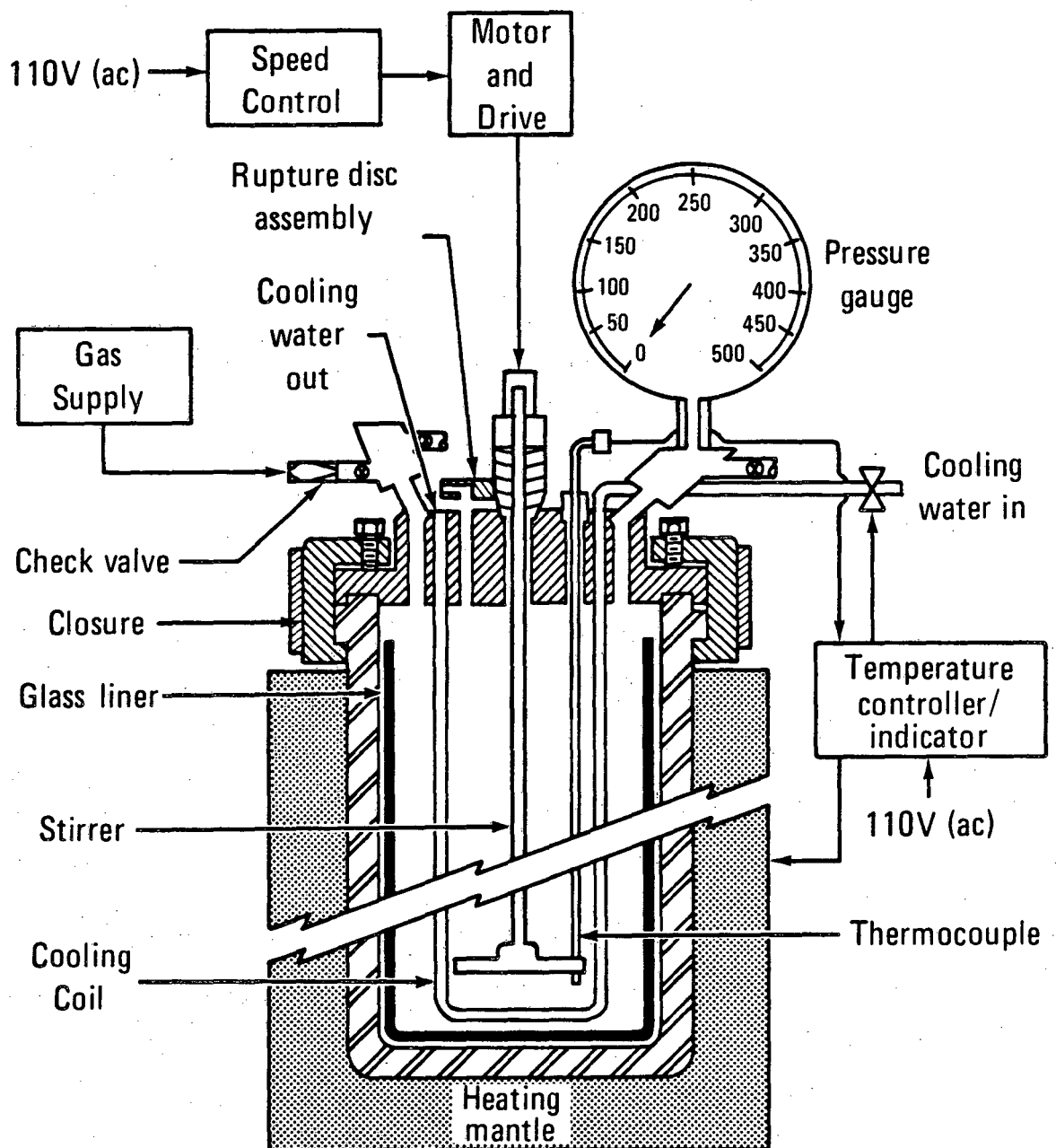
B. Experimental Apparatus

1. Parr Autoclave

Most of the experiments were performed in a 300 ml Parr autoclave reactor manufactured by Parr Instrument Company in Moline, Illinois. A picture of the Parr reactor is shown in Fig. 8.

The reactor was made entirely of type 316 stainless steel. Heating was achieved by an external electrical heater. The reactor was fitted with inlet and outlet gas lines which allowed gas to be charged and discharged. Reactants, in this case wood flour, acid, and alcohol, were weighed consecutively into a glass liner which was designed to fit snugly the interior of the reactor. Stirring of the reactants was provided by a mechanical stirrer on a vertical shaft propelled by a dc motor. During stirring, cooling water was used to cool the packing glands for this shaft; it proved necessary to replace the packing after every 10-15 runs, depending on severity of the experiments.

Temperature control was provided by a thermocouple, temperature controller, and cooling water supply. A deviation from set-point temperature in the reactor, sensed by the thermocouple and relayed to the controller, would either activate the heater or the cooling-water flow. Temperature control of $\pm 2^\circ\text{C}$ was achieved through this mode of operation.



XBL809-1877

Fig. 8. The 350-ml Parr Autoclave Reactor.

2. Other Apparatus

Other major equipment used include pyrex glass soxhlet extractors, a Büchi rotary evaporator, two vacuum ovens, and a vacuum distillation unit for solvent recovery study.

C. Experimental Procedure

The procedure described below was used in most of the experiments. Wood flour, as is, was weighed into the reactor glass liner. Process solvent in the ratio of 4 gm solvent/1 gm wood was next weighed into the liner. A predetermined small amount of sulfuric acid was then transferred into the liner through a disposable pipette. Weighings were done with an accuracy of ± 0.005 gram.

The loaded glass liner was lowered carefully into the Parr auto-clave reactor, which was then bolted shut with high-pressure screws. Approximately 1000 psig of nitrogen was charged into the reactor for a leak test. If the reactor proved leak-free, the nitrogen charge was bled off, and replaced several times with fresh nitrogen with intervening bleed-off to provide virtually complete removal of air from the reactor. After the last bleed, atmospheric-pressure nitrogen remained in the reactor.

The heater was heated red hot prior to lowering the reactor in the heater, in order to insure a minimum heating time. This point was counted as time zero and a stopclock was started. Temperature and pressure were monitored every two minutes until reaction temperature was reached, and every five minutes at reaction conditions. It took roughly 40 minutes to get up to 250°C. A temperature change of 4°C,

i.e. $\pm 2^{\circ}\text{C}$ at reaction temperature of 250°C could bring about a pressure change of up to 80 psig depending on the solvents used; this pressure fluctuation occasionally made data-taking rather difficult.

Once a predetermined reaction time was completed, the reactor was removed from the heater. The cooling water was turned on to give a maximum water through the internal cooling loop. Simultaneously, a bucket of cold water was also raised around the reactor to immerse it. This combination cooling was extremely effective, so that a typical time to cool from 250°C to 50°C was 2.5 to 3 minutes. During cooling the pressure dropped rapidly to a level slightly higher than atmospheric; the residual gas in the reactor was usually vented, but in some cases, was collected in pre-evacuated gas sampling cylinders.

The reactor was opened and its entire contents were poured into a numbered, dried, and pre-weighed thimble placed in a beaker. The remaining unpoured material in the glass liner was carefully scraped into the thimble with a stainless steel laboratory scrapper; using this method, material balances of 95-plus percent were usually achieved. The liquid, both alcohol and converted wood, was allowed to pass through the thimble into the beaker. This process took 2 hours or longer (in some cases, five hours) depending on the viscosity of the fluid. The collected liquid was then evaporated under vacuum so as to recover and measure the soluble fraction of wood-derived material. The remaining gluey solid or unconverted wood in the thimble was subjected to acetone extraction in a soxhlet extractor, overnight or until the wash acetone was entirely colorless. The

thimble was then removed from the extractor, placed into a clean beaker, and dried in a vacuum oven maintained at 2 torr and 110°C temperature. After 24 hours the thimble was weighed, replaced in the vacuum oven for another 24 hours, then weighed again. If the weights agreed to within the accuracy of the balance, the drying process was terminated. A sample (~0.5g) of the residue was sent for elemental analysis, and the remainder was stored in a vacuum dessicator.

The acetone wash together with extracted material was placed in a vacuum evaporator. The acetone was evaporated, condensed, and collected under a steady stream of nitrogen, and the recovered acetone soluble fraction was weighed. In some runs both the solvent-soluble and acetone-soluble materials were subjected to toluene soxhlet extraction. The percent acetone insolubles were used primarily as a solubility indicator to evaluate the process effectiveness at various process conditions. In retrospect, the wood was converted into solvent and acetone solubles, acetone insoluble (residue or unconverted wood), plus a small quantity of gas which was later determined to be predominantly carbon dioxide.

D. Chemical Analysis

1. Elemental Analysis

In most cases, the recovered soluble fractions and the insoluble wood were sent for elemental analyses which were performed by Mr. V. T. Tashinian and Ms. D. James of the University of California's Micro-Analytical Laboratory. The carbon and hydrogen analyses were carried out via the Perkin-Elmer Model 240 automated elemental

analyzer. Inorganic ash was obtained by weight difference before and after combusting the sample at 800°C. In some experiments involving use of inorganic catalysts such as zinc and ferric chlorides, both zinc and iron were analyzed after sample digestion in a mixture of sulfuric acid and hydrogen peroxide via the Perkin-Elmer Model-360 atomic adsorption units.

2. Solvent Incorporation

In solvent incorporation study, unincorporated solvent was recovered via vacuum distillation. The various collected liquid samples during distillation were analysed for the process solvent used, and for water. Knowing the amount of solvent (on a dry basis) both initially and after the reaction enabled one to calculate the amount incorporated by difference. The alcohol and water analyses were performed on a Model-920 Varian Gas Chromatograph equipped with a 1/4" x 7' column packed with Porapak Q and using a thermoconductivity detector. Helium flow rate was set at 60 ml/min., with filament current at 150 mA. For analysis, 2-microliter samples were injected into the injector port which was set at a temperature of 220°C depending on the solvents involved. A thermal conductivity detector was used to measure alcohol and water. Standards of known concentration of alcohol in water and vice versa were injected routinely to calibrate the instrument, results being in the form of peaks recorded on a Model 9176 Varian chart recorder.

3. Gas Analysis

Gases collected were analysed on a Carle Analytical Gas Chromatograph equipped with dual columns, one specifically for

hydrogen analysis. The column temperature and the filament current were set at 75°C and 200 mA, respectively. One-microliter samples were injected through a fixed-volume sample-injection loop to insure maximum reproducibility. Carrier gases were helium and nitrogen, and their flow rates were set at 60 and 40 ml/min. respectively. The GC results were obtained as peaks recorded on a Model 023 Varian Integrator. A standard gas which contained 29.02% hydrogen, 24.2% carbon monoxide, 3.34% carbon dioxide, 5.01% methane, 4.89% ethylene, 1.71% propane, 4.93% propylene, and the rest helium was used to calibrate the result obtained.

4. Klason Lignin Test

In some experiments the resultant insoluble or unconverted material obtained was subjected to lignin determination. In the test, concentrated sulfuric acid is used to dissolve the carbohydrates, and the lignin is measured as residue.

A dry sample of one gram was weighed and placed into a beaker along with 15 ml of 72% sulfuric acid added with stirring. The mixture was allowed to stand for two hours in a water bath at 18-20°C, with frequent stirring. It was then washed into a 1-liter beaker or flask, water (~550 ml) was added for dilution to 3% sulfuric acid concentration, and the solution was boiled for four hours under reflux.

The insoluble lignin component was allowed to settle, and the mixture was then filtered through a dry filtering crucible. The lignin retained in the crucible was washed free of acid with about 200 ml of hot water. The crucible and contents were then dried in a

vacuum oven overnight and weighed; drying and weighing were repeated until the weight was constant. Insoluble content (lignin) was expressed as weight percent of the initial dry sample.

E. Additional Analysis

1. Scanning Electron Microscopy (SEM)

For several experiments, the insoluble materials were subjected to SEM to examine their structure. The technique was also applied to untreated wood. The sample was sprinkled onto a special SEM mount, and subsequently sputter-coated with gold to render it conductive. The surface was then examined in the AMR 1000 Scanning Electron Microscope located in the Materials and Molecular Research Division of the Lawrence Berkeley Laboratory. Usually several magnification shots per sample, from low to high, were taken.

2. Gel Permeation Chromatography (GPC)

Products obtained from the four selected process solvents were analysed by GPC for their molecular-weight distribution. Each sample for GPC analysis was dissolved as a 5% solution in tetrahydrofuran (THF), and filtered through 0.45 μm Millipore filters. About 5 to 10 μl of sample was injected into the Perkin Elmer Series-2 High Pressure Liquid Chromatograph equipped with a Varian GPC column suitable for molecular weight ranges from 100 or less to 2000 or more. THF was used as eluting solvent at a flow rate of 0.8 ml/min., and the eluate was monitored by UV absorbance at 245 nm. Dimethoxy phenyl propanol (MW=196) and polystyrene (1% solution) were used as standards.

CHAPTER V

RESULTS AND DISCUSSIONSA. Preliminary Process Feasibility

The effectiveness of the solvent mixtures for solvolysis, measured as product acetone solubles, can be seen in Table 7. These results can be compared with Seth's for solubilizing wood by hydrogenation under similar reaction conditions (Table 8). Solvolysis showed some advantages over hydrogenation. The difference in performance was particularly pronounced in the phenol-water system, with even the unacidified water (RP 2 and 5) surpassing the performance of the hydrotreating medium. Ferric and zinc chlorides were used as acidification agents in RP 12, 17, and 29, with the amounts of wood solubilized comparable to those when sulfuric acid was the catalyst. In all cases considered (except for phenol), the insoluble residue was never below 20%.

In order to probe the nature of the insoluble residue, the Klason lignin test was performed on residues from runs RP 2 and RP 3; lignin was the major component (>80%). The finding suggests that the aqueous systems do not depolymerize the lignin. In terms of the structure of wood cells (Fig. 3a,b), lignin is the glueing agent that glues the fibrous cellulose together. Since penetration of process liquid into the fibrous elements should be greatly enhanced if this gluey lignin layer is first dissolved, it is surprising that considerable carbohydrate, but not much lignin, was dissolved in the treatment.

Table 7. Solubilities of Wood in Alcohol and Acidified-Water Mixtures With and Without Additives.

Expt. #	Solvent	Acetone Insolubles (%)
RP 8	Methanol*	47.81
4	Methanol	27.82
7	Ethanol*	39.25
3	Ethanol	25.30
11	Phenol	4.18
2	Water	42.64
5	Water**	45.73
12	10% FeCl ₃ /Ethanol***	34.23
17	5% FeCl ₃ /Ethanol***	28.10
29	5% ZnCl ₂ /Methanol***	24.67

Process Conditions:

- Solvent = 50/50 : alcohol/water (pH = 2.5)
- Solvent/wood = 4/1
- 400 initial psig CO/H₂ (1:1)
- 250°C, 1 hr.

Notes:

- * pH = 2.0, 180°C, 1 hr.
- ** pH \cong 7.0
- *** Acid salts used instead of H₂SO₄

Table 8. Conversions of Wood Treated with Inorganic Salts and Hydrogen Donor Solvent. (Ref. 120)

Inorganic Salts	Acetone Insolubles (%)
Molybdic Acid	63.3
Zinc Chloride	56.2
Antimony Tribromide	63.1
Nickel Chloride	47.7
Ferric Chloride	39.7
Ferric Chloride*	48.9
Sodium Carbonate*	48.0
Copper Chromite	57.7
Ferric Sulfate	56.0
None	49.8

Process Conditions:

- Wood = 12g
- Tetralin = 48g
- Water = 19g
- Acid salt = 1g
- 200 initial psig hydrogen
- 250° C, 1 hr.

Note:

* Under carbon monoxide instead of hydrogen

An experiment using conditions similar to those of RP 3 was conducted in an one-liter autoclave reactor, and produced sufficient insoluble material for further testing. Two experiments were performed to provide more information about the residue. First, the Kraft pulping reaction was carried out, in which 15 grams of residue was digested in 2.5 grams of 1.1 N NaOH and 1.5 grams of sodium sulfide at 180°C for 3 hours. Second, another portion of the residue was subjected to the lignin alcoholysis reaction, using butanol and 0.2% HCl at 160°C for 3 hours. In both tests, considerable residue (up to 90%) remained undissolved, indicating a more inert lignin-like material. This finding suggests that lignin either dissolves and then repolymerizes, or undergoes irreversible crosslinking during the treatment. From a process standpoint, it is important to investigate ways to maximize solubilization or minimize insoluble residue. Lowering the temperature, shortening the residence time, or introducing synthesis gas at different pressures, might work in this direction. Finally, the possibility of using wood chips, or preferably moist chips, instead of dry wood flour (65 mesh) appeared to need investigation.

The results cited showed that an acidified medium of alcohol (or phenol) and water is able to solubilize more than 50% of the wood and thus tend to validate the proposed process concept.

B. Solvent Selection Study

To identify solvents that could best solubilize wood, a list of wood-derivable solvents was drawn up through a literature study. Experiments were performed with these solvents to evaluate their

effectiveness in wood solubilization under the same reaction conditions as in the feasibility study. In addition to sulfuric acid, acetic and formic acids were also used.

Table 9 shows the experimental results. They reveal that mixtures of water and hydroxy-organics such as cyclohexanol, phenol, cresol, or catechol are good solvents for wood. The percent insoluble varied from 6.6% in cyclohexanol to as low as 1.02% in catechol. Generally, the aliphatic alcohols (cellulose-derivable) did not achieve as much solubilization as the lignin-derivable phenols or alcohols.

That neutral water (RP 5) alone was able to solubilize more than 50% wood prompted a look at alcohol-water mixtures with no added acid (Table 10). The results clearly indicated that solvents without acid have a greatly reduced capacity for solubilization. Organic acids such as acetic and formic were then tested as substitutes for sulfuric acid. Owing to their weaker acidity, about 20 times as much was used to achieve the required pH, and the experimental results (Table 11) demonstrate that organic acids were just as good as sulfuric acid. However, because of the much larger amount needed, it was then decided to stay with sulfuric acid.

For selected runs, the gas chromatograms showed that the reactor gas compositions before and after reaction were nearly identical, except for a very small amount of carbon dioxide (about 1% of the mixture) in the off gas. Thus, it appears that the synthesis gas did not participate in the solvolysis, a welcome but not surprising result. (One would not expect synthesis gas to react at 250°C without a

Table 9. Solubilities of Wood in Selected Alcohol and Acidified-Water Mixtures.

Expt. #	Solvent	Acetone Insolubles (%)
	Cellulose-derivable:	
RP 8	Methanol*	47.81
4	Methanol	27.82
7	Ethanol*	39.25
3	Ethanol	25.30
25T	Ethanol**	50.08
21	Propanol	19.43
23	Butanol	16.52
34	Pentanol	18.77
35	Hexanol	13.80
19	Ethylene glycol	15.29
20	Glycerol	26.67
	Lignin-derivable:	
30	Cyclohexanol	6.60
11	Phenol	4.18
22	Catechol	1.02
31	Cresol	4.33
32	Guaiacol	4.78
2	Water	42.64
28	Water***	45.73

Process Condition:

- solvent = 50/50 : alcohol/water (pH = 2.5)
- solvent/wood = 4/1
- gas = 400 initial psig CO/H₂ (1:1)
- 250°C, 1 hr.

* pH = 2.0, 180°C

** 300°C

*** pH \cong 7.0

Table 10. Solubilities of Wood in Alcohol-Water Mixtures.

Expt. #	Solvent	Acetone Insolubles (%)
RP 30 NA	Cyclohexanol	83.82
11 NA	Phenol	68.27
32 NA	Guaiacol	74.25

Process Conditions:

- Solvent = 50/50 : alcohol/water
- Solvent/wood = 4/1
- 400 initial psig CO/H₂ (1:1)
- 250° C, 1 hr.

Table 11. Effects of Organic Acids Versus Sulfuric Acid Additives on Wood Solubility.

Expt. #	Acid - Solvent	Acetone Insolubles (%)
RP 23A	Acetic - Butanol	21.73
35A	Formic - Hexanol	17.25
11A	Acetic - Phenol	9.00
19A	Formic - Ethylene Glycol	19.62
23	Sulfuric - Butanol	16.52
35	Sulfuric - Hexanol	13.80
11	Sulfuric - Phenol	4.18
19	Sulfuric - Ethylene Glycol	15.19

Process Conditions:

- Solvent = 50/50 : alcohol/water (pH = 2.5)
- Solvent/wood = 4/1
- 400 initial psig CO/H₂ (1:1)
- 250° C, 1 hr.

catalyst.) In order to verify the non-participation of synthesis gas, several experiments were repeated using 400 psig of nitrogen with the same conversions (Table 12). The results prompted us to use 15 psia of nitrogen in all subsequent experiments.

The batch reactor's long heat-up time was always a concern in these runs. Characteristically, it took 40 minutes to heat to 250°C, about two-thirds of the time at reaction temperature. Besides long heat-up, water also imposes stricter pressure specifications on equipment because of its high vapor pressure. In an effort to improve the situation, it was decided to try pure alcohols as process solvents because of their lower heat capacity (and usually lower vapor pressure). Sulfuric acid was again added, in an amount comparable to that for the alcohol-water runs. These systems took an average of only 25 minutes to reach 250°C. Moreover, on the basis of insolubles, the pure alcohols achieved better solubilization (Table 13) than alcohol-water mixtures.

Based on the experiments reported so far, four alcohols (or hydroxyorganics) were chosen for further study: two cellulose-derivable, butanol and ethylene glycol; and two lignin-derivable, cyclohexanol and phenol.

C. Effects of Process Parameters

1. Temperature

Figures 9 through 12 are plots of percent unconverted (residual insoluble wood) versus reaction temperature, from 120° to 300°C, for phenol and three alcohols. Experimental conditions and numerical data are listed in Tables 14 through 17.

Table 12. Solubilities of Wood in Alcohol-Water Mixtures Under Inert Atmosphere.

Expt. #	Solvent	Acetone Insolubles (%)
RP 23N	Butanol	20.33
23	Butanol*	16.52
35N	Hexanol	12.67
35	Hexanol*	13.80
11N	Phenol	2.37
11	Phenol*	4.18
11N1	Phenol**	5.76

Process Conditions:

- Solvent = 50/50 : alcohol/water (pH = 2.5)
- Solvent/wood = 4/1.
- 400 initial psig N₂
- 250° C, 1 hr.

Notes:

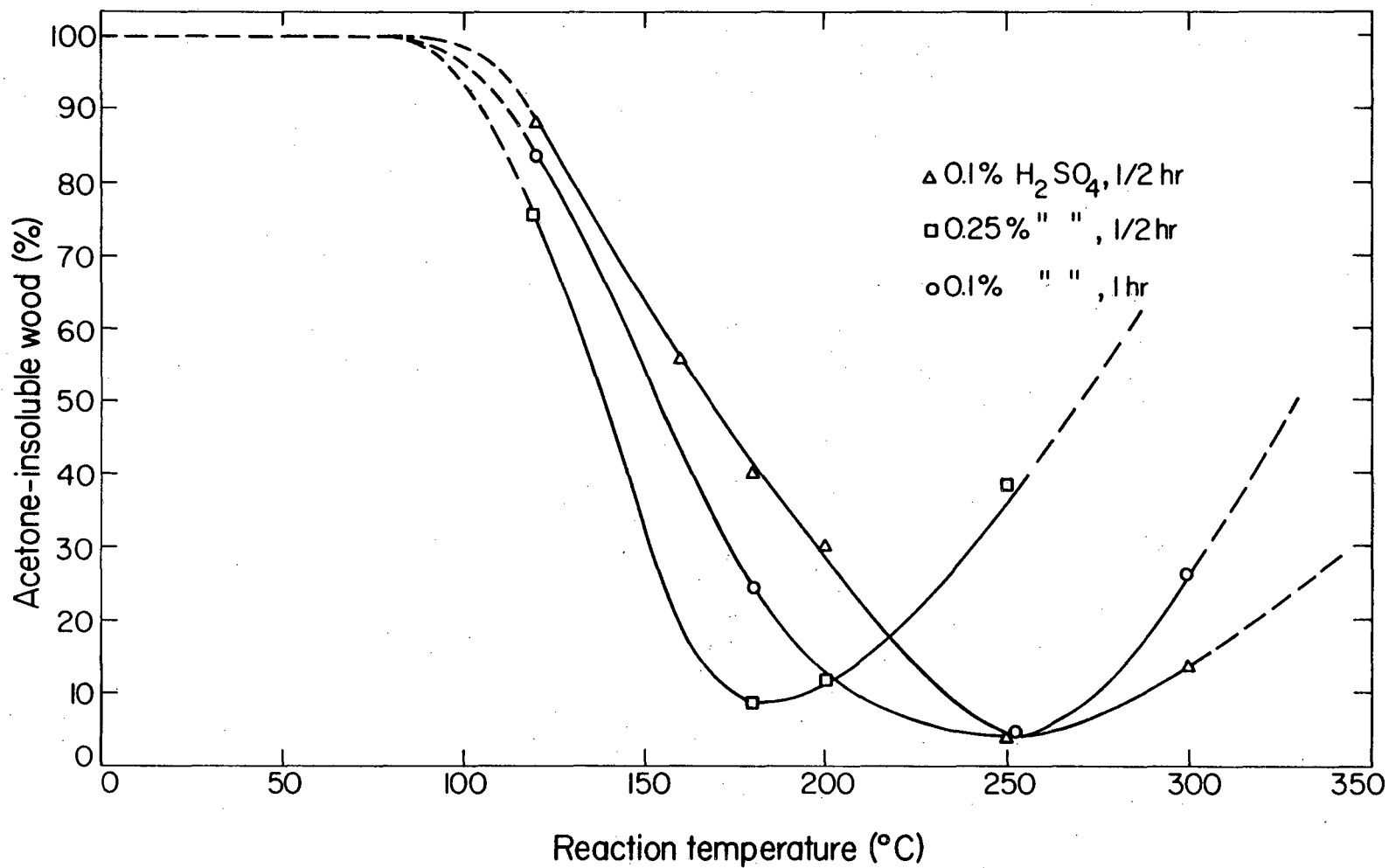
- * 400 initial psig CO/H₂ (1:1)
- ** ~ 15 psia N₂

Table 13. Solubilities of Wood in Alcohols with Small Amount of Sulfuric Acid.

Expt. #	Solvent	Acetone Insolubles (%)
RP 50	Butanol	16.92
51	Hexanol	8.70
191	Phenol	1.35
156	Cyclohexanol	4.32
208	Ethylene Glycol	3.99

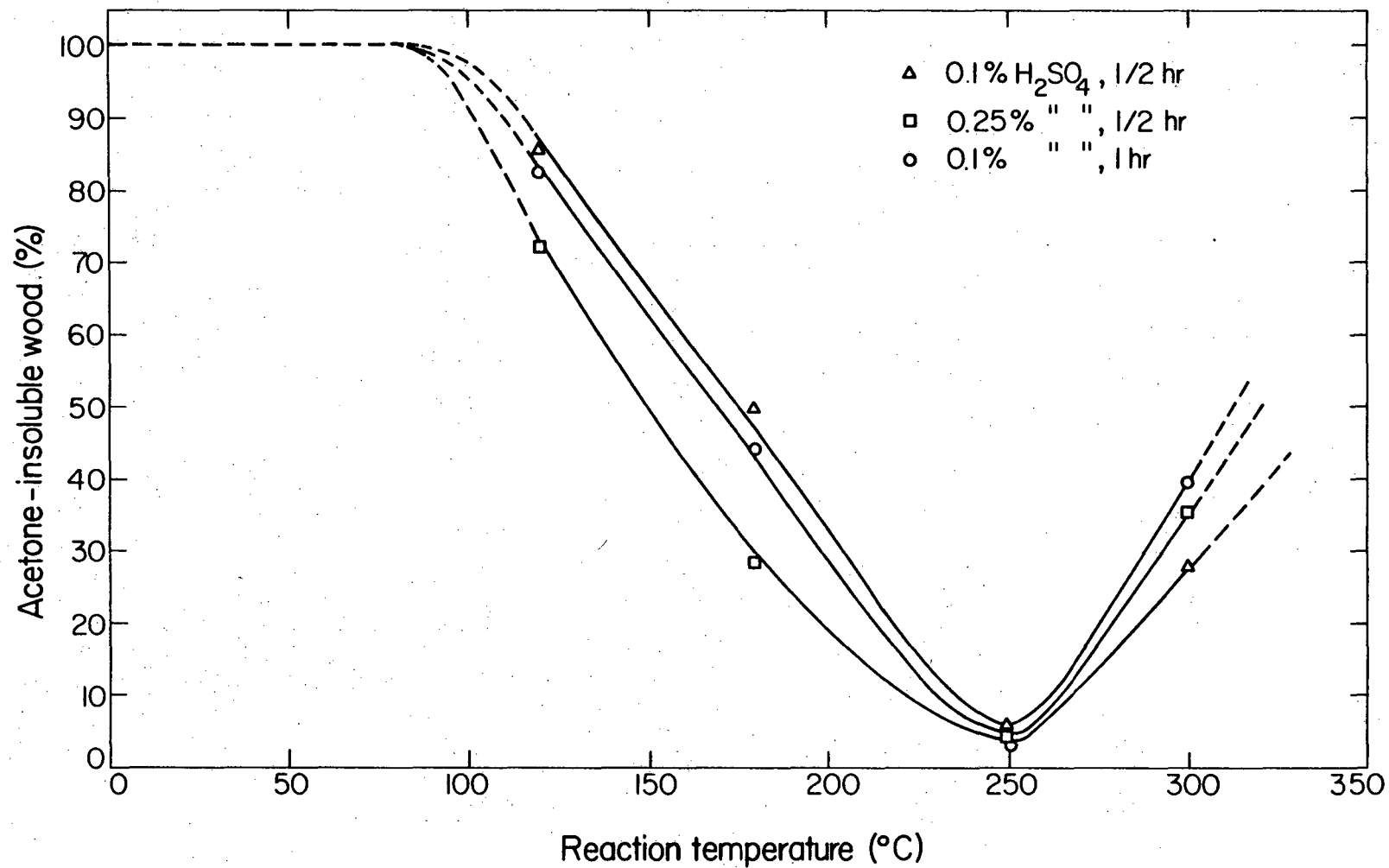
Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂
- 0.1 wt-% H₂SO₄ in Solvent
- 250° C, 1 hr.



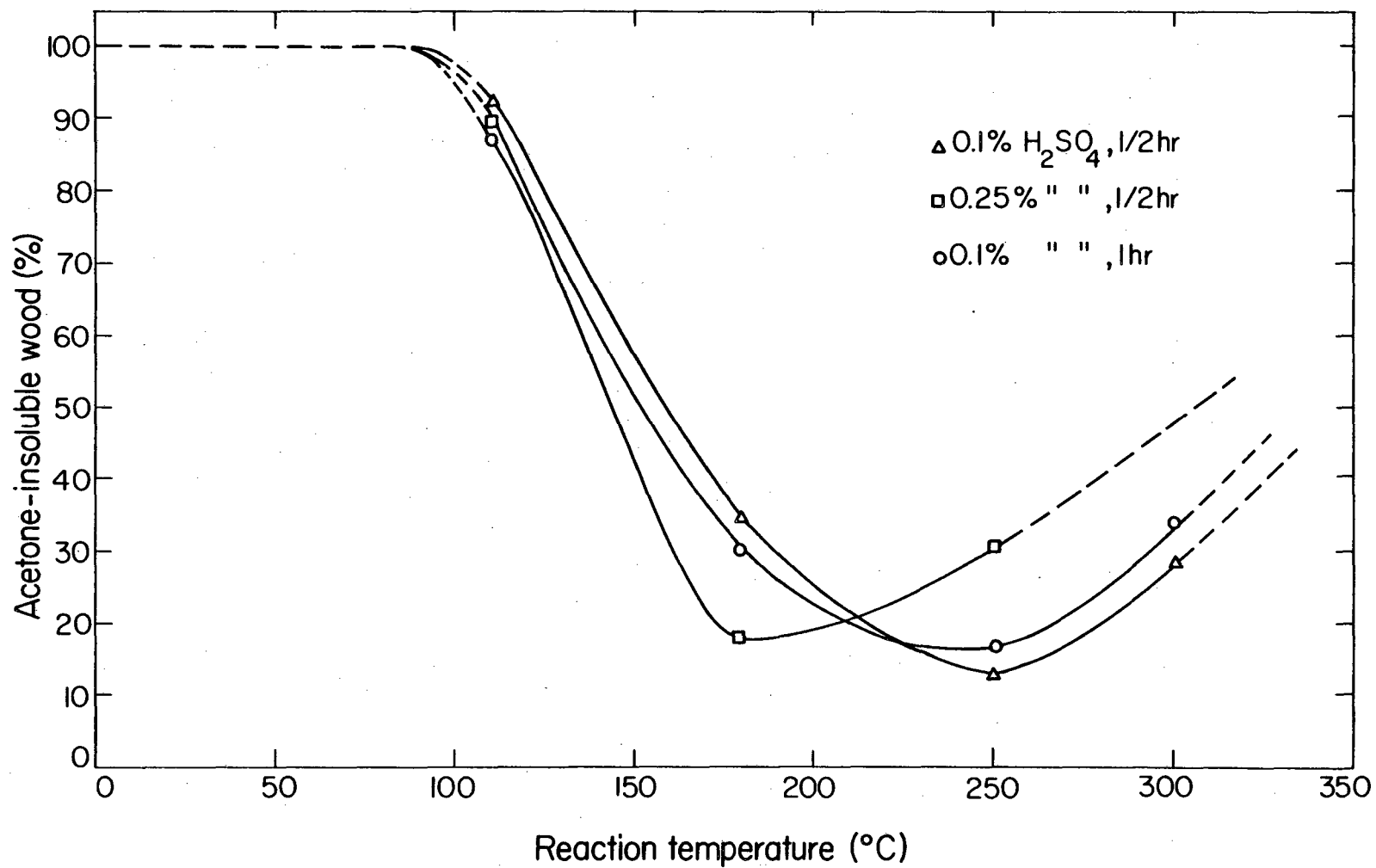
XBL 816-992

Fig. 9. Solubilities of Wood Versus Reaction Temperatures in Butanol.



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Fig. 10. Solubilities of Wood Versus Reaction Temperatures in Ethylene Glycol.



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Fig. 11. Solubilities of Wood Versus Reaction Temperatures in Cyclohexanol.

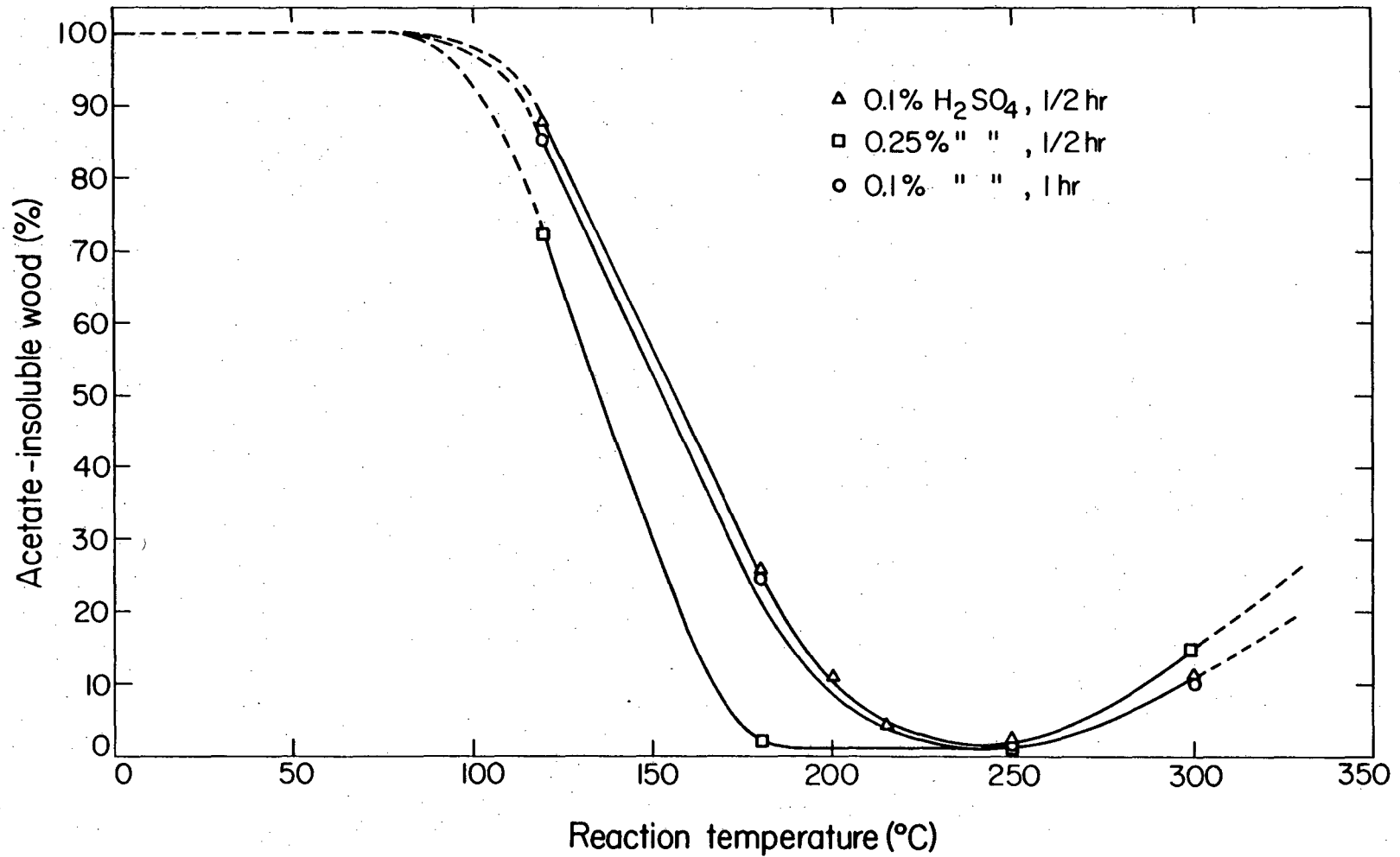


Fig. 12. Solubilities of Wood Versus Reaction Temperatures in Phenol.

Table 14: Wood Solvolysis in Butanol; Temperature Effect

Expt. #	Acid Conc. (%)	Time (hr.)	Temp. (°C)	Acetone Insolubles (%)
RP 230 44 56 65	0.1	0.5	120 180 250 300	92.50 34.50 13.19 32.09
RP 232 54 50 231	0.1	1	120 180 250 300	84.52 30.20 16.92 30.50
RP 47 49 57	0.25	0.5	120 180 250	89.70 18.17 30.18

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

Table 15: Wood Solvolysis in Ethylene Glycol; Temperature Effect

Expt. #	Acid Conc. (%)	Time (hr.)	Temp. (°C)	Acetone Insolubles (%)
RP 237 76 82 236	0.1	0.5	120 180 250 300	85.50 49.58 5.49 27.52
RP 235 243 208 236	0.1	1	120 180 250 300	82.63 44.00 3.99 39.43
RP 88 75 77 244	0.25	0.5	120 180 250 300	72.25 28.79 3.52 35.04

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

Table 16: Wood Solvolysis in Cyclohexanol; Temperature Effect

Expt. #	Acid Conc. (%)	Time (hr.)	Temp. (°C)	Acetone Insolubles (%)
RP 249 55 101 229	0.1	0.5	120 180 250 300	88.12 34.92 3.52 13.60
RP 255 89 156 248	0.1	1	120 180 250 300	83.00 24.47 4.32 26.28
RP 71 48 114 80 74	0.25	0.5	120 180 180 200 250	75.41 8.06 8.91 11.79 38.47

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

Table 17: Wood Solvolysis in Phenol; Temperature Effect

Expt. #	Acid Conc. (%)	Time (hr.)	Temp. (°C)	Acetone Insolubles (%)
RP 102	0.1	0.5	120	87.50
70			180	26.20
94			200	12.97
RK 9			215	3.88
RP 102			250	1.25
241			300	11.08
RP 98	0.25	0.5	120	72.48
69			180	1.90
96			250	1.17
240			300	14.93
RP 250	0.1	1	120	85.00
186			180	25.34
191			250	1.35
242			300	11.10

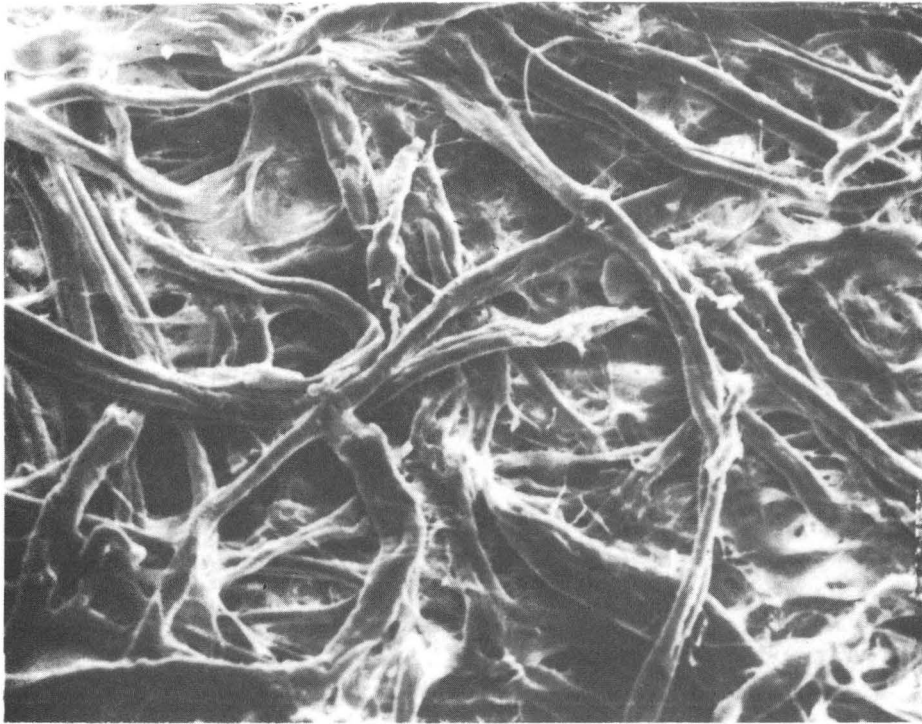
Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

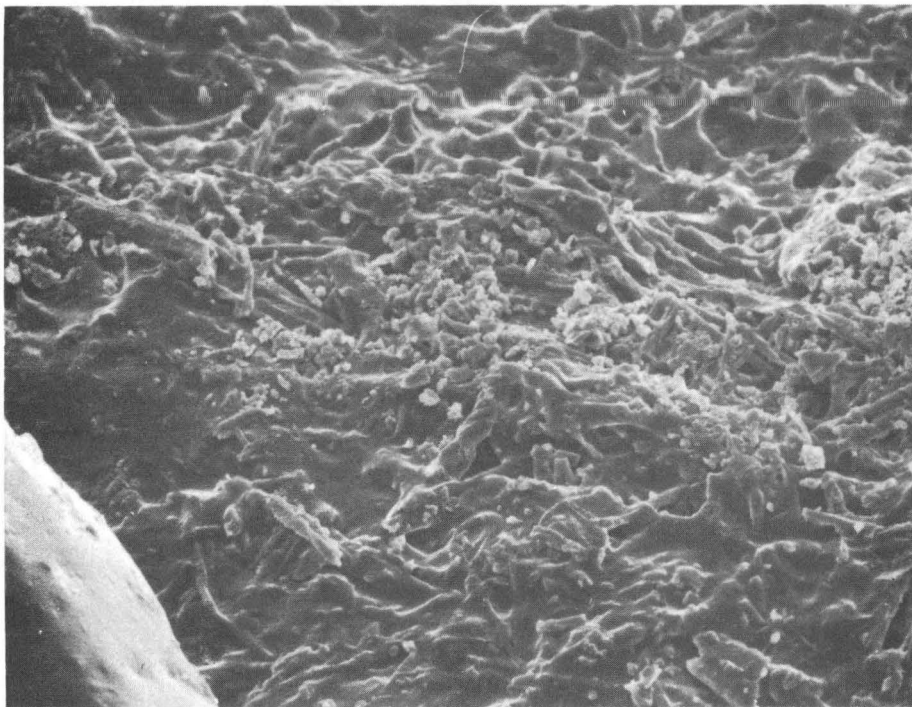
All four curves show a maximum wood solubilization at an intermediate temperature. For example, for the 0.1% acid runs, the optimum temperature is 250°C. Except for ethylene glycol, 0.25% acid requires a lower temperature, 180°C, for an equally good conversion. Thus, for good solubilization, a lower temperature requires a higher acid concentration, and vice versa.

Rapid solubilization commences above 120°C, and ceases in the range of 180° to 250°C. Above 250° to 300°C, the solubility always decreases, indicating repolymerization of the previously depolymerized wood. Higher acid concentration (0.25%) promotes the repolymerizations more effectively than lower (0.1%).

The repolymerized material was black and charred in appearance, and did not resemble any material previously obtained. In order to collect enough of this material for further testing, a one-liter autoclave run using the conditions of RP 65 was made. The resulting solid was subjected to solvolysis using phenol at condition of 0.1% acid, 250°C, and 0.5 hour. Only 20% solubility was obtained, demonstrating the dissimilarity between this solid and the wood feed. Under the scanning electron microscope, the repolymerized material appeared porous (Fig. 13), with small holes covering the entire surface. Subjecting the material to the Klason lignin test, none was dissolved, indicating the absence of carbohydrates. Elemental analyses showed O/C and H/C at 0.42 and 1.21, respectively, for the material indicating its similarity to lignin which have O/C and H/C of 0.4 and 1.4. An attempt to determine its molecular weight by gel permeation



(a)



(b)

XBB 823-1770

Fig. 13. Scanning Electron Micrograph of (a) Untreated Wood Flour (5KX), (b) Repolymerized Product (5KX).

chromatography failed, due to its insolubility in as polar a solvent as tetrahydrofuran. Clearly, from a process point of view, the repolymerization should be avoided.

2. Acid Concentration

Figures 14 through 17 show plots of percent unconverted wood versus amounts of acid used for runs employing acid concentrations ranging from 0.01 to 0.75 weight-% in solvent. Experimental conditions and numerical data are listed in Tables 18 through 21.

At each temperature, except for phenol runs, the curves indicate optimum acid concentrations corresponding to maximum solubilization. For good conversion (>90%), 0.1% acid requires a temperature of 250°C, while 180°C is sufficient for 0.25% acid. Very low solubility (<15%) was observed at 0.01% acid, while considerable conversion was obtained at or above 0.05% (especially at 250°C). At both 180° and 250°C, acid strengths above 0.25% generally brought about an increase in insoluble residue, except for phenol.

The insoluble material obtained at high acid concentrations physically resembled the porous solid obtained previously. Elemental analyses showed its O/C and H/C to be 0.52 and 1.18, respectively, very near the previous results. However, in the Klason lignin test, over half of the solid was dissolved indicating that the majority components were carbohydrates. These results suggest that the repolymerized solid obtained at high acid concentration contains C-O bonds, while the one obtained at high temperature contains newly formed C-C bonds.

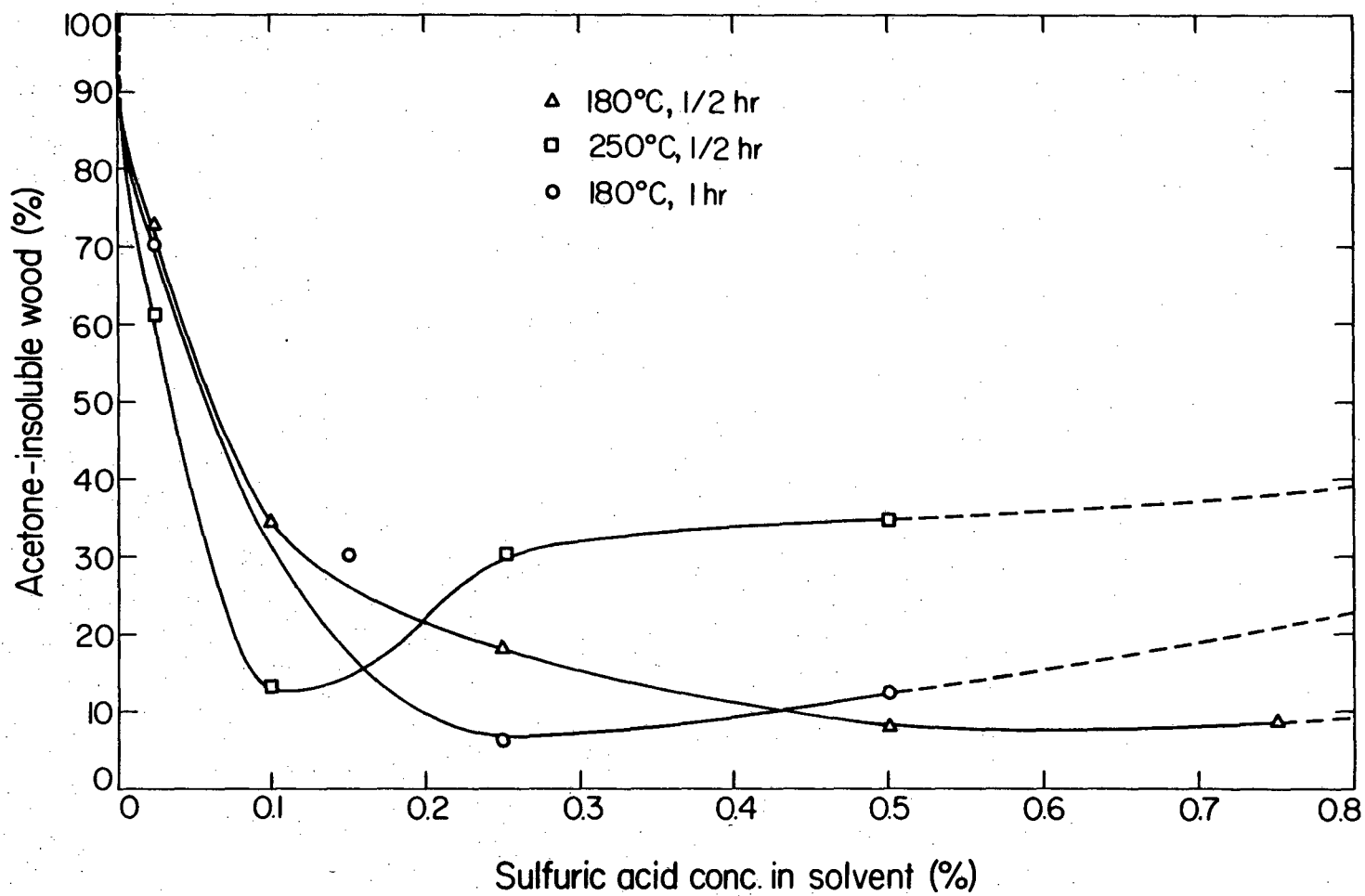


Fig. 14. Solubilities of Wood Versus Acid Concentrations in Butanol.

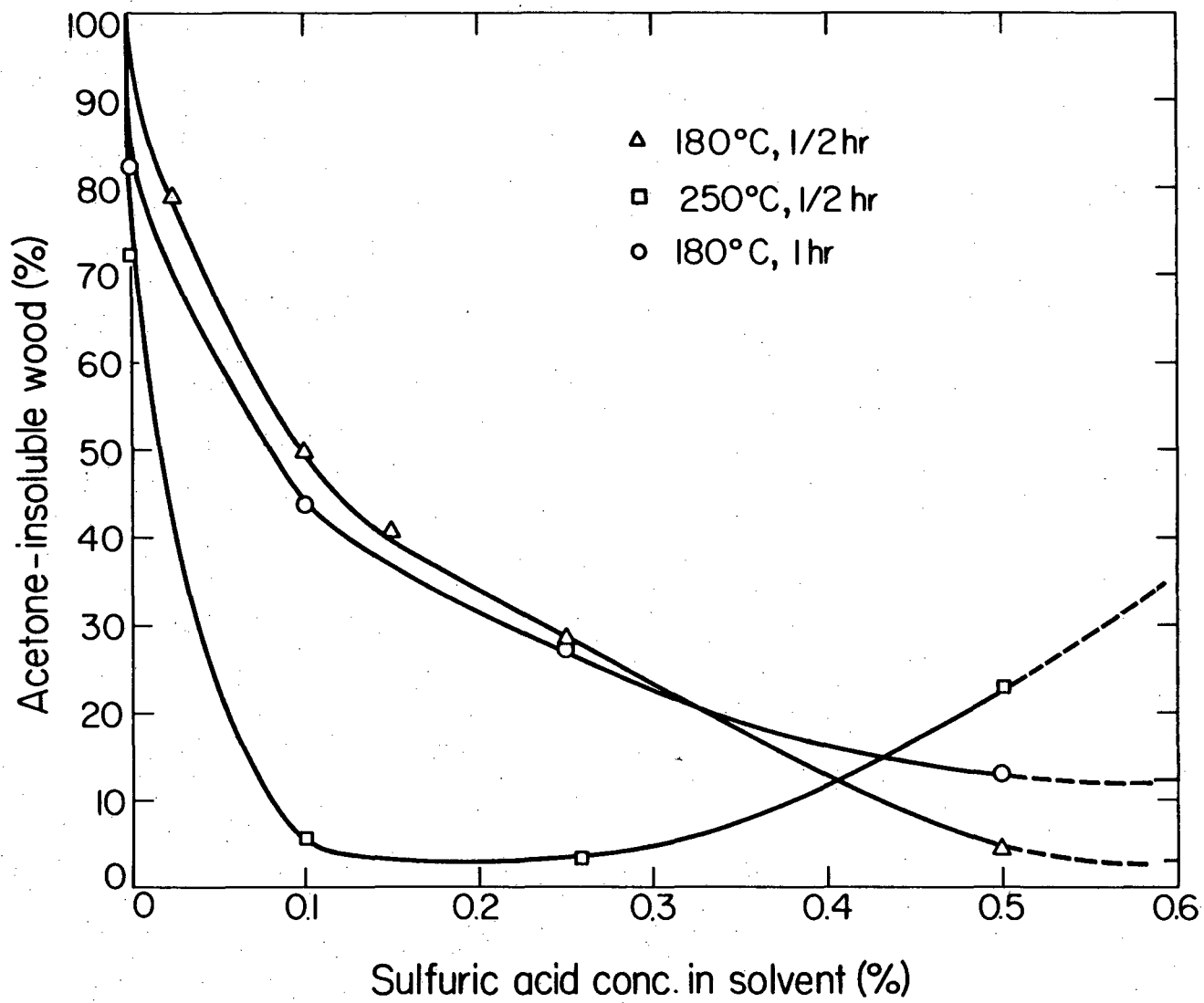


Fig. 15.

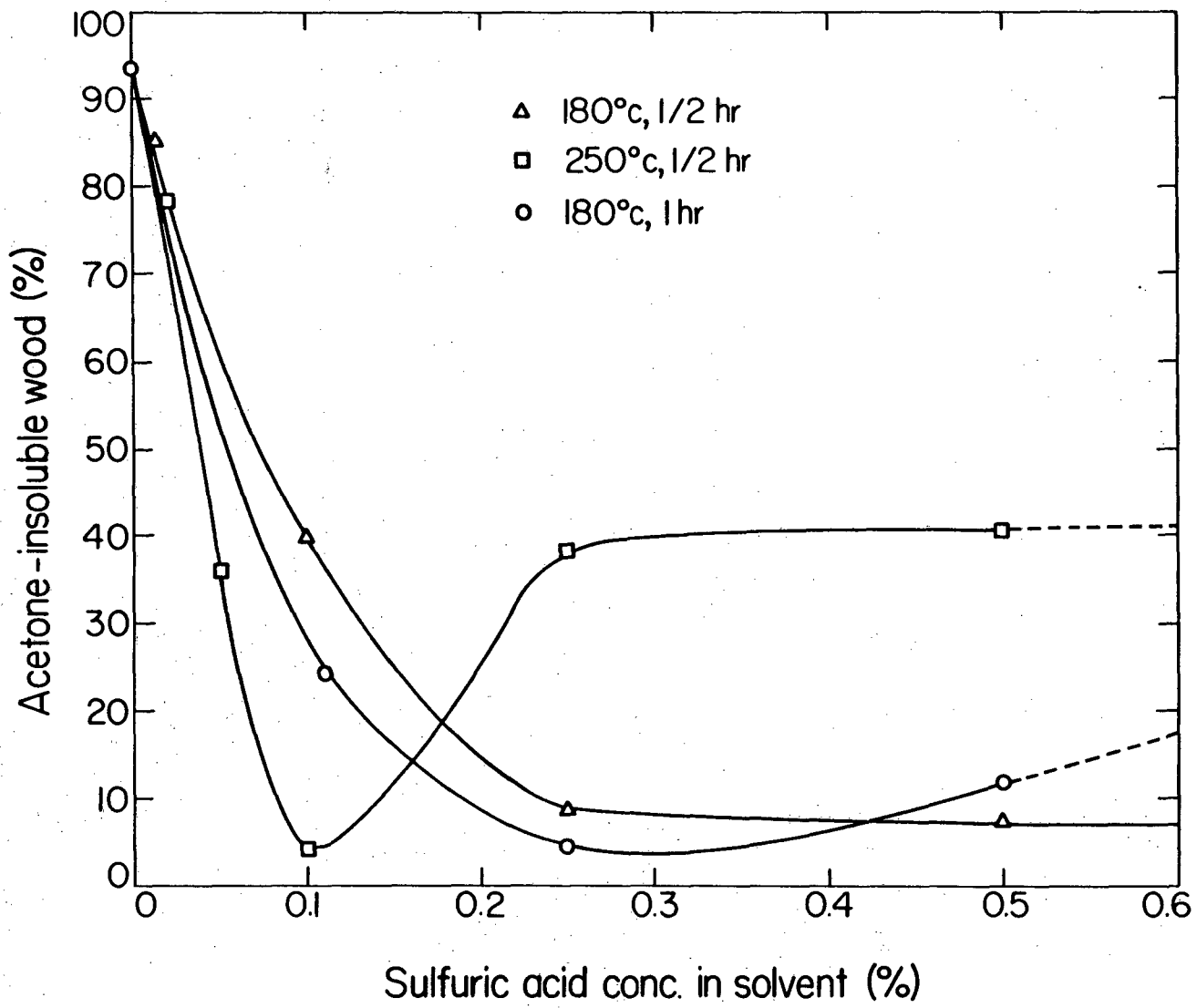
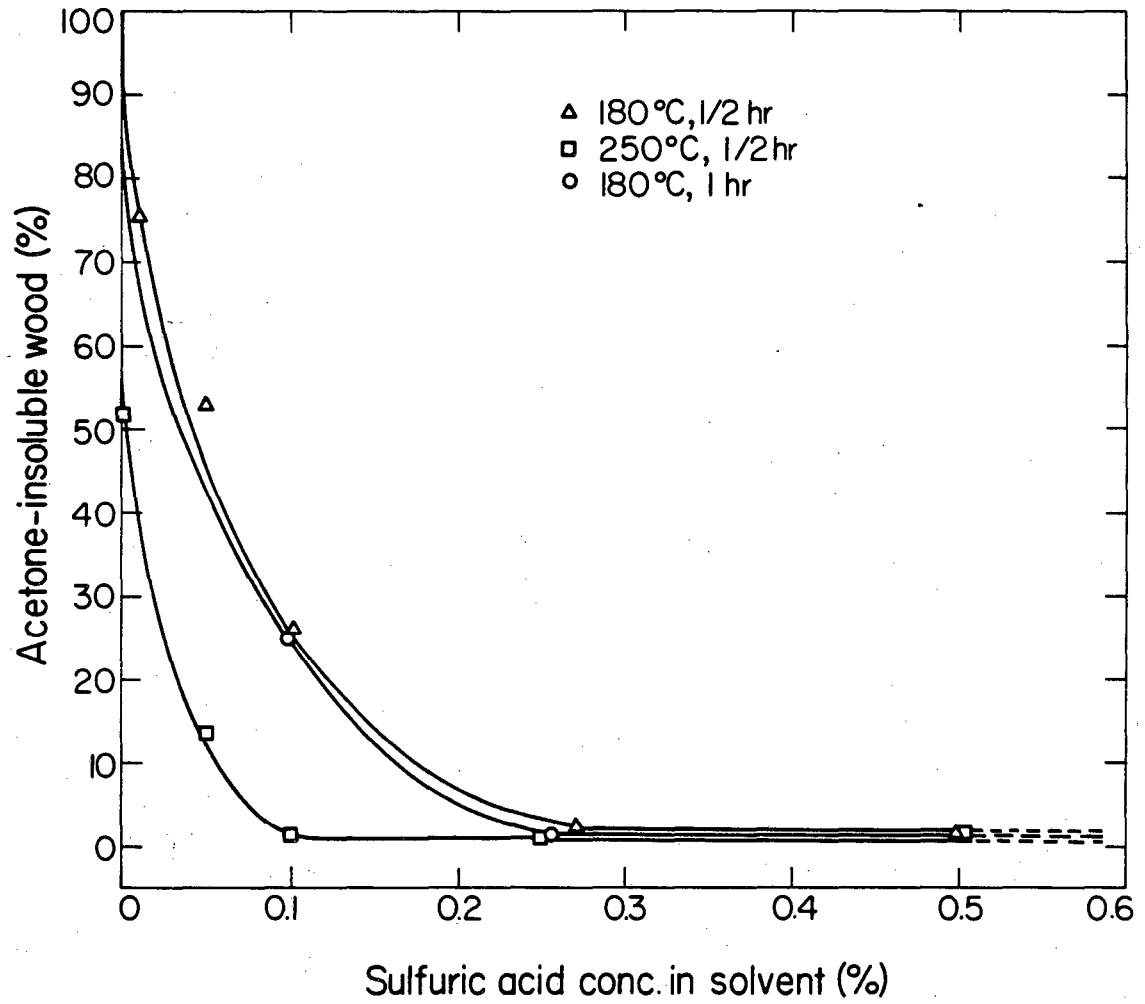


Fig. 16.



XBL 816-999

Fig. 17. Solubilities of Wood Versus Acid Concentrations in Phenol.

Table 18: Wood Solvolysis in Butanol; Acid Concentration Effect

Expt. #	Temp. (°C)	Time (hr.)	Acid Conc. (%)	Acetone Insolubles (%)
RP 233 44 49 46 68	180	0.5	0.025 0.1 0.25 0.52 0.75	73.08 34.50 18.17 8.13 8.64
RP 252 54 52 182 43	180	1	0.025 0.15 0.25 0.5 0.52	70.03 30.20 6.67 9.21 12.23
RP 234 56 57 58	250	0.5	0.025 0.11 0.25 0.50	61.12 13.19 30.18 34.73

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

Table 19: Wood Solvolysis in Ethylene Glycol; Acid Concentration Effect

Expt. #	Temp. (°C)	Time (hr.)	Acid Conc. (%)	Acetone Insolubles (%)
RP 247 238 76 75 41	180	0.5	0.025 0.1 0.15 0.25 0.5	79.03 49.58 40.59 28.79 4.69
RP 239 251 78 86	180	1	0 0.1 0.25 0.5	82.50 44.17 27.77 13.19
RP 87 82 77 81	250	0.5	0 0.1 0.27 0.5	72.50 5.49 3.52 23.20

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

Table 20: Wood Solvolysis in Cyclohexanol; Acid Concentration Effect

Expt. #	Temp. (°C)	Time (hr.)	Acid Conc. (%)	Acetone Insolubles (%)
RP 228	180	0.5	0.01	85.01
55			0.1	34.92
48			0.25	8.06
114			0.25	8.91
45			0.5	7.40
RP 91	180	1	0	93.48
89			0.1	24.47
73			0.25	4.47
42			0.5	11.73
RP 155	250	0.5	0.01	78.39
253			0.05	36.00
101			0.1	3.52
74			0.25	38.17
254			0.50	40.50

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

Table 21: Wood Solvolysis in Phenol; Acid Concentration Effect

Expt. #	Temp. (°C)	Time (hr.)	Acid Conc. (%)	Acetone Insolubles (%)
RP 261 RK 8 RP 70 69 95	180	0.5	0.01 0.05 0.12 0.27 0.5	77.00 53.04 26.20 1.90 1.32
RK 5 RP 186 97	180	1	0 0.1 0.25	73.20 25.34 1.83
RP 245 RA 10 RP 102 117 96 246	250	0.5	0 0.05 0.1 0.1 0.25 0.5	51.60 14.36 1.25 0.81 1.17 1.50

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

In real process situations, low sulfuric acid concentration is preferred, not only for reduced chemical costs, but also because of lesser opportunity for repolymerization. Thus, 0.1% acid at 250°C is probably preferable to 0.25% acid at 180°C.

3. Residence Time

The effect of reaction time on wood solubility is shown in Tables 22 through 25 and Figures 18 through 21. The time given is the sum of heating time and the time at reaction temperature; typical heating times from room to 180°C and 250°C are 14 and 25 minutes, respectively.

As is characteristic of slow heating in batch equipment, there is always some uncertainty in interpreting conversion versus time results; especially so if a system achieves considerable conversion during heat-up as in runs at 0.1% acid and 250°C, where more than 80% of the wood is solubilized when the reaction mixture is immediately cooled upon reaching 250°C. It is, however, possible to draw some conclusions about time dependence which will be discussed at a latter point.

Most of the conversion-time plots show the existence of an optimum time beyond which the yield of soluble material starts to decrease. For 180°C runs, the optimum time at reaction temperature is about 1 hour, whereas at 250°C 0.5 hour is sufficient. Conversion during heat-up to 180°C is much less than during heat-up to 250°C. In 0.1% acid-phenol run, heat-up from room temperature to 180°C solubilized 55% of the wood, with 25% more dissolved from 180° to 215°C, and 10%

Table 22: Wood Solvolysis in Butanol; Residence Time Effect

Expt. #	Acid Conc. (%)	Temp. (°C)	Heat-up Time (min.)	Time at Temp. (min.)	Acetone Insolubles (%)
RP 165 180 171 60 227 44 54	0.1	180	18.3 18.8 17.1 21.0 — 22.0 18.8	0 3.75 7.5 15.0 22.5 30.0 60.0	80.07 64.22 54.94 47.55 46.25 34.50 30.20
RP 167 173 56 50	0.1	250	43.2 41.3 45.0 44.0	0 7.5 30.0 60.0	7.26 6.91 13.19 16.92
RP 166 172 53 49 52 64	0.25	180	17.6 17.0 23.0 19.0 24.0 20.0	0 7.5 15.0 30.0 60.0 75.0	51.31 35.25 24.69 18.17 6.67 6.72
RP 169 181 59 46 43	0.5	180	16.9 17.9 22.0 24.0 22.0	0 7.5 15.0 30.0 60.0	38.40 23.80 10.77 8.13 12.23

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

Table 23: Wood Solvolysis in Ethylene Glycol; Residence Time Effect

Expt. #	Acid Conc. (%)	Temp. (°C)	Heat-up Time (min.)	Time at Temp. (min.)	Acetone Insolubles (%)
RP 206	0.1	250	23.0	0	23.31
223			—	7.5	9.76
207			22.5	15.0	5.30
82			22.0	30.0	5.49
208			25.3	60.0	3.99
224			—	90.0	21.78
225			—	90.0	20.82
RP 204	0.25	180	16.1	0	48.97
221			—	3.75	43.25
220			—	7.5	39.25
205			15.5	15.0	34.78
75			14.0	30.0	28.79
78			15.0	60.0	27.77
RP 90	0.25	150	22.0	0	4.47
84			23.0	15.0	2.97
77			23.0	30.0	3.52
83			22.0	60.0	3.96
222			—	90.0	31.58

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂

Table 24: Wood Solvolysis in Cyclohexanol; Residence Time Effect

Expt. #	Acid Conc. (%)	Temp. (°C)	Heat-up Time (min.)	Time at Temp. (min.)	Acetone Insolubles (%)
RP 152	0.1	180	16.6	0	73.04
148			—	3.75	56.24
161			16.7	7.5	49.63
162			17.8	15.0	41.09
55			18	30.0	34.92
89			14	60.0	24.47
RP 150	0.1	250	26.9	0	15.53
174			27.5	37.5	11.69
164			25.8	7.5	10.54
151			27.5	15.0	7.26
147			—	22.5	4.84
101			—	30.0	3.52
156			28.0	60.0	4.32
RP 178	0.25	180	15.0	0	55.78
154			16.6	3.75	36.92
153			17.9	7.51	17.49
177			15.0	15.0	10.06
114			14.0	30.0	8.91
73			14.0	60.0	4.47

Process Conditions:

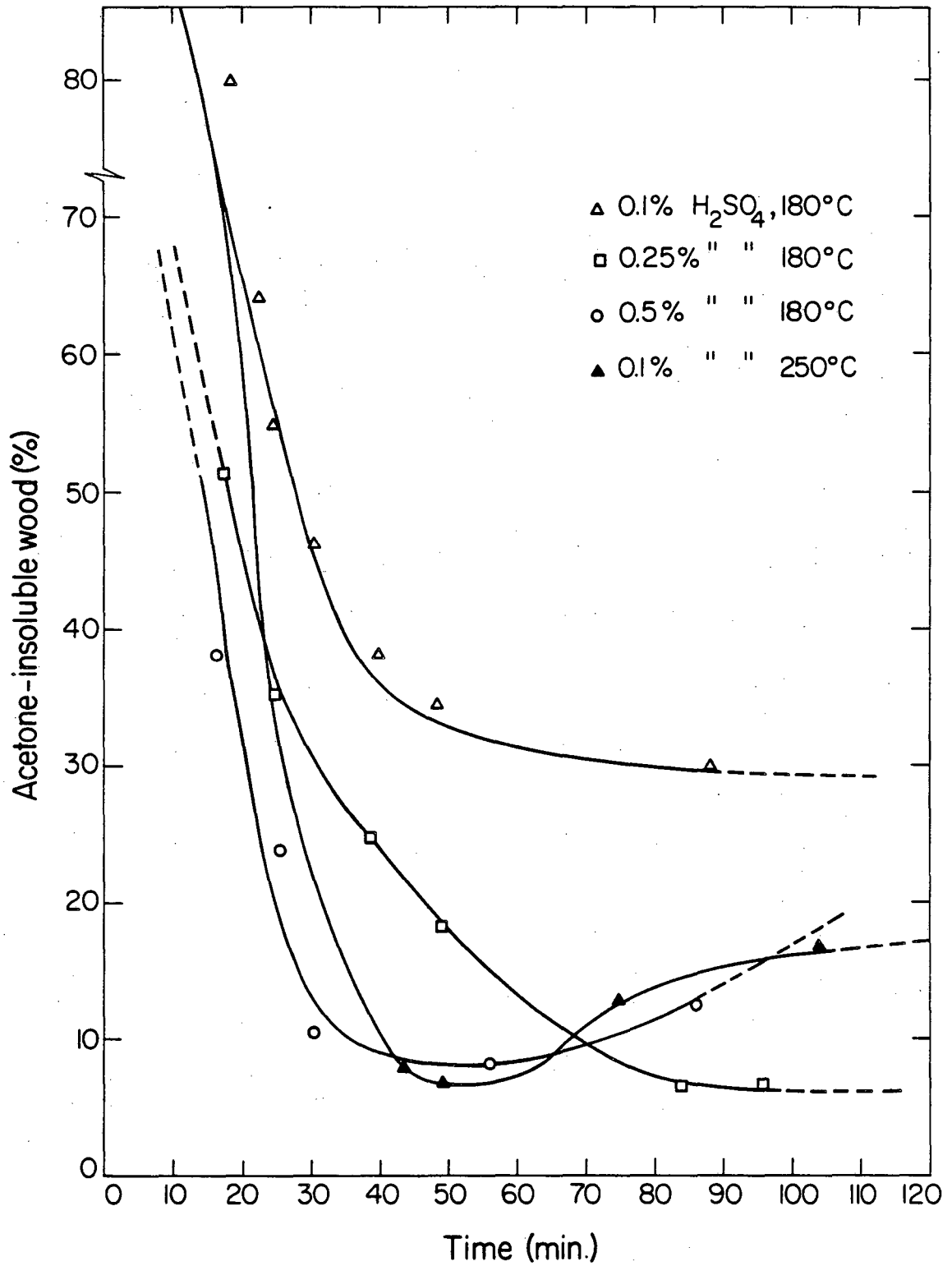
- Solvent/wood = 4/1
- 15 psia N₂

Table 25: Wood Solvolysis in Phenol; Residence Time Effect.

Expt. #	Acid Conc. (%)	Temp. (%)	Heat-up Time (min.)	Time at Temp. (min.)	Acetone Insolubles (%)
RP 196	0.1	180	13.5	0	53.50
149			-	3.75	42.37
193			13.9	7.5	36.30
185			12.3	15.0	35.67
194			15.0	22.5	28.85
70			14.0	30.0	26.20
186			14.8	60.0	25.34
RK 10			0.1	215	24.5
11	20.8	3.75			16.50
11A	-	3.75			15.01
12	20.5	7.5			12.83
13	21.5	15.0			6.74
9	24.0	30.0			3.88
14	-	60.0			3.42
RP 187	0.1	250			26.0
195			26.1	3.75	2.77
189			27.2	7.5	1.68
190			24.6	15.0	2.14
117			27.0	30.0	0.81
102			25.0	30.0	1.25
191			24.8	60.0	1.35
RP 103			0.25	180	13.6
192	14.3	7.5			10.54
RK 6	14.9	11.0			4.04
RP 93	-	15.0			3.82
69	12.5	30.0			1.90
97	13.8	60.0			1.83

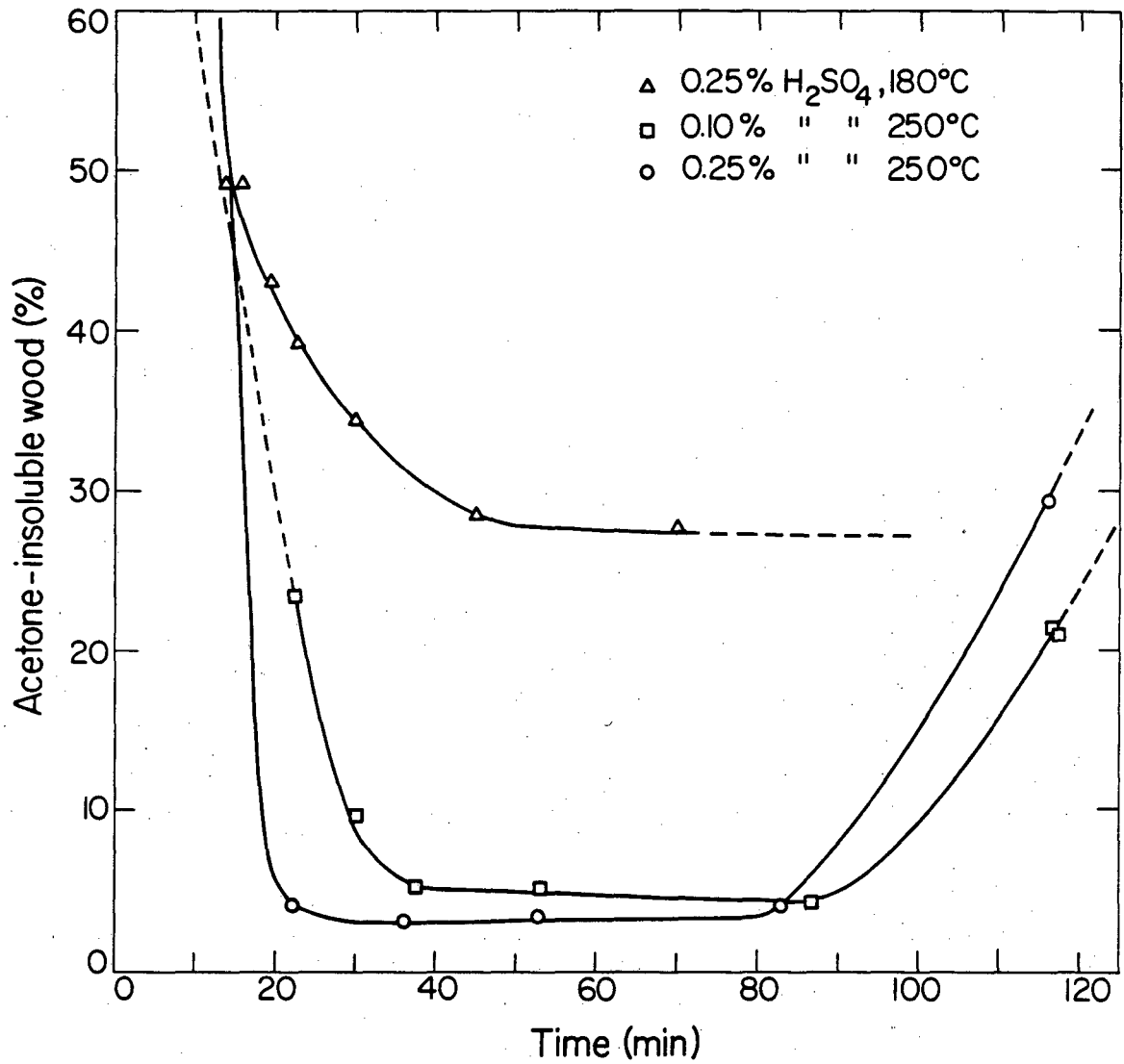
Process Conditions:

- Solvent /wood = 4/1
- 15 psia N₂



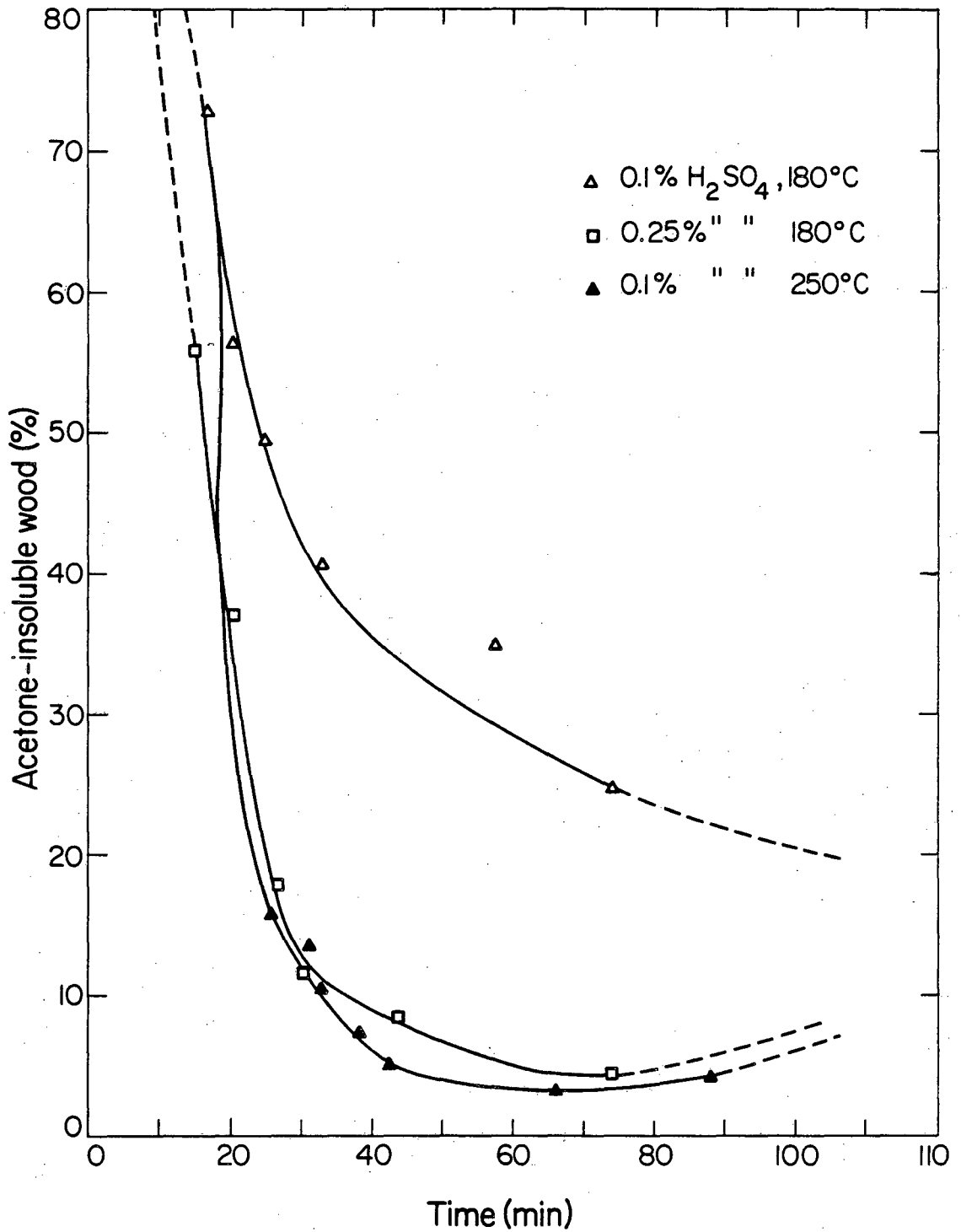
XBL 816-994

Fig. 18. Solubilities of Wood Versus Residence Time in Butanol.



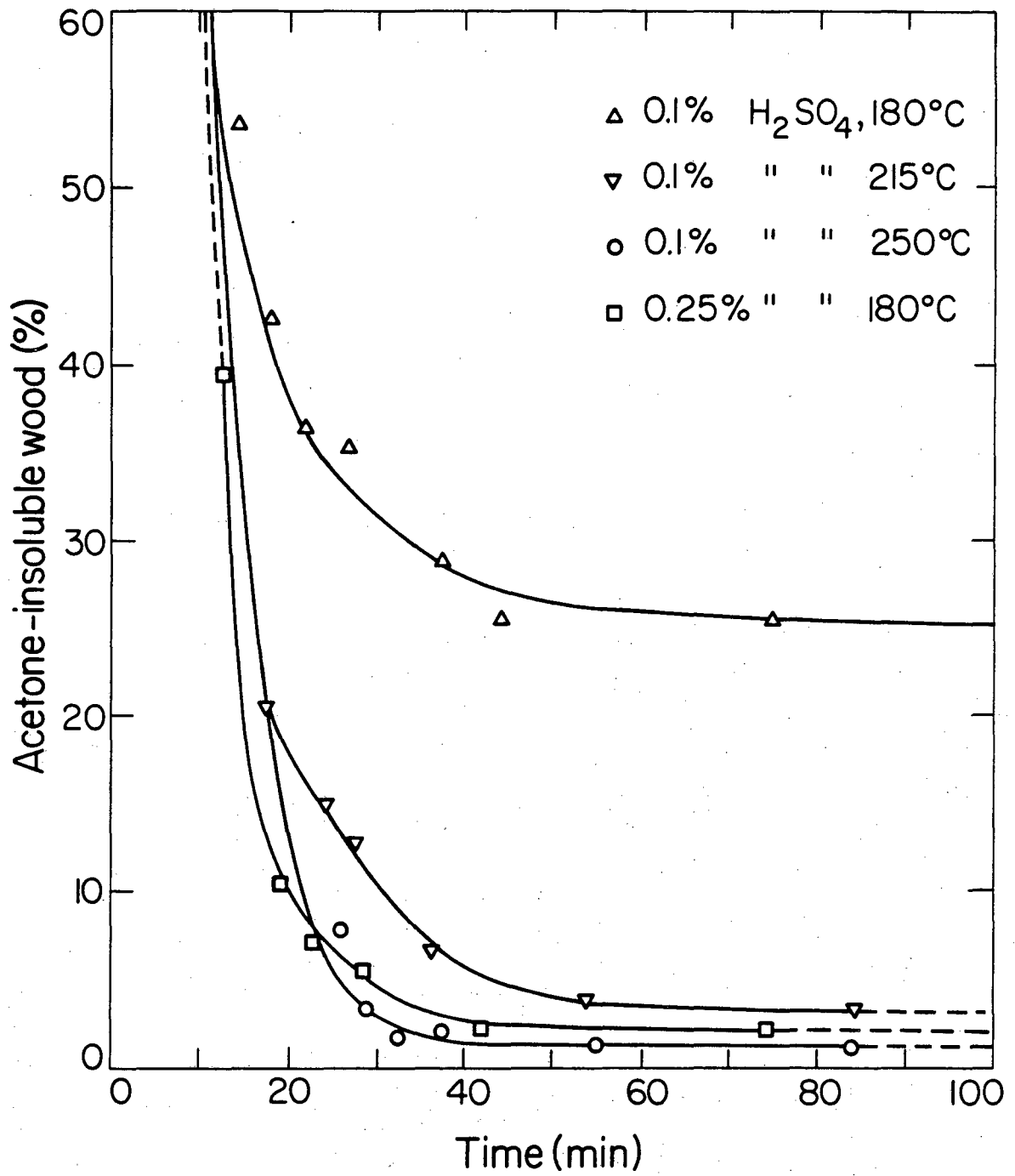
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Fig. 19. Solubilities of Wood Versus Residence Time in Ethylene Glycol.



XBL 816-995

Fig. 20. Solubilities of Wood Versus Residence Time in Cyclohexanol.



XBL 816-997

Fig. 21. Solubilities of Wood Versus Residence Time in Phenol.

more from 215° to 250°C. For an hour at reaction temperature, conversions at 180°C, 215°C, and 250°C are roughly 75%, 95%, and 99%, respectively. Reaction rates evidently are falling off as time progresses. The rapid initial dissolution rate but progressively slowing down is probably due to product inhibition effect.

Upon adding 0.15% more acid to a system which has reacted at 180°C for 0.5 hour, an additional 30 minutes at 180°C gives a conversion comparable to that of 0.25% acid at 180°C and 0.5 hour in a direct run. A similar result was obtained by adding 0.2% acid to a system which previously had been run with 0.05% acid at 180°C for 0.5 hour. These results suggest that the slowing down of the dissolution rate as reaction progresses is caused by a decrease in acid concentration. In other words, adding additional acid to a "dead" system revives it. Apparently, part of the wood-derived products complexes with, or consumes the acid, to an extent faster than 0.1% but less than 0.25%.

Raising the temperature of a product mixture with 0.1% acid, run for 0.5 hour at 180°C (or at 215°C) to 250°C, gives a conversion comparable to that with 0.1% acid, run for 0.5 hour at 250°C. These results suggest that the acid-consuming reaction may be partly reversed at higher reaction temperatures, although other reasonable interpretations are also possible.

4. Solvent to Wood Ratio

Based on Seth's (120) results, a four-to-one ratio (weight) of solvent to wood was chosen for all experimental runs. The process would be improved if an equally good conversion were obtained at a lower solvent ratio. Therefore, this factor was also investigated.

Cyclohexanol was used as test solvent, in ratios from 2:1 to 6:1 under experimental conditions which had given maximum solubilization at 4:1 ratio. The result of the experiments is tabulated in Table 26 and plotted in Figure 22. Duplicate runs were made for the 4:1 case, so that experimental reproducibility could be assessed.

The plot indicates that wood solubility varies more or less linearly from 2:1 to 4:1. No additional solubility was obtained beyond 4:1. Observation prior to the reactions suggested that a 4:1 ratio corresponded to a minimum amount of solvent needed to wet adequately the wood flour. For ratios higher than 4:1, similar wood solubility was obtained, suggesting that only a minimum overall wetting of the wood is essential to yield good dissolution. There is, therefore, no process advantage in increasing the solvent-to-wood ratio beyond 4:1.

5. Speed of Stirring

Some recent work in organosolv pulping (95,97) have indicated degree of agitation to be a factor in the overall delignification rate. The published results show that with no agitation, the reaction took two to three times longer to achieve the same degree of lignin removal than with full agitation. Because of the basis of solvolysis concept, we have evaluated the stirring effect in our system. The results are listed in Table 27 and Figure 23.

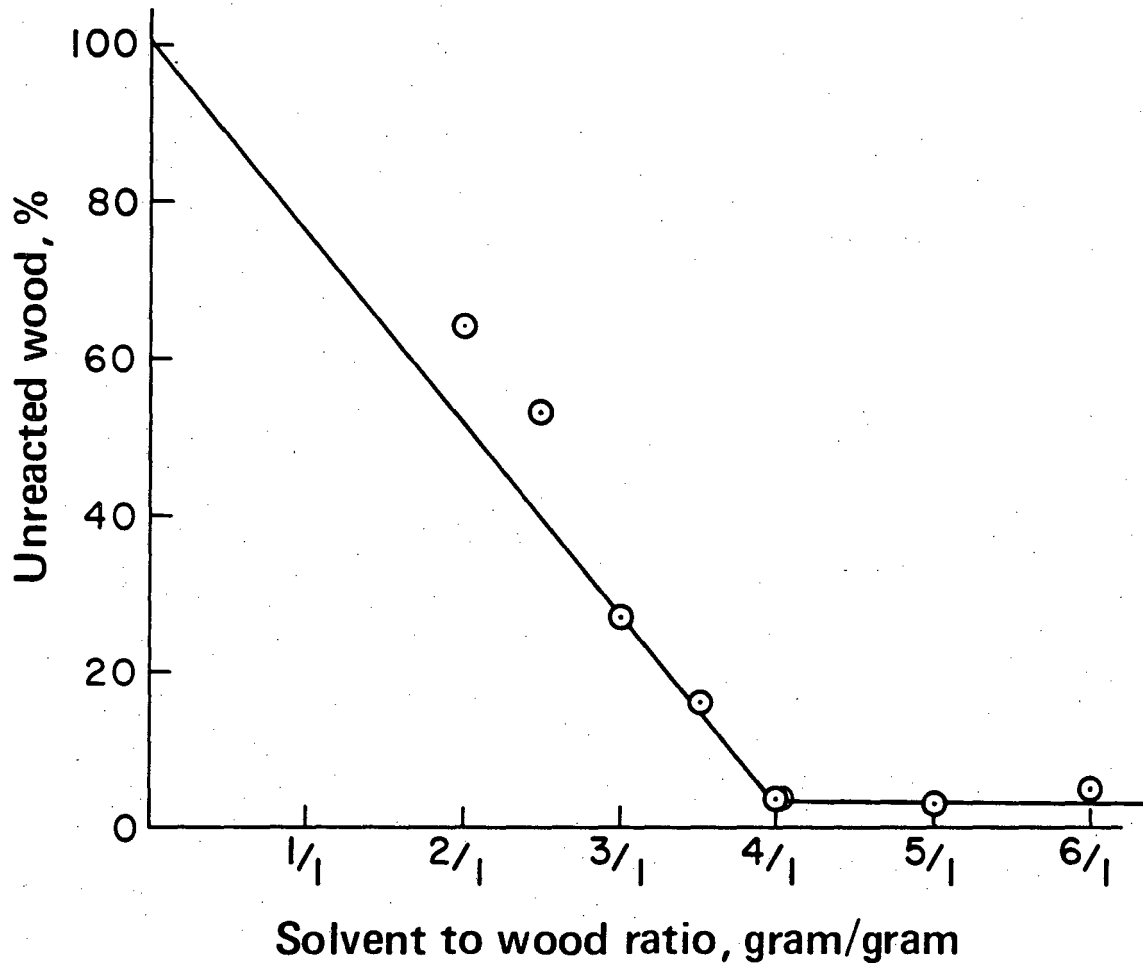
The results indicate that stirring at 360 RPM achieved similar, if not slightly better, solubilization compared with no agitation. In these runs, most insoluble material was observed to cling around the

Table 26. Solubilities of Wood Using Different Solvent to Wood Ratio Feed.

Expt. #	Solvent : Wood (gm/gm)	Acetone Insolubles (%)
RSW 1	2:1	48.17
2	2.5:1	25.27
3	3:1	13.42
4	3.5:1	9.45
RP 101	4:1	3.52
RP 163	4:1	3.08
RSW 5	5:1	3.37
RSW 6	6:1	4.67

Process Condition:

- Solvent = cyclohexanol
- 15 psia N₂
- 0.1 wt-% H₂SO₄ in Solvent, 250° C, ½ hr.
- Speed of stirring = 140 RPM



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Fig. 22. Solubilities of Wood at Various Solvent to Wood Ratio.

Table 27. Solubilities of Wood Versus Degree of Agitation.

Expt. #	Speed of Stirring (RPM)	Acetone Insolubles (%)
RSS 1	0	6.23
2	80	3.43
3	80	3.65
4	118	3.52
5	140	3.17
6	160	6.02
7	172	4.14
8	184	4.57
9	204	5.56
10	220	4.55
11	240	5.32
12	274	4.78
RP 101	360	3.52
RP 163	360	3.08

Process Condition:

- solvent = cyclohexanol
- solvent/wood = 4/1
- 15 psia N₂
- 0.1 wt-% H₂SO₄ in solvent, 250°C, ½ hr.

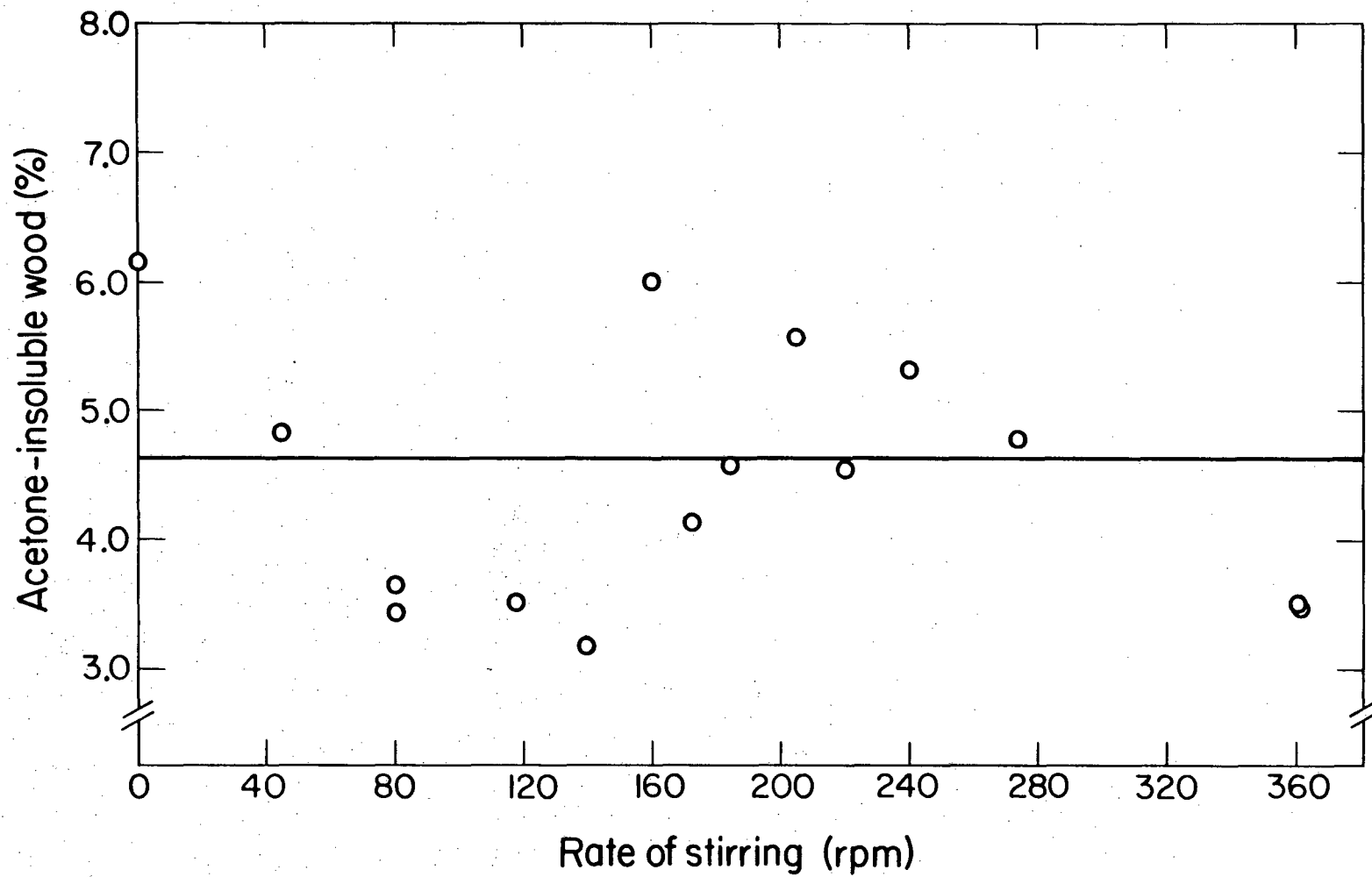


Fig. 23. Solubilities of Wood Versus Rate of Stirring.

stirrer shaft, indicating that this could be a characteristic of the reactor and its stirring arrangement. The scattered data points between 140 and 360 RPM may be related to the above observation. The fact that no agitation is essentially as effective as vigorous agitation indicates that solvolysis is not limited by external mass transfer.

In a continuous process, the lack of dependence of agitation means probable independence of Reynolds number. This improves our flexibility in optimizing reactor size, permits use of viscous slurry, allows use of larger pipe diameter for feed and product, and above all reduces cost.

6. Wood Particle Size

Recent literature (95,97) also suggests that delignification using a mixture of alcohol and water in equal amount is limited by internal diffusion. To evaluate their findings in our system, we treated wood of different particle sizes ranging from wood flour (65 mesh) to wood chips (1/4" to 1/8"). Chips are an eventual preference due to their already widespread usability in the pulping industry.

Table 28 lists the results obtained. Most experiments were repeated to insure accuracy and demonstrate reproducibility. The results indicate that the amount of insolubles differs by only 1% between 65 and 10 mesh wood flour, a figure well within experimental and analytical error. Even using wood chips, substantial dissolution was observed.

Table 28. Solubilities of Wood of Different Particle Sizes.

Expt. #	Particle Size (mesh)	Acetone Insolubles (%)
RM 11	regular chips ($\frac{1}{4}$ - $\frac{5}{8}$ '' x $\frac{1}{8}$ '')	13.81
12*	"	1.03
13**	"	5.82
14***	"	11.67
8	8	4.40
9	8	5.27
10	8	4.03
6	10	7.23
7	10	10.45
4	16	7.88
5	16	9.13
3	20	8.24
1	30	6.33
2	30	8.06
RSS 1	65	6.23

Process Condition:

- solvent = cyclohexanol
- solvent/wood = 4/1
- 15 psia N₂
- 0.1 wt-% H₂SO₄ in solvent, 250° C, ½ hr.

- * solvent = Phenol
- ** solvent = Ethylene Glycol
- *** solvent = Butanol

The insoluble materials from the chip runs were dark brownish in color, mushy in appearance, and did not conform to physical integrity of wood chips. To determine the processability of this solid, one of the chip runs was conducted for a slightly longer period, 35 minutes at 250°C instead of 30 minutes. The run netted 6% insolubles, suggesting that equally good solubilization in chips and flour under similar conditions are possible.

From the reaction standpoint, the finding that both particle size and stirring speed exert such a negligible influence on solubilization suggests that solvolysis is a kinetic controlled reaction. It would be of interest to determine the various kinetic parameters that characterize solvolysis.

7. Wood Moisture Content

A process to handle moist wood feed would reduce or eliminate the drying step prior to solvolysis, which could be advantageous. "Green" wood contains as much as 50% water when logged. After several weeks of shipping and open-air storage, the wood's moisture falls to the 10-15% level. Such field-dried logs are further dried to 4% before they are chipped and pulped. Chips and flour can absorb moisture from humid air, and may require re-drying before they are processed.

Experimental runs were made to evaluate the solubilization of wood flour at moisture levels of 9% (as received), 15% (field-dried), and 50% (green wood), with each of the four solvents. The conditions were 0.1% acid and 250°C for 0.5 hour, or, for butanol, 0.25% acid and 180°C for 1 hour.

Table 29 gives the experimental results. The trend suggests that higher wood moisture reduces solubilization. The reduction, however, is small. For example, wood conversions were 98.75% and 94.51% for the 9% moist wood in phenol and ethylene glycol, versus 95.90% and 97.22% at 15% moisture, and versus 96.19% and an average of 90.89% at 50% moisture. It thus appears that both chips or flour from green or field-dried wood can be solvolyzed just as well as the 9% moisture wood. The big difference appears to be in the operating pressure. Evidenced by the data (Table 29), the difference in operating pressure at 250°C varies from 100 psig (phenol) to as much as 500 psig (cyclohexanol) for the field-dried and green wood. High operating pressure translates into stricter equipment specifications and thus high capital expenditure.

In addition to the earlier result that chips can be solvolyzed thus eliminating the grinding process, the use of green wood further improves process economics by avoiding drying the feed. From an overall process standpoint, green-wood solvolysis has opened up the possibility of solubilizing wood or other biomass on the spot where it is logged or collected. This could impact positively on the usually prohibitively high transportation and collection charges related to biomass operation.

8. Solvent Incorporation

Solvent consumption is an important process factor that requires investigation. All four solvents were studied under process conditions that produced the least amount of residue. Vacuum distillation

Table 29. Solubilities of Wood of Different Moisture Levels.

Expt. #	Solvent	Moisture (% in wood)	Acetone Insolubles (%)	Maximum Pressure attained (psig)
RP 52	Butanol*	9	6.67	135
106	**	15	6.96	130
140	**	15	6.04	135
107	**	50	8.36	255
159	**	50	7.33	270
82	Ethylene Glycol	9	5.49	175
110	"	15	2.78	180
142	"	50	7.81	380
179	"	50	10.40	365
101	Cyclohexanol	9	3.52	210
108	"	15	5.73	360
175	"	15	6.38	350
160	"	50	5.98	545
143	"	50	6.15	560
102	Phenol	9	1.25	225
112	"	15	4.10	265
113	"	50	3.81	350

Process Conditions:

- Solvent/wood = 4/1
- Speed of stirring = 140 RPM
- 15 psia N₂
- 0.1% wt-% H₂SO₄ in solvent, 250° C, ½ hr.

Note:

* 0.25% wt-% H₂SO₄ in Butanol, 180° C, 1 hr.

was used to recover unincorporated solvent. Prior to distillation, a predetermined amount of sodium hydroxide was added, in order to neutralize the acid remaining in the system and thus avoid condensation reactions during distillation. Table 30 lists the results of this study.

The amounts of solvent incorporated averaged at about 2.5% (relative to solvent used) or about 9.5% (relative to initial dry wood), except for phenol of which more than 17% (based on solvent) or 75% (based on dry wood feed) was not recovered. Along with solvent incorporated, water was formed during solvolysis (Table 30). Roughly 10% (based on initial dry wood) water was formed in solvents except phenol which netted more than 23% water. It is interesting to note that the amount of water formed is proportional to the amount of solvent incorporated.

Since neither hydrogen nor carbon monoxide is required in solvolysis, a net water formation could only be explained by dehydration reactions. This net water formation serves both a desirable and undesirable purpose. It is desirable because wood oxygen is reduced and more importantly, bonds that crosslink wood are broken to form low-molecular-weight fragments. On the other hand, it is undesirable because in reducing oxygen, hydrogen goes with it and in effect lowers the amount of hydrogen in the solvolytic product.

Table 30. Amounts of Solvent Incorporated and Water Formed During Solvolysis.

Solvent	Solvent Incorporated (%) based on		Water Produced (% initial dry wood)
	initial dry solvent	initial dry wood	
Butanol*	2.32	10.18	12.38
Ethylene Glycol	2.24	9.84	9.96
Cyclohexanol	2.87	12.60	11.14
Phenol	17.56	77.14	23.30

Process Conditions:

- Solvent/wood = 4/1
- Speed of stirring = 140 RPM
- 15 psia N₂
- 0.1% wt-% H₂SO₄ in Solvent, 250°C, ½ hr.

Note:

* 0.25% wt-% H₂SO₄ in Butanol, 180°C, 1 hr.

9. Product Characteristics

(a) Appearance

After unincorporated solvent is removed by distillation, the residual solvolytic product appears as a shiny, tar-like, viscous material at 100°C. It hardens when temperatures drop below 100°C.

Examining with the scanning electron microscope (Figure 24), the product displays a crystal-like structure. The absence of cellulosic fibers is indicative of complete structural destruction of the woody structure.

(b) Elemental Analysis

Table 31 shows the elemental compositions of the solvolytic products. The product oxygen contents vary from 20 to 35% (by weight), which correspond to roughly 15 to 40% oxygen reduction based on original wood oxygen.

Recalling earlier result that phenol solvolysis produces the largest amount of water among the four solvents, it correlates well with the elemental result that the phenol treated product has the least amount of oxygen, and, as shown in the next section, the lowest softening point. Since a low oxygen and low molecular weight product is desirable, it will be of interest to relate the oxygen (and hydrogen) contents of the product to the process parameters and the nature of the solvents.

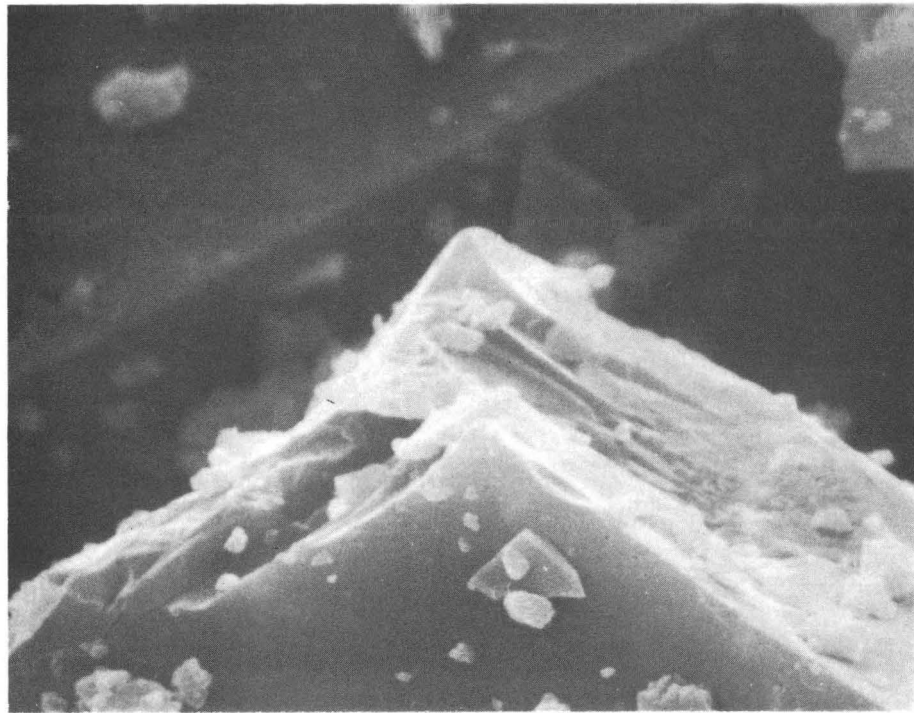
(c) Properties

The acetone-soluble solvolytic products are partially soluble in toluene. Toluene solubility ranges from less than 6% to slightly more

Fig. 24. Scanning Electron Micrograph of (a) Wood Flour Before Solvolysis (5KX); (b) Cyclohexanol Treated (250°C, 0.1 wt% H₂SO₄, 0.5 hr) Solvolytic Product (5KX).



(a)



(b)

XBB 823-1769

Fig. 24.

Table 31. Elemental Content of the Solvolytic Products.

Product/Solvent System	Carbon	Hydrogen	Oxygen	atomic ratio		Oxygen Removed, % based on initial dry wood
				H/C	O/C	
Butanol**	61.12 57.62*	6.14 4.77*	32.02 34.50*	0.99*	0.45*	14.90
Ethylene Glycol	59.19 58.71*	5.44 5.67*	34.65 33.34*	1.16*	0.43*	17.76
Cyclohexanol	62.88 62.16*	6.06 5.21*	30.35 32.63*	1.01*	0.39*	19.51
Phenol	74.32 73.52*	5.31 4.52*	18.91 21.79*	0.74*	0.22*	46.25

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂
- 0.1 wt-% H₂SO₄ in Solvent, 250°C, ½ hr.

Notes:

- * Corrected for incorporated solvent i.e. on solvent free basis
- ** 0.25 wt-% H₂SO₄ in Butanol, 180°C, 1 hr.

than 25% (Table 32). Toluene is chosen as a solubility test solvent because its solubles are presumably of better quality - less oxygenates, lower molecular weight, and lower melting (or softening) than acetone solubles.

All four toluene solubles are light brown in color. At room temperature, the acetone solubles are soft bitumen-like solids, while the toluene solubles are highly viscous liquids. Upon heating, both solubles soften and start to flow. Table 32 depicts their softening temperature.

(d) Molecular Weight

Gel permeation-chromatography (GPC) was used to determine the molecular weight distribution of the solvolytic products. Table 33 displays the GPC results. The median molecular weight of the acetone solubles ranges from 260 to 350, with the phenol treated product ranks the lowest. This is indicative that a more severe depolymerization occurred in the phenol system. The median molecular weights for toluene solubles of cyclohexanol and phenol are both around 200.

10. Solvolysis Kinetics

Following the plots of acetone-insoluble wood versus time (Fig. 18 through 21), two kinetic models are proposed to describe the solvolysis behavior: an acid-sulfation equilibrium model, and an organic acids production model.

(a) Acid-Sulfation Equilibrium Model

The model involves the assumption that the wood-derived products W-OH form sulfate esters with sulfuric acid in two steps:

Table 32. Solubilities of the Solvolytic Products in Toluene.

Product/Solvent System	Acetone solubles softening Temp. (°C)	Toluene Solubles	
		% initial dry wood	softening Temp. (°C)
Butanol*	151	5.59	**
Ethylene Glycol	145	15.12	**
Cyclohexanol	137	22.17	32
Phenol	85	25.45	**

Process Conditions:

- Solvent/wood = 4/1
- 15 psia N₂
- 0.1 wt-% H₂SO₄ in Solvent, 250°C, ½ hr.

Notes:

- * 0.25 wt-% H₂SO₄ in Butanol, 180°C, 1 hr.
- ** a viscous liquid at room temperature

Untreated Wood (oven-dry):

Acetone Solubility = 2.42%
Toluene Solubility = 0.24%

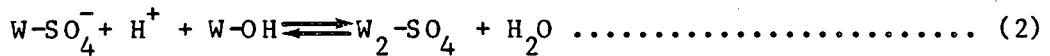
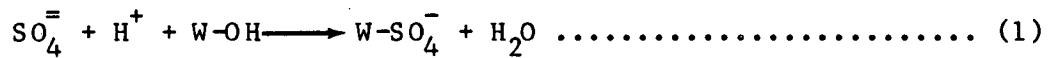
Table 33. Molecular Weights of the Solvolytic Products.

Product/Solvent System	Median Molecular Weight
Butanol	300
Ethylene Glycol	350
Cyclohexanol - AS*	350
TS**	200
Phenol - AS*	260
TS**	180
Albany oil (LBL process)	~ 300-400

Notes:

* AS : Acetone Soluble

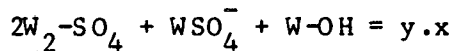
** TS : Toluene Soluble



It is also assumed that reaction (1) is irreversible, and that reaction (2) does not commence unless reaction (1) is essentially completed. This second assumption is supported by results of wood hydrolysis reactions (121,122), in which the end pH of the hydrolyzing medium usually rises by 1 to 2 units.

The equilibrium constant for reaction (2) is fitted by estimating that the residual acidity is 2%, 5%, and 10% of the starting acid for 180°C, 215°C, and 250°C, respectively. These values account for the behavior that the 250°C runs solubilize more wood than 180°C.

Total W-OH is given by $\text{W-OH} = y \cdot x$, where y = proportion of reactive W-OH group per unit conversion. The W-OH balance is:



The available H^+ is then:

$$(\text{H}^+) = \frac{1}{2} (\text{H}^+)_0 - \text{W}_2\text{-SO}_4^-, \text{ where } (\text{H}^+)_0 = \text{amount of starting acid.}$$

The H^+ consumed in the first reaction is:

$$\frac{1}{2} (\text{H}^+)_0 = \text{W}_2\text{-SO}_4^- + \text{W-SO}_4^-$$

Therefore, the equilibrium equation takes the form

$$K = \frac{(W_2-SO_4)}{(W-SO_4^-)(H^+)(W-OH)} = \frac{(W_2-SO_4)}{(H^+)^2(y \cdot x - H^+ - 2W_2-SO_4)}$$

Knowing K at reaction temperature, one can calculate K during heat-up by applying Van Hoff's equation:

$$\ln K = a + \frac{b}{T}, \text{ where } a, b \text{ are constants.}$$

The following table gives a sample calculation for the phenol system at 0.1 wt.-% acid:

°C	TEMP. °K	X %	H ⁺	K
180	453	75	0.0025	338,000
215	488	85	0.005	43,900
250	523	98	0.01	6,000

Plugging in the K values and their respective temperatures, a and b are determined to be 14,000 and -20, respectively.

The following rate equation was found to fit the conversion-time data closely:

$$\frac{dx}{dt} = k_o e^{\frac{-E}{RT}} (H^+)(1-x)$$

where x = Wood conversion (percent acetone-solubles), k_o = rate constant (min^{-1}), E = activation energy (14000Cal/gmole), T = temperature ($^{\circ}\text{K}$), and H^+ = percent of available acid.

To calculate conversion during reaction heat-up, the following heat-up equation is used (T_c is temperature in $^{\circ}\text{C}$):

$$\frac{dT_c}{dt} = C_2(300 - T_c) \quad \text{or} \quad T_c = 300 - e^{-(C_1 + C_2)t}$$

where C_1 and C_2 are constants; C_1 and C_2 are determined when the heat-up equation is fitted with the experimental data.

Numerical integration of the rate equation was carried out on a Hewlett-Packard (HP-85) computer. The strategy diagram and the computer program are given in the appendix. Table 34 tabulates the k_o s for all four solvents. Figures 25 through 31 show the calculated conversion-time plots together with experimental data points for phenol and cyclohexanol systems at various acid concentrations and process temperatures.

(b) Organic Acids Production Model

Recent work (121,122) in Lawrence Berkeley Laboratory's Biomass group has indicated the formation or liberation of organic acids during wood liquefaction. The residual activity is considered to be due to catalysis by the organic acids, which appear to ionize more at high temperature.

The model assumes that sulfuric acid is continuously and irreversibly consumed, and that wood-derived organic acids are continuously

Table 34. Table of Rate Constants for the Acid-Sulfation Equilibrium Model.

$$\frac{dx}{dt} = k_0 e^{\frac{-14000}{RT}} H(1-x)$$

Solvent System	Process Conditions Acid Conc. (%), Temp. (°C)	Rate Constants, k_0 (min.^{-1})
Butanol	0.1%, 180°C 0.1%, 250°C 0.25%, 180°C	0.5×10^7
Ethylene Glycol	0.1%, 250°C 0.25%, 180°C 0.25%, 250°C	0.5×10^7
Cyclohexanol	0.1%, 180°C 0.1%, 250°C 0.25%, 180°C	0.75×10^7
Phenol	0.1%, 180°C 0.1%, 215°C 0.1%, 250°C 0.25%, 180°C	2.5×10^7

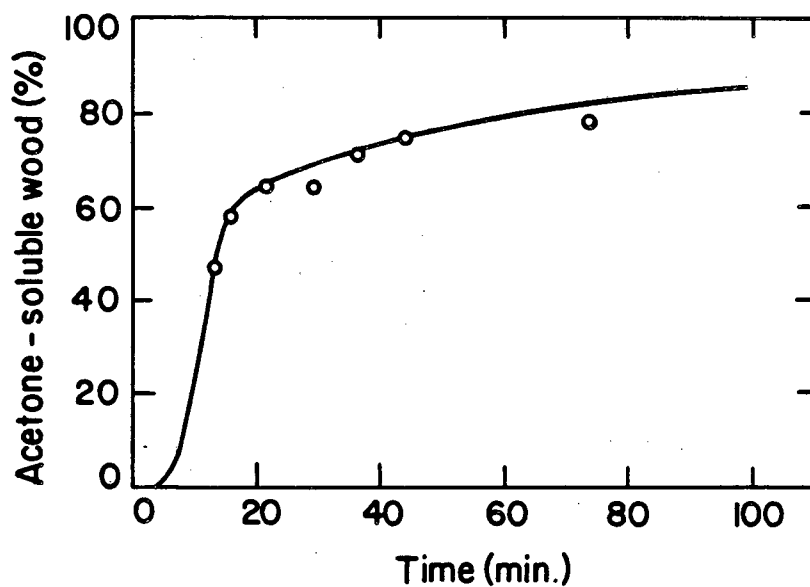
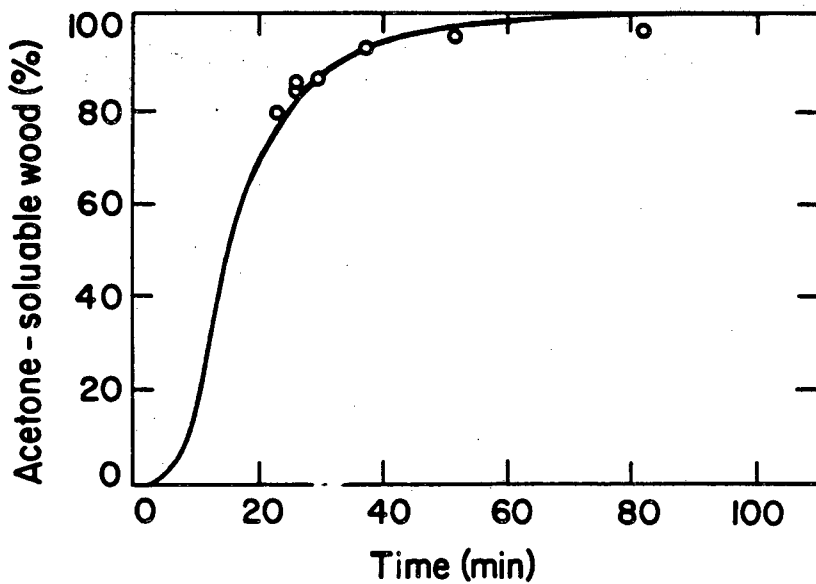


Fig. 25. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in phenol at 180°C.



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Fig. 26. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in phenol at 215°C.

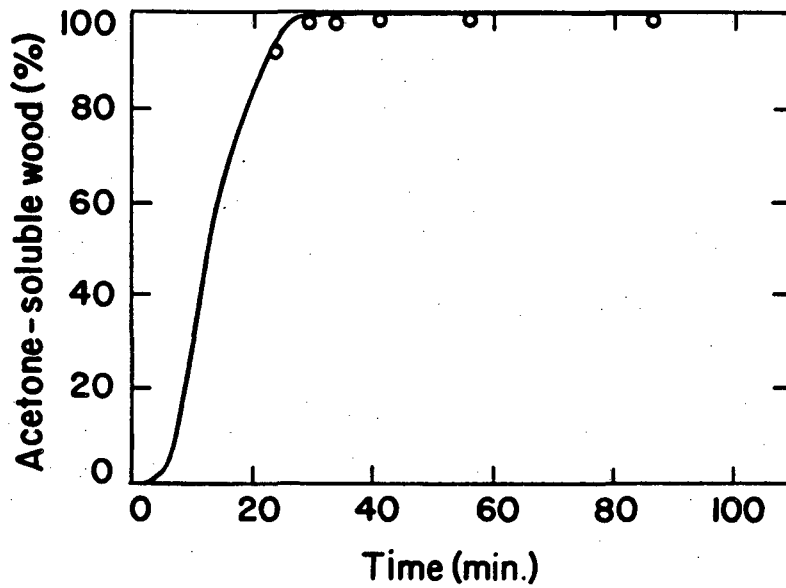


Fig. 27. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H₂SO₄ in phenol at 250°C.

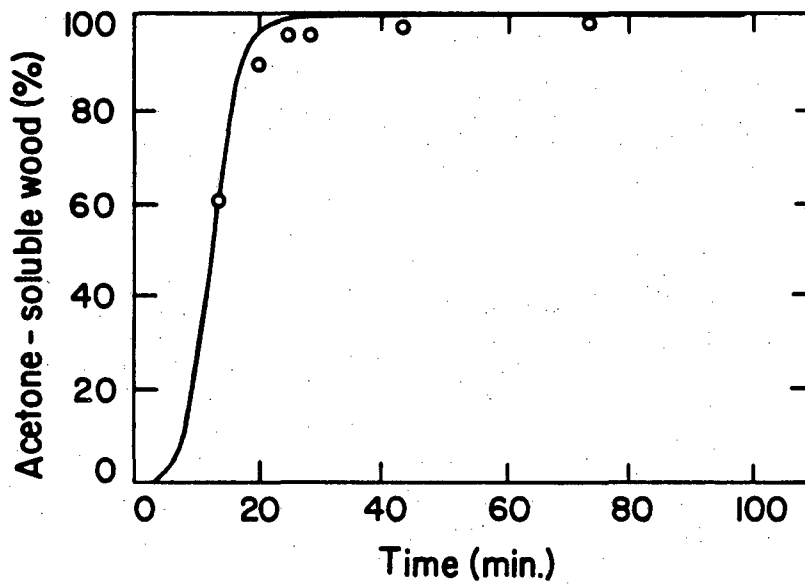


Fig. 28. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.25 wt% H₂SO₄ in phenol at 180°C.

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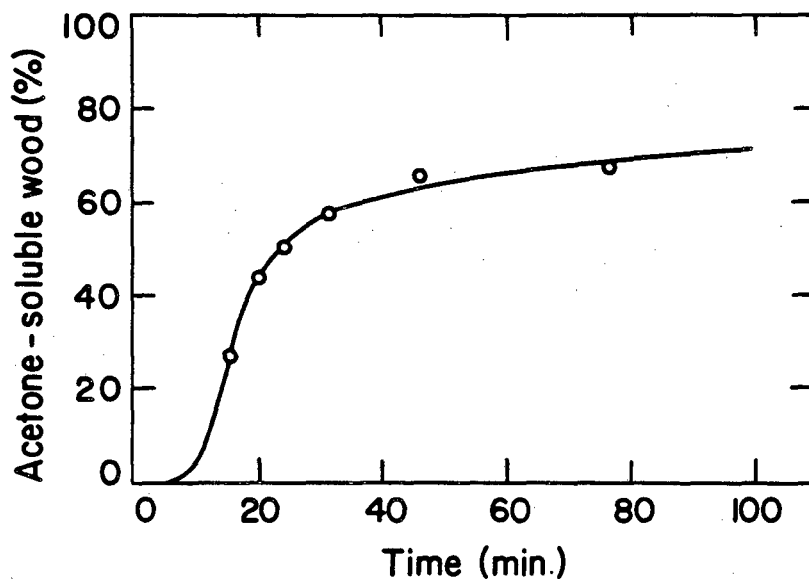
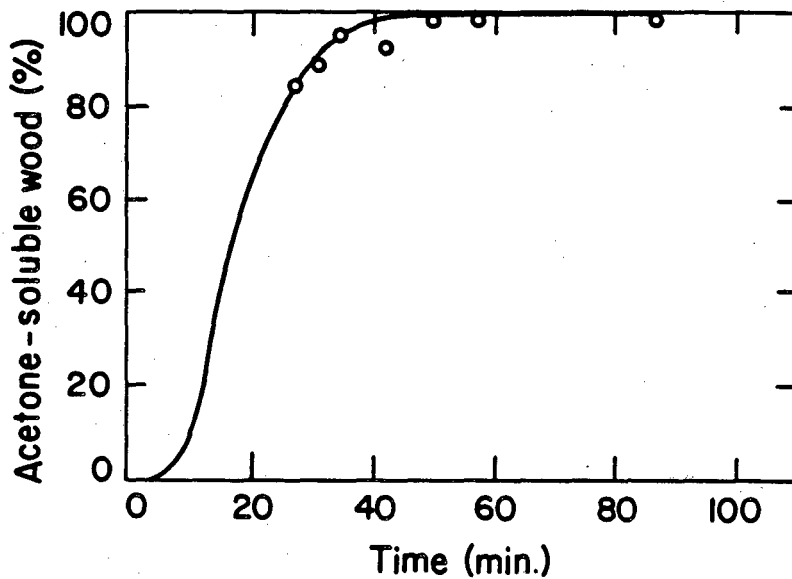


Fig. 29. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in Cyclohexanol at 180°C.



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Fig. 30. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in Cyclohexanol at 250°C.

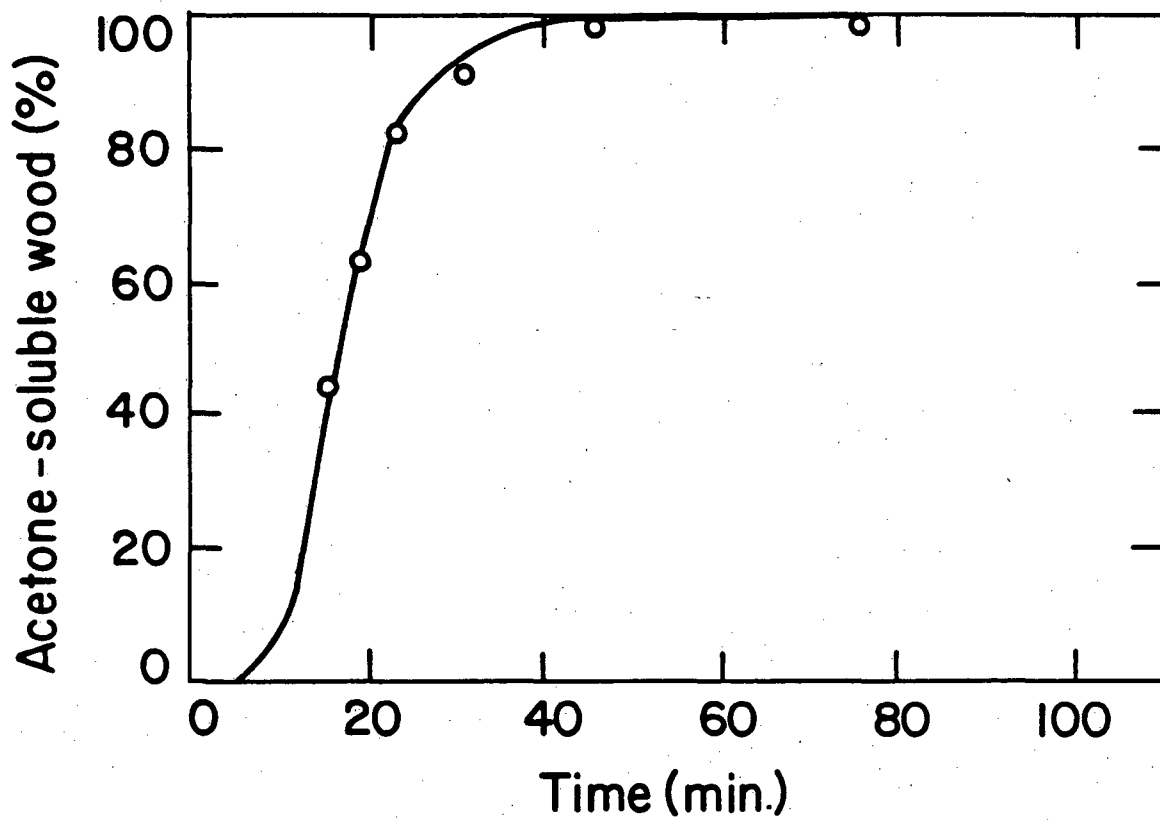
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Fig. 31. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.25 wt% H_2SO_4 in Cyclohexanol at 180°C.

produced. The following kinetic equation is used to computer fit the experimental data:

$$\frac{dx}{dt} = (k_1 H + k_2 W)(1-x)$$

where $k_1 H$ and $k_2 W$, respectively account for acid consumption and organic acids production; therefore,

$$\frac{dx}{dt} = K_{10} e^{\frac{-E_1}{RT}} (H_o^+ - y \cdot x) + K_{20} e^{\frac{-E_2}{RT}} z x^n (1-x)$$

where x = percent acetone-soluble wood, k_{10} and k_{20} are rate constants (min^{-1}), E_1 and $E_2 = 14$ and 30 KCal/gmole, respectively, $H = (H^+)_o - y \cdot x$ = percent available acid, and z = organic acids produced per unit conversion.

To compute conversion during heat-up, the same time-temperature dependence equations as in the acid-sulfation equilibrium model was used here. The k_1 and k_2 are tabulated in Table 35. Figures 32 and through 36 depict the conversion-time plots for phenol and cyclohexanol systems. The strategy diagram and computer program for the model are given in the Appendix.

Table 35. Table of Rate Constants for the Organic Acids Production Model.

$$\frac{dx}{dt} = \left(k_1 e^{\frac{-14000}{RT}} H + k_2 e^{\frac{-30000}{RT}} z x^{0.5} \right) (1-x)$$

Solvent System	Process Conditions Acid Conc.(%), Temp.(°C)	Rate Constants (min. ⁻¹)	
		k ₁ x10 ⁷	k ₂ (10 ¹³)·z
Butanol	0.1%, 180°C	0.5	0.1
	0.1%, 250°C		
	0.25%, 180°C		
Ethylene Glycol	0.1%, 250°C	0.5	0.075
	0.25%, 180°C		
	0.25%, 250°C		
Cyclohexanol	0.1%, 180°C	0.75	0.15
	0.1%, 250°C		
	0.25%, 180°C		
Phenol	0.1%, 180°C	2.5	0.35
	0.1%, 215°C		
	0.1%, 250°C		
	0.25%, 180°C		

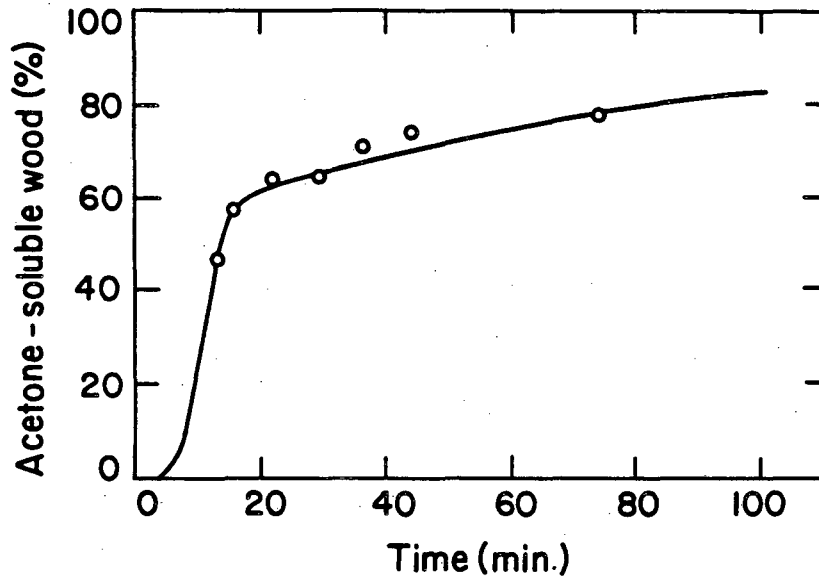


Fig. 32. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in phenol at 180°C.

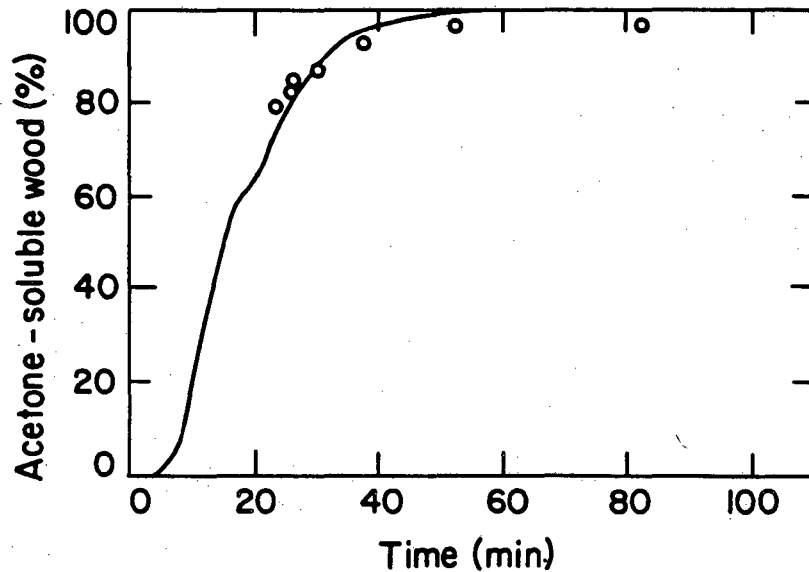
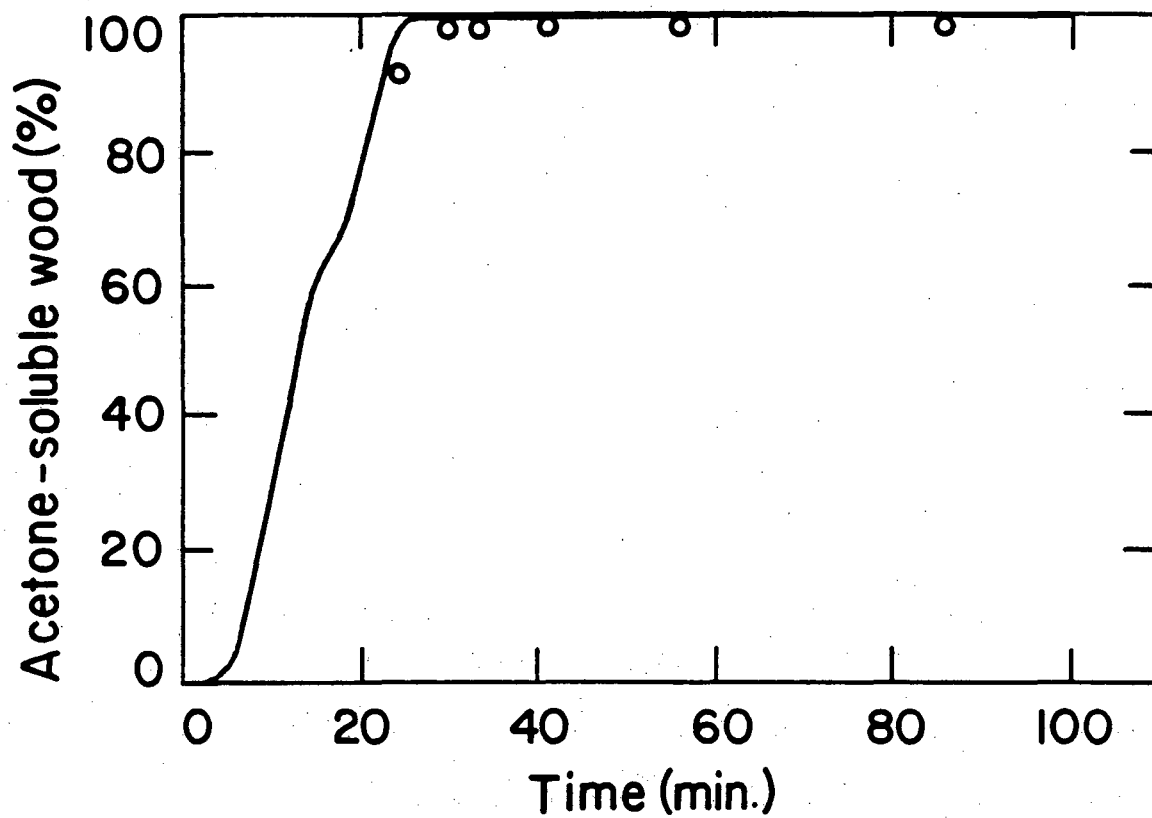


Fig. 33. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in phenol at 215°C.

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XBL 816-984

Fig. 34. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in phenol at 250°C.

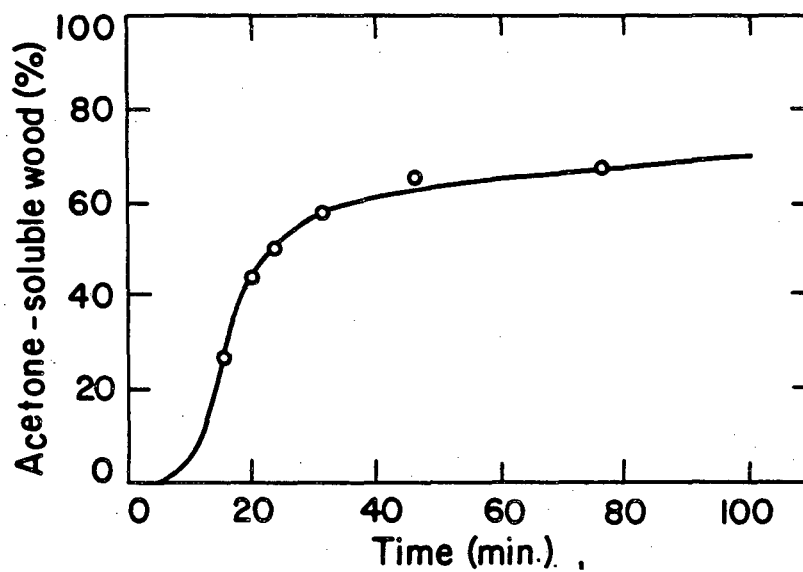
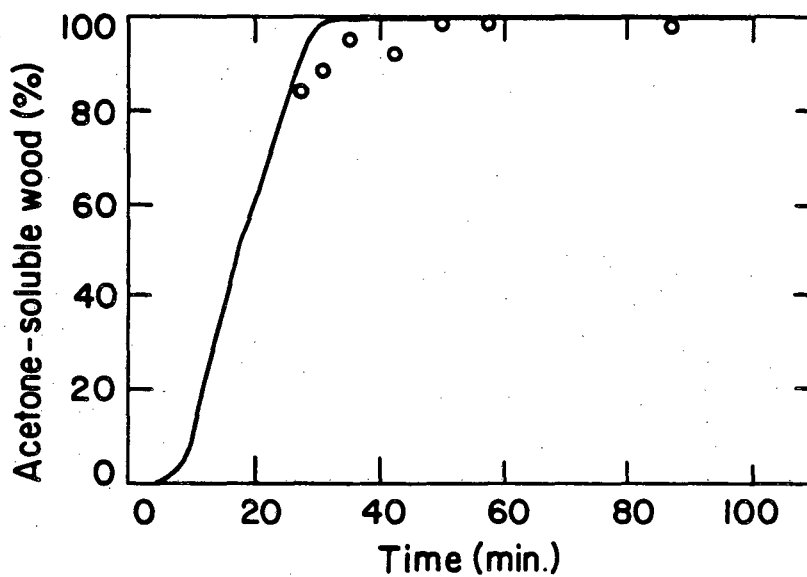


Fig. 35. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in Cyclohexanol at 180°C.



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Fig. 36. Percent Acetone-Insoluble Wood Versus Reaction Time; 0.1 wt% H_2SO_4 in Cyclohexanol at 250°C.

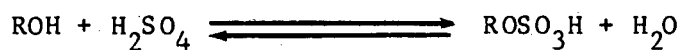
CHAPTER VI

SOLVOLYSIS PROCESS CHEMISTRY

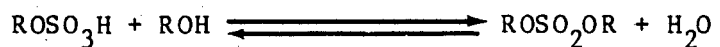
Earlier work at PERC laid the chemical foundations of a high temperature, high pressure process to liquefy wood. The reaction occurred via a controlled pyrolysis (thermal degradation) accompanied by reductive reactions with carbon monoxide as reductant. Due to the lower process temperature and the absence of reducing gas, the solvolysis reaction mechanism must be very different. In order to understand better the interactions in a system of acid, alcohol, and wood, the chemistry of such system will be explored here. Firstly, reaction of acid and alcohol in the absence of wood will be discussed. Secondly, reaction of alcohol and wood will be examined. Finally the acid-alcohol-wood system will be discussed with the goal of identifying those bonds that are broken leading to wood solubilization.

A. Sulfuric Acid-Alcohol

The reaction of sulfuric acid and alcohol can be represented by the following equations:



In excess alcohol,



In most sulfation reactions studied, excess acid was used. Reactions involving a small amount of acid have rarely been investigated. If we recall that acid is also consumed by some of the wood-derived products, the fact that significant slowing down in wood dissolution occurs only when over half of the wood is dissolved suggests that the acid consumption by process alcohol compared to consumption by wood-derived products is relatively minor.

B. Alcohol-Wood

Many researchers have published their alcohol-wood reactions findings but few have attempted to explain the reaction mechanism involved. Experiments were conducted to evaluate how wood interacts with alcohol. The results are shown in Table 36.

In the absence of acid, incomplete wood solubilization is achieved. The insoluble wood ranges from 51.6% in phenol to 89.5% in butanol. It is interesting to note that water alone is able to solubilize close to 60% of the wood, a figure surpassing phenol. The relatively high solubility in water might in part be due to the organic acid fraction of the hemicelluloses. The acid freed as a result of hemicellulose dissolution could be consumed by the alcohol, whereas with no acid consuming reaction in water the acid is available to attack wood. Another possible explanation is the length of heat-up time. Because of higher heat capacity, water takes twice as long to heat and hence allows more time for wood to dissolve.

C. Acid-Alcohol Wood

Comparing the result of runs with and without acid (Table 36), wood solubilization is clearly enhanced by acid. Although acidity is

Table 36. Solubilities of Wood in Alcohols With and Without Sulfuric Acid.

Solvent	Acidity pKa	Acetone Insolubles (%)	
		without acid	with acid
Butanol*	16.1	89.50	6.67
Ethylene Glycol	14.4	72.50	5.49
Cyclohexanol	15.5	81.82	3.52
Phenol	9.9	51.60	1.25
Water	15.8	41.68	32.83

Process conditions:

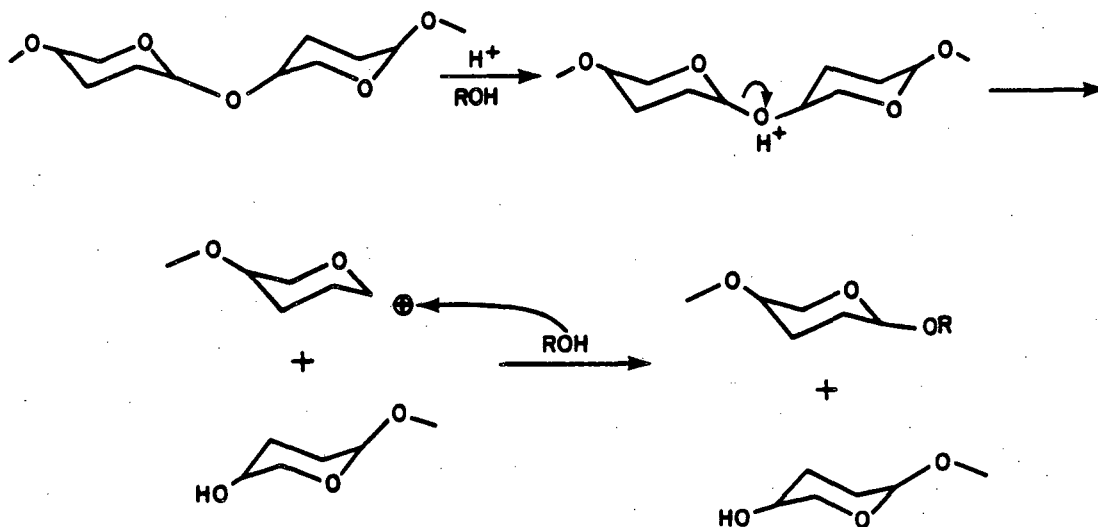
- 0.1% wt-% H₂SO₄ in Solvent
- 250° C, ½ hr
- 15 psia N₂

Note:

* 0.25% wt-% H₂SO₄, 180° C, 1 hr.

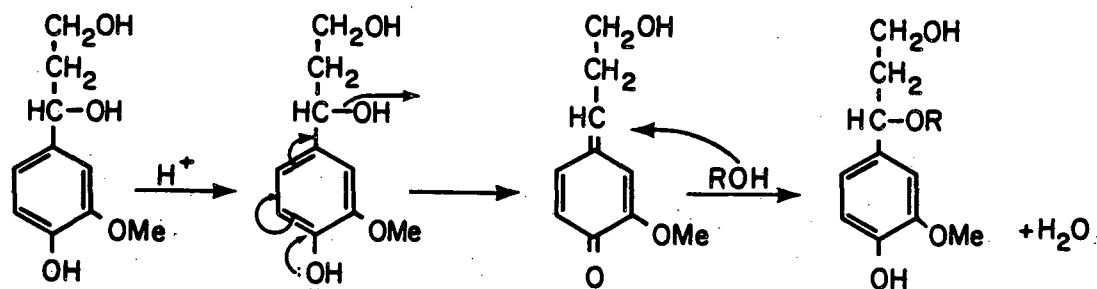
a factor that influences dissolution, phenol with its lowest pKa is still too weak an acid to show any catalytic action on the solubilization.

In the presence of acid, the cellulose and hemicellulose are believed to be depolymerized by acidic hydrolysis. The mechanism (123-125) calls for the formation of intermediate carbonium ions which are stabilized by alkoxy groups (or phenyl from phenol) in alcoholic medium. This transacetalization reaction would explain the solvent-incorporation result reported earlier.



XBL 816-913

If heating continues, the depolymerized carbohydrates dehydrate to yield hydroxymethylfurfural and water. This water elimination reaction is documented (125) to occur at or above $180^\circ C$, and in our case, the claim is supported by the formation of water. In using phenol, more highly depolymerized product, as indicated by its lower molecular

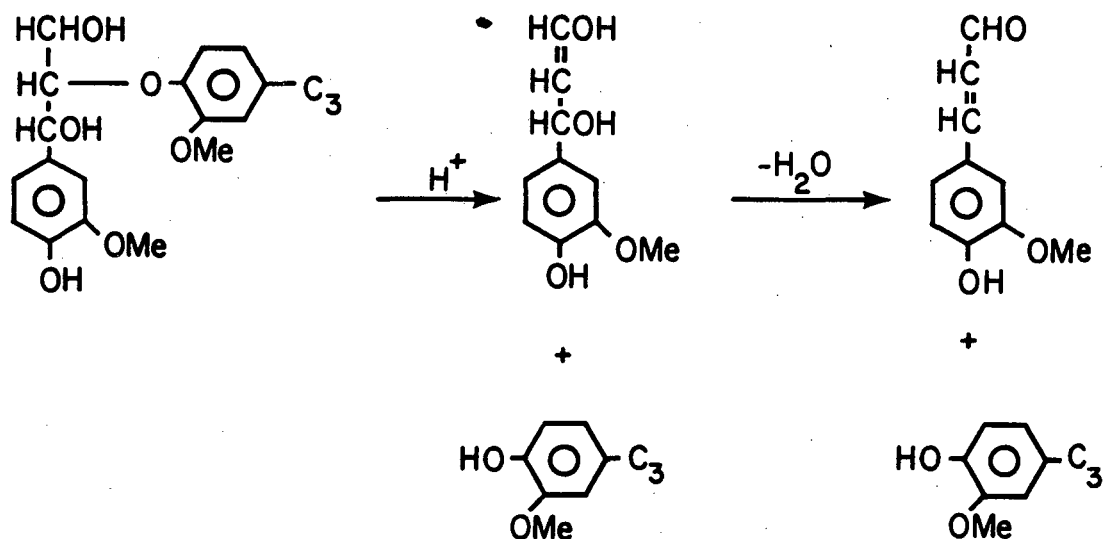


lignin monomer unit

XBL 816-908

Nikitin's proposed quinomethide mechanism was supported by Larsson and Lindberg (129), who performed a kinetic study on acidic hydrolysis of vanillyl methyl ether, taken as a lignin model compound. The mechanism proposed consists of quinomethide formation followed by α -ether bond scissioning. Kratzl et al. (130) also reported that quinomethide was involved in hydrolyzing cyclic α -aryl ether, another lignin model compound.

While it is possible to explain α -carbon etheric bond cleavage using Nikitin's theory, the fact that β -carbon etheric bonds account for half of the lignin crosslinks suggests that other mechanisms also operate during lignin solvolysis. Kratzl et al. (130) observed β -carbon-oxygen bond cleavage by performing an acid-catalyzed solvolysis of guaiacyl glycerol- β -acryl-ether at 185°C . Their proposed mechanism involves removal of γ -proton and elimination of guaiacyl, followed by elimination of the benzylic hydroxyl function as water.



XBL 816-910

More evidence was given by Hibbert (131) who isolated and identified four guaiacyl ketones (Figure 37, structures iv to vii) from the water soluble products obtained from the reaction of spruce wood and boiling ethanol. He believed the ketones were formed from β -hydroxy coniferyl alcohol (iii) or its keto form (ii), both are lignin monomer units. Adler and coworkers (132,133) extended Hibbert's assumption by demonstrating that α -arylglycerol β -ether (i), a recognized feature in lignin structure, also yielded the same ketones. Figure 37 illustrates the mechanism of ketones formation. The mechanism involves protonation of etheric oxygen followed by bond cleavage to form carbonium ion which is 'capped' by a hydroxyl group. In our case, alkoxyl (or phenyl) would be the capping agent, another mechanism for solvent incorporation.

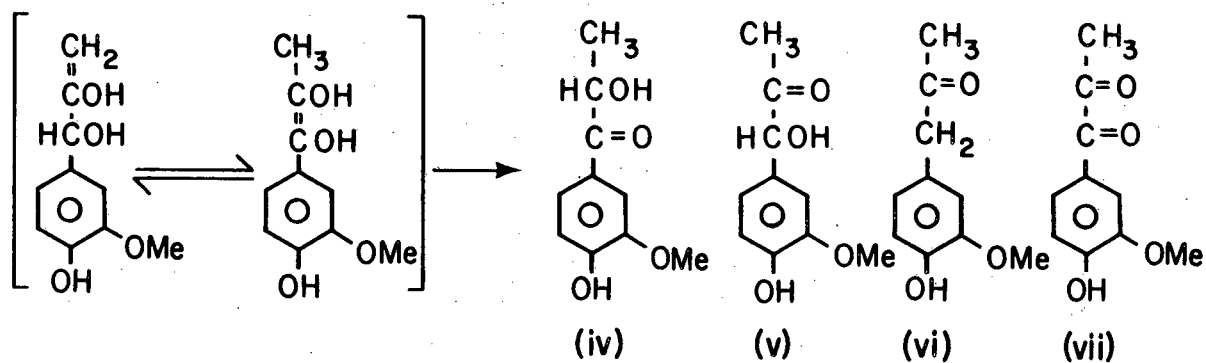
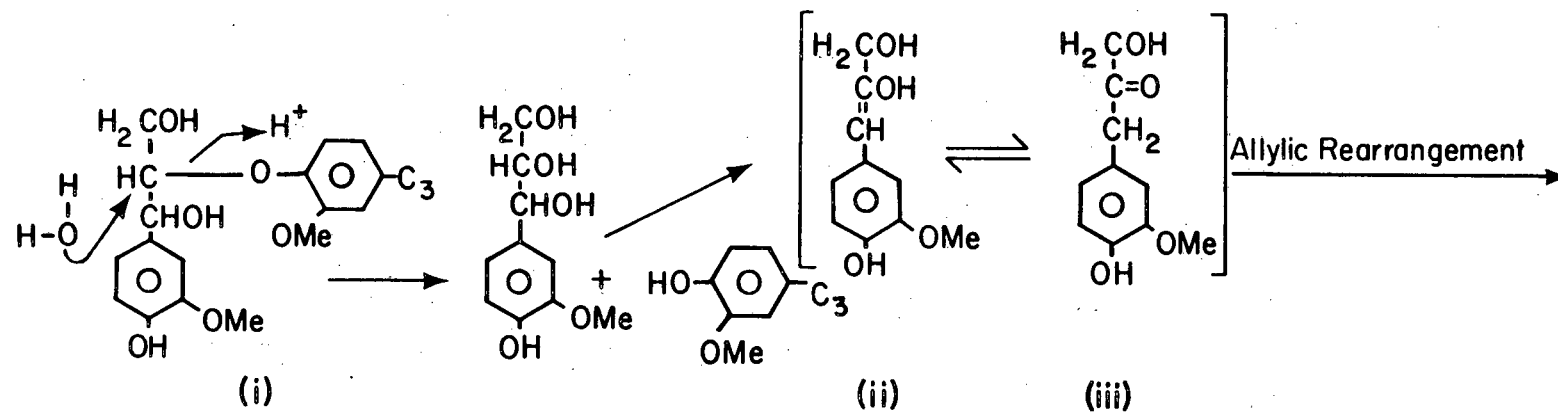


Fig. 37. The Mechanisms of α -aryl Glycerol β -ether Hydrolysis Yielding Hibbert Ketones.

XBL 816-911

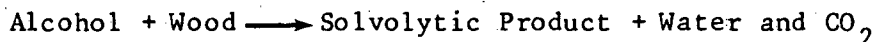
D. An Overall Picture

By fitting experimental observations and literature information into an overall picture, we can put together a reaction sequence leading to wood solubilization (Figure 38). The primary steps include protonation, bond cleavage and species stabilization.

Following the formation of hydronium ions, protonation is believed to occur rapidly such that C-O bonds cleavage can be achieved quickly. The resultant carbonium ion intermediates must be capped for stabilization if repolymerization is to be avoided. Alkoxy or phenyl groups are believed to serve the role of capping agents. The presence of hydronium ions also causes the depolymerized wood species to release water which lowers the product wood oxygen. At elevated temperatures (>250°C) and/or prolonged heating (>1 hr.), excessive dehydration causes the depolymerized wood to repolymerize and form acetone insolubles.

E. Liquefaction Stoichiometry

For better understanding of the solvolysis reactions, the following equation can be used to describe the chemical results:



At optimum process conditions, wood is almost entirely converted or solubilized. Among the by-products, water accounts for the majority (10 - 24% of dry starting wood), carbon dioxide makes up 99% of the off gas (0 - 4.5% of dry starting wood) with the rest shared among carbon monoxide, methane and ethane.

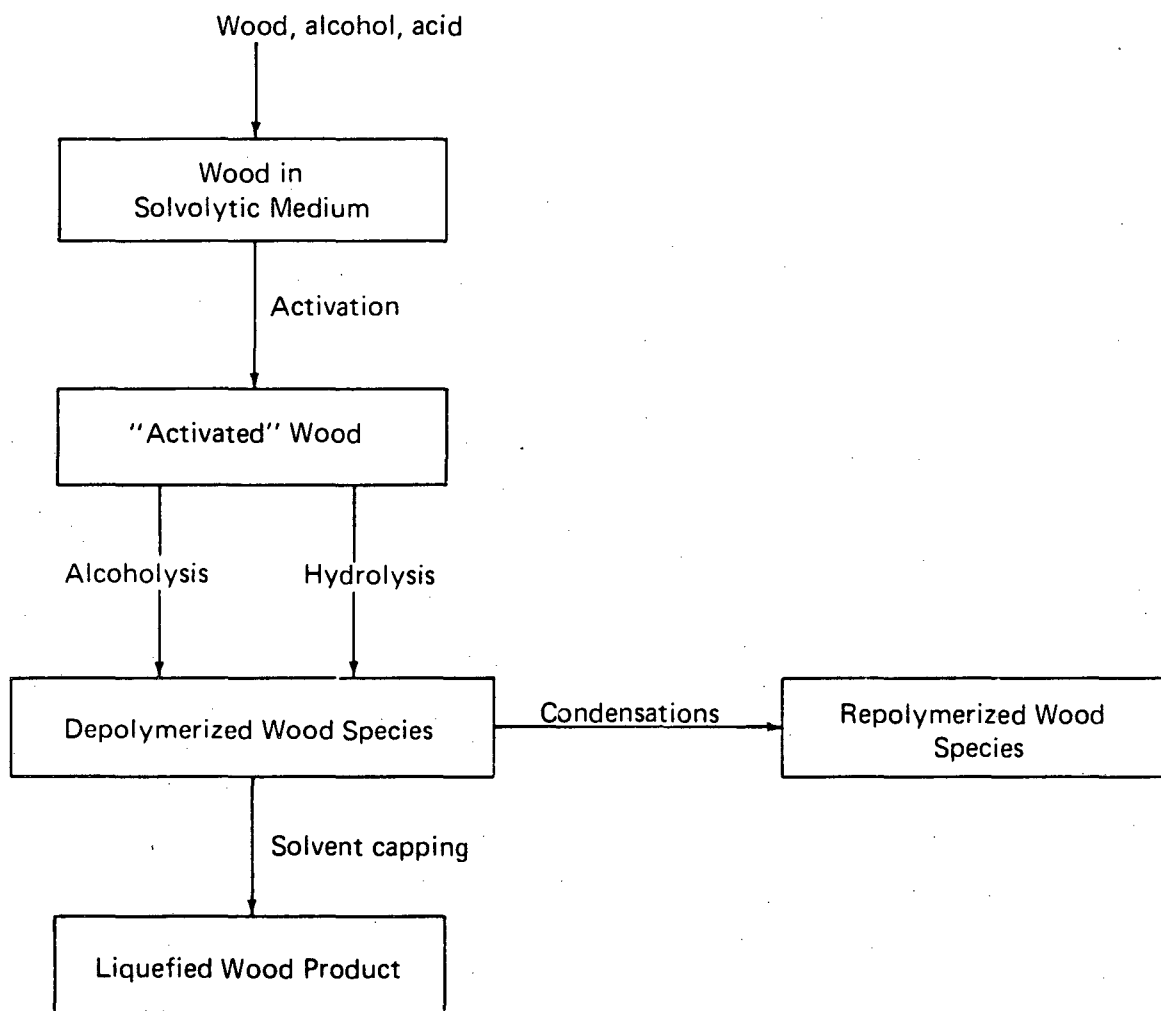
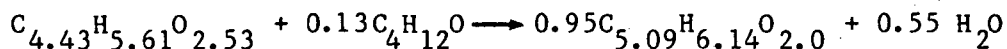


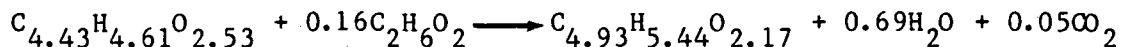
Fig. 38. Reactions Sequence Leading to Wood Solubilization in a Solvolytic Medium.

Below is a summary of equations for the four-solvent systems:

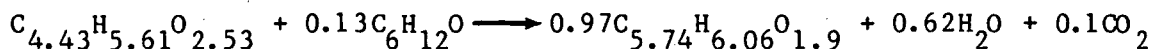
1. Butanol:



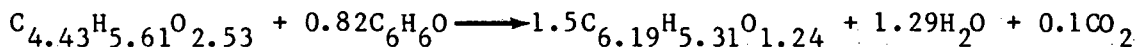
2. Ethylene Glycol:



3. Cyclohexanol:



4. Phenol:



The bases for the above equations are:

1. One hundred grams of starting wood (dry). Starting wood (dry) has 53.17% carbon, 5.61% hydrogen, 40.54% oxygen, also a few tenths of one percent of nitrogen, sulfur, and inorganic ash which are assumed negligible and thus not accounted for in the wood's formula.
2. Carbon dioxide was assumed to be the only gaseous product whose amount was calculated using ideal gas behavior.
3. Data for solvent incorporated, water produced, and product elemental compositions came from Tables 30 and 31.

F. Product Hydrogenation Prospect

The solvolytic product contains considerable amounts of oxygen (20-30%). In order to realize a higher heating value, further deoxygenation is necessary. One option is to catalytically

hydrogenate the product. Hydrogenation entails the advantage of reducing the phenolics in the product to cyclohexanols which are recycled to slurry the feed. This lessens the amount of solvent incorporated.

Figure 39 shows the heating value of biomass-derived oil and related organic materials as a function of oxygen content. A representative atomic hydrogen to carbon ratio of various fuels is shown in Figure 40. A good mid-range transportation fuel (diesel-jet fuel mixture) may be represented as a pure hydrocarbon containing 12-15% hydrogen by weight. The composition of this fuel and other petroleum derived liquid fuels are contrasted with PERC/LBL oil, our solvolytic products, and other solid fuels in Figure 41. Rough calculations show that for 100 lb of solvolytic product, 1.5×10^{15} SCF of hydrogen is required to make mid-range transportation fuel. This large amount of needed hydrogen could be a limiting factor in process economics.

Fig. 39. Higher Heating Values of Biomass-Derived Oils and Related Organic Materials as a Function of Oxygen Content.

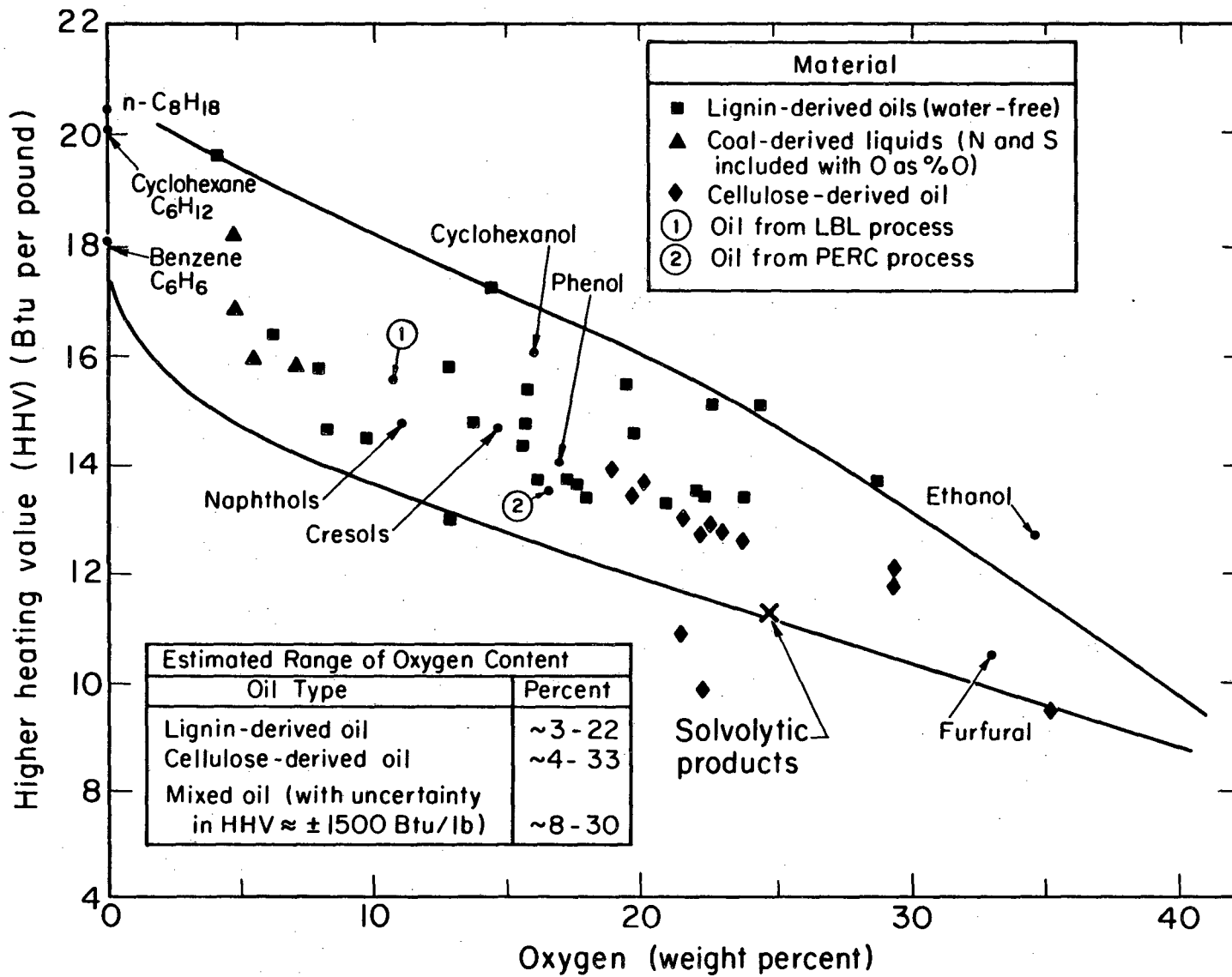
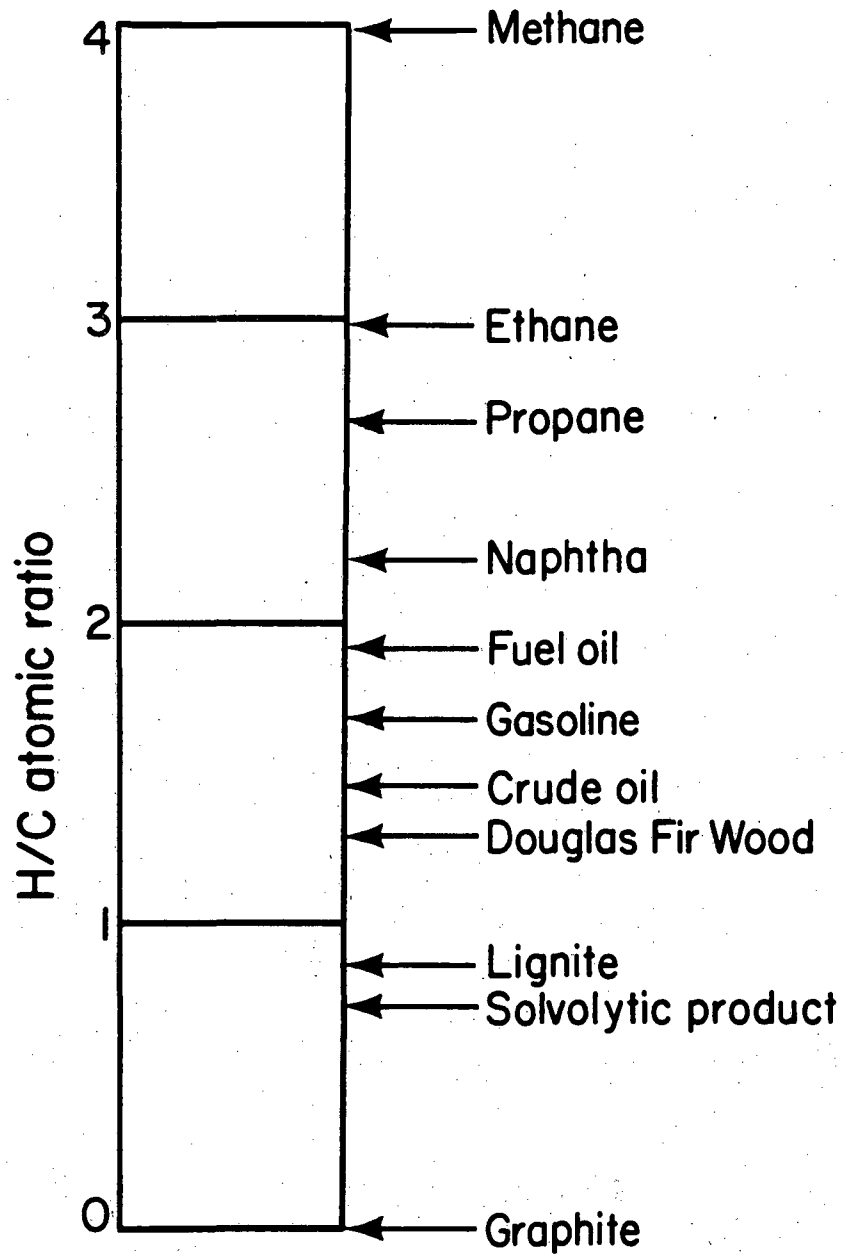


Fig. 39.

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Fig. 40. Atomic Hydrogen to Carbon Ratio of Various Fuels.

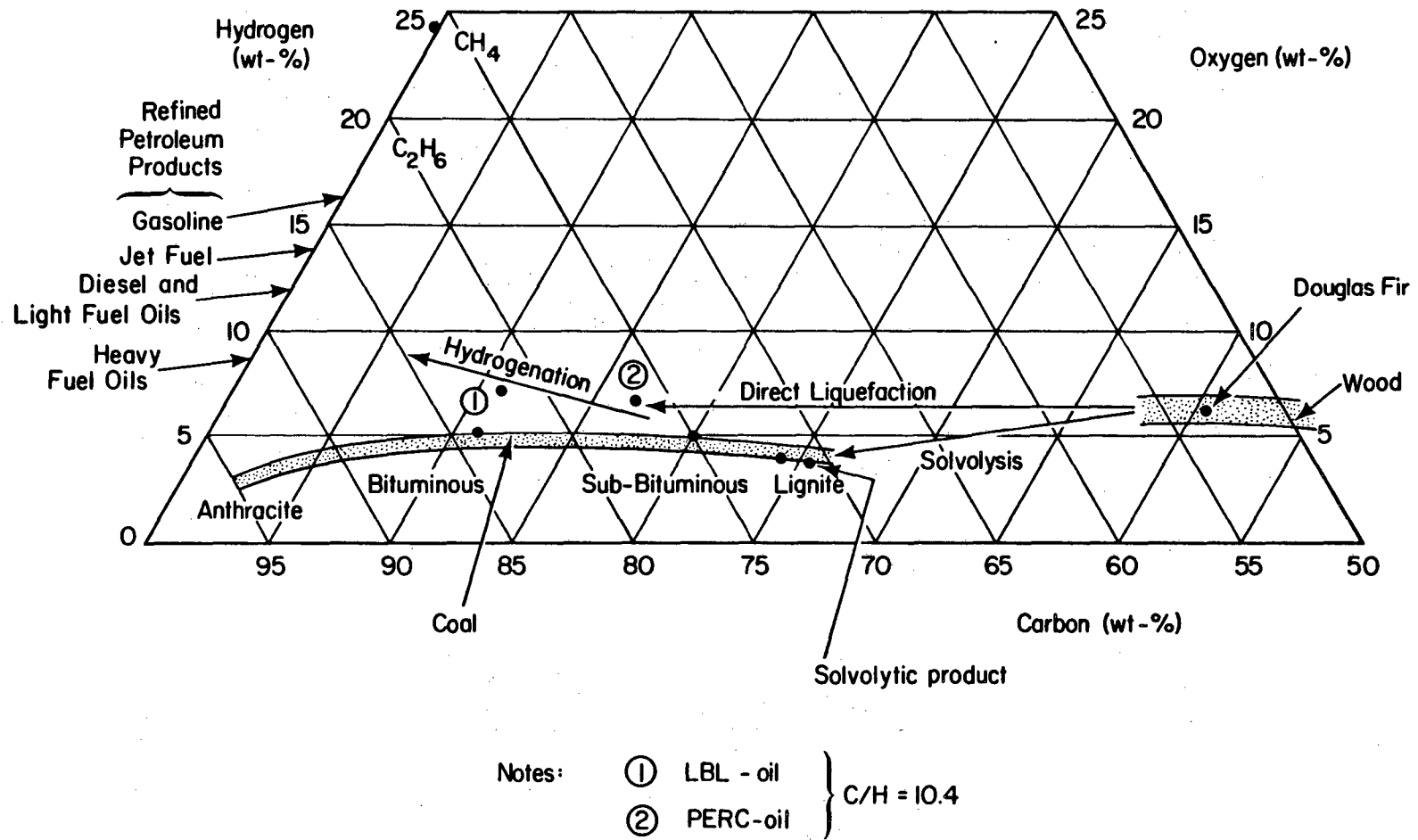


Fig. 41. Hydrogenation Prospects of the Solvolytic Wood Products.

CHAPTER VII

CONCLUSIONS

The process feasibility of utilizing simultaneous lignin alcoholysis and cellulose hydrolysis to dissolve wood is established. A system consisting of small amounts of sulfuric acid and a potentially wood-derived alcohol is demonstrated to be capable of cleaving the bonds which crosslink the polymeric wood structure. At 0.1 wt% sulfuric acid in phenol, it takes less than 30 minutes at 250°C to render over 95% of the wood acetone soluble whereas the original wood is less than 2% acetone soluble. No hydrogen or synthesis gas is required. Other solvents almost equally effective are cyclohexanol, ethylene glycol, and butanol.

A 4 to 1 solvent to wood ratio is found to adequately wet the wood and yield good overall conversion. Both speed of stirring and wood particle size exert small, essentially negligible, effects on conversion, indicating that wood solvolysis is kinetically controlled. Kinetic models have been generated to computer fit the experimental data; the results show that solvolysis is first order in wood and in available acidic protons.

From 10 - 75% (dry wood basis) of the solvents is found to be retained in the product. This is probably due to solvent alkoxylation (phenylation in the case of phenol) occurring during bond cleavage. Water, roughly 10 - 25% (dry wood basis) depending on solvent used, is generated during wood solvolysis. Its formation appears to be caused by dehydration and by condensation reactions responsible for wood

deoxygenation. At higher severity conditions, wood solubility drops accompanied by less solvent incorporation or more water formation. This indicates solvent alkoxylation is a means of stabilizing depolymerized wood fragments to keep them from repolymerizing.

The mechanism of wood solvolysis is believed to involve protonation of etheric oxygens which are the major links in lignin and carbohydrates. The protonation is quickly followed by bond scission, generating reactive radicals which are prone to recombine unless stabilizers are present. Under inert atmosphere, the solvent is believed to play the role of a stabilizer. Oxygen reduction is mainly achieved by dehydration and/or mild condensation reactions.

This work has demonstrated that wood solubilization may take place at conditions considerably milder than the current PERC process (360°C, 2000 psig CO). Better understanding of wood behavior in a medium of acid and alcohol could well pave the way for wood liquefaction processes which are less energy and capital intensive and more energy efficient with a better product distribution.

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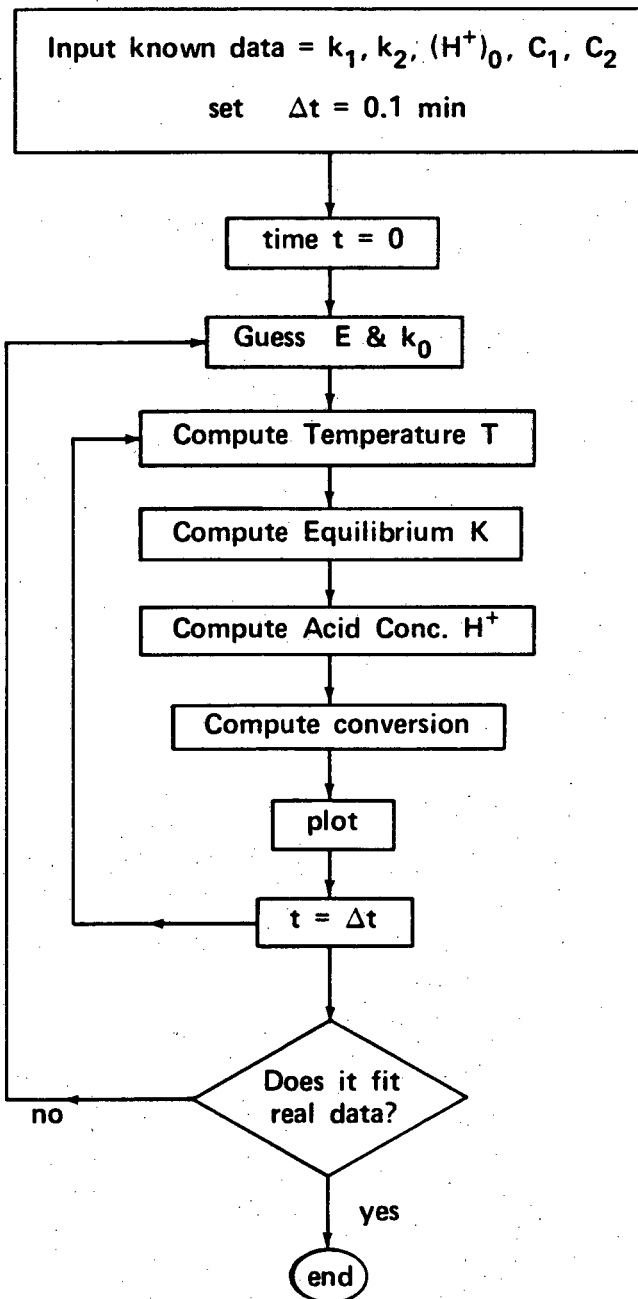
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APPENDIX

A. Acid-sulfation Equilibrium Model

1. Program Flow Sheet



2. Program

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1 | -----
31 | PROGRAM ACID-BO MODEL
61 | -----
81 | CALCULATES AND DRAWS THE
   | CURVE OF CONVERSION VS
   | TIME
131 |
151 |
181 | Initialize The Variables.
210 | GOSUB 871
241 |
271 | Set The Variables.
301 | GOSUB 4771
331 |
361 | Draw The Graph Axis
391 | GOSUB 5551
421 |
451 | Plot The Data Points.
481 | GOSUB 6421
511 |
541 | Compute And Draw The Curve
571 | GOSUB 2181
580 |
582 | Print graph and variables
585 | GOSUB 8940
601 |
631 | END
731 |
751 |
781 |
811 | -----
   |
   | SUBROUTINE Initializes the
   | Variables
   |
   | T1=20
101 | T2=180
102 | T2=RXN TEMP
1021 | K0=10^7
1031 | K0=RATE CONSTANT
1051 | E=14000
1061 | E=ACTIVATION ENERGY
1081 | H= 1
1111 | K1=-20
1141 | K2=14000
1171 | Y= .16
1190 | C1=-.0509
1201 | A9= 1
1231 |
1261 | RETURN
1291 |
1321 |
1351 |
1381 | -----
1411 |
1441 | SUBROUTINE Initializes T,
1471 | X, And S, And Defines The
1501 | Time-Temp And The Temp-
1531 | Equilibrium FUNCTIONS.
1561 | WHERE T=THE TEMPERATURE,
1563 | X=THE CONVERSION
1591 |
1621 | T=20
1651 | X=0
1711 | Y= .16
1741 |
1771 | DEFINE THE EQUILIBRIUM AND
   | TEMPERATURE FUNCTION
   |
   | S.
1801 |
1831 | Define The Time-Temp Func
   | tion.
1861 | DEF FNT(N) = 300-EXP(5.6348
   | +C1*N)+273.15
1891 |
1921 | Define The Temp-Equilibri
   | um Function.
1951 | DEF FNK(N) = EXP(K1+K2/N)
1981 |
2011 | RETURN
2041 |
2071 |
2101 |
2131 | -----
2161 |
2191 | SUBROUTINE To Compute And
   | Draw The Curve.
2221 |
2251 |
2281 | Initialize T, X, And S,
2282 | And define the time-Temp
2283 | And the Temp-Equil const
2284 | functions.
2341 | GOSUB 1411
2371 |
2401 | MOVE 0,0
2431 |
2461 | DO LOOP TO CALCULATE THE
   | CURVE.
2491 |
2521 | FOR I=A9 TO 100 STEP A9
2551 | IF T=T2+273.15 THEN GOTO 26
   | 41 | T2 IS THE MAX TEMP
2581 | T=FNT(I) | Find Temp
2611 | IF T>T2+273.15 THEN T=T2+27
   | 3.15
2641 | K=FNK(T) | Find The Equilib
   | rium Const
2671 |
2701 | IF Y*X>.05 THEN GOSUB 3211
   | ELSE H= 1-Y*X
2731 |
2821 | GOSUB 3631 | Compute Delta
   | X

```

```

2851 |
2881 | CALCULATE THE NEW X
2911 X=X+X1
2941 |
2971 | PLOT THE POINT (time,X)
3001 DRAW I,X
3031 NEXT I
3050 |
3061 RETURN
3091 |
3121 |
3151 |
3181 | -----

3211 |
3241 | SUBROUTINE To Compute H
3244 |
3246 |
3271 FOR J=1 TO 4
3301 K9=1/K
3331 D=.1-Y*X
3361 M=K9-.05*K9/H
3391 H1=(D+SQR(D^2-4*M))/2
3421 H2=(H1+H)/2
3451 NEXT J
3460 |
3481 H=H2
3541 |
3571 RETURN
3580 |
3581 |
3582 |
3601 | -----

3631 |
3651 | SUBROUTINE Computes Delta
      X
3691 |
3721 |
3751 X1=A9*K0*EXP(-E/(1.987*T))*
      H*(1-X)
3781 |
3791 RETURN
3811 |
3840 |
3841 |
3871 |
3901 | -----

4600 |
4610 | SUBROUTINE to set the
4611 | variables
4620 |
4741 |
4771 DISP "THE VALUES OF THE CON
      STANTS ARE:"
4801 DISP "T1=";T1
4831 DISP "T2=";T2
4861 DISP "E=";E
4891 DISP "K0=";K0
4921 DISP "H=";H

4951 DISP "K1=";K1
4981 DISP "K2=";K2
5011 DISP "Y=";Y
5041 DISP "A9=";A9
5071 DISP
5101 DISP
5131 DISP "ARE YOU GOING TO CHAN
      GE ANY OF THE VARIABLES? A
      NSWER EITHER YES OR NO."
5161 |
5191 INPUT J1$
5221 |
5251 IF NUM(J1$)=NUM("N") THEN R
      ETURN
5281 IF NUM(J1$)=NUM("Y") THEN G
      OTO 5341 ELSE GOTO 5131
5311 |
5341 DISP "AFTER EACH VARIABLE A
      ND ITS VALUE ARE ENTERED, P
      RESS ENDLIN."
5371 DISP "AFTER ALL OF THE CHAN
      GES ARE MADE, PRESS CONT."
5401 PAUSE
5420 |
5431 GOTO 4771
5461 |
5491 |
5521 |
5525 | -----

5551 REM SUBROUTINE DRAWS AXIS
5581 |
5611 |
5641 GCLER
5671 SCALE -10,110,-.1,1.1
5701 XAXIS 0,5,0,110
5731 YAXIS 0,.05,0,1
5761 |
5791 REM * LABEL X-AXIS *
5821 |
5851 LDIR 0
5881 FOR X=0 TO 100 STEP 20
5911 MOVE X-2,5,-.1
5941 LABEL VAL$(X)
5971 NEXT X
6001 |
6031 REM * LABEL Y-AXIS *
6061 |
6091 LDIR 0
6121 FOR Y=0 TO 1 STEP .1
6151 MOVE -10,Y-.03
6181 LABEL VAL$(Y)
6211 NEXT Y
6230 |
6241 MOVE 0,0
6271 |
6301 RETURN
6331 |
6361 |
6391 |

```

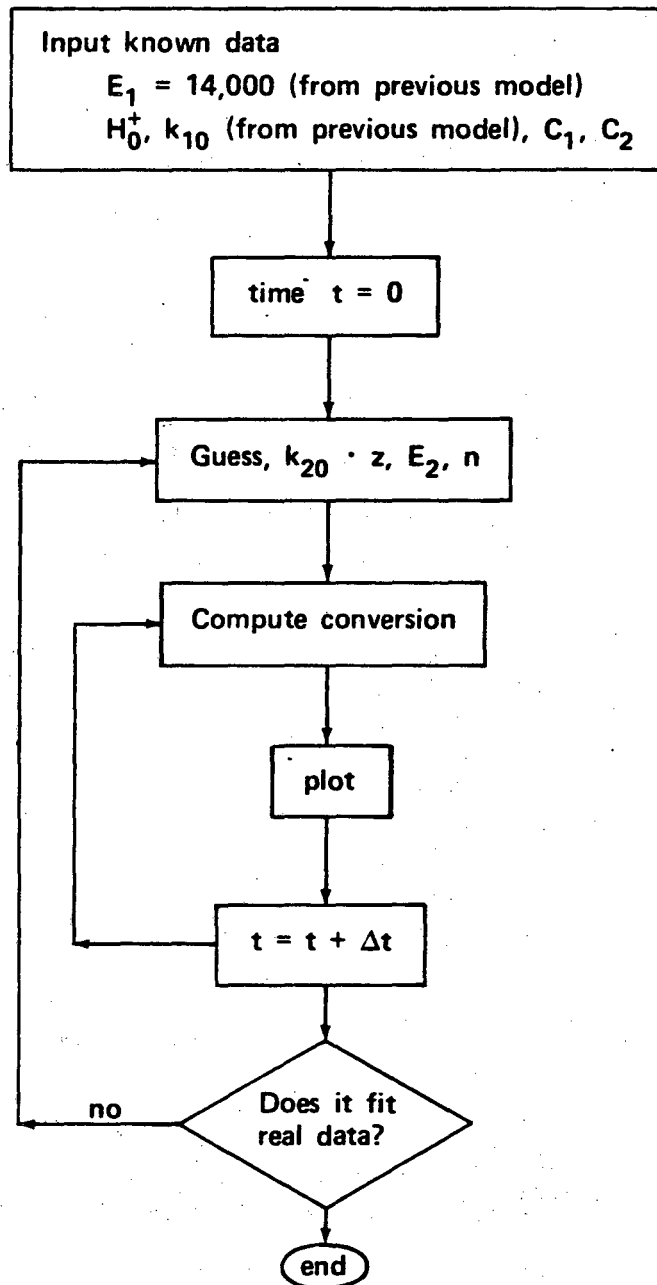
```

6400 | -----
6421 | SUBROUTINE PLOTS THE DATA
      | POINTS
6451 |
6481 |
6511 | READ N
6541 | FOR I=1 TO N
6571 | READ X,Y
6601 |
6631 | GOSUB 6811 ! GRAPH POINTS
6661 |
6691 | NEXT I
6721 |
6735 | RETURN
6730 |
6735 |
6751 | DATA 7,13 9, 47,17 7, 58,21
      | 4, 64,28 9, 64,36 4, 71,43
      | 9, 74,73 9, 75 ! DATA AT
      | 1%@180c
6781 |
6785 |
6790 |
6795 | -----
6811 | REM * PLOT CROSS *
6820 |
6824 |
6841 | MOVE X,Y
6871 | IMOVE 0, 025 @ IDRAW 0, - 05
6901 | IMOVE 1,5, 025 @ IDRAW -3,0
6920 |
6931 | RETURN
6932 |
6933 |
6934 |
6937 | -----
6940 | SUBROUTINE to Print
6941 | graph and variables.
6942 |
6943 |
6945 | COPY
6950 | PRINT "T1=";T1,"T2=";T2,
      | " E=";E,"K0=";K0," H=";H
      | "K1=";K1,"K2=";K2," Y="
6955 | PRINT "A1=";A1,"A9=";A9
6960 |
6965 | RETURN
6966 |
6968 |
6970 |
6972 | -----
6991 |
7021 | DATA 7,13 1, 47,15 7, 58,21
      | 4, 64,28 9, 64,36 4, 71,43
      | 9, 74,73 9, 78 ! DATA AT
      | 1%@180c
7051 | DATA 7,23 3, 79,26, 835,26,
      | 85,29 8, 87,37 3, 93,52 3,
      | 96,82 3, 97 ! DATA AT 1%@
      | 2150
7081 | DATA 7,23 8, 92,29 6, 98,33
      | 3, 98,40 8, 985,55 8, 99,5
      | 5,8, 99,85 8, 99 ! DATA AT
      | 1%@2500
7090 | DATA 6,13 8, 61,19 9, 9,24,
      | 8, 96,28 8, 96,43 8, 98,73,
      | 8, 99 ! DATA AT 25%@180c
7111 | -----
7141 | ! DATA FOR CYCLOHEXANOL
7171 | DATA 6,15 65, 27,20 4, 438,
      | 24,15, 504,31 65, 58,46 65,
      | 65,76 65, 675 ! DATA AT 1
      | % @180c
7201 | DATA 7,27 15, 845,30 9, 884
      | 34,65, 95,42 15, 927,49 65
      | 982,57 15, 985,87 15, 987
7231 | ! DATA AT 1% @2500
7240 | DATA 6,15 5, 442,19 25, 631
      | 23, 825,30 5, 909,45 5, 98
      | 1,75 5, 985 ! DATA AT 25%@
      | 1800
7261 | -----
7291 | ! DATA FOR BUTANOL
7321 | DATA 7,18, 199,22 75, 358,2
      | 6 5, 451,34, 523,41 5, 538,
      | 49, 595,79, 648 ! DATA AT
      | 1% @ 1800
7351 | DATA 4,43 4, 927,50 9, 931,
      | 73 4, 868,103 4, 831 ! DATA
      | AT 1% @ 2500
7381 | DATA 6,20 1, 487,27 6, 648,
      | 35 1, 823,50 1, 898,80 1, 9
      | 33,95 1, 963 ! DATA AT 25%
      | @ 1800
7411 | -----
7420 | ! DATA FOR ETHYLENE GLYCOL
7441 | DATA 5,23 2, 767,30 7, 902,
      | 38 2, 947,53 2, 945,83 2, 9
      | 6 ! DATA AT 1% @ 2500
7471 | DATA 6,15 15, 51,18 9, 668,
      | 22 65, 708,30 15, 802,45 15
      | 852,75 15, 952 ! DATA AT
      | 25% @1800
7501 | DATA 4,22 5, 955,37 5, 97,5
      | 2,5, 965,82 5, 96 ! DATA AT
      | 25% @ 2500

```

B. Organic Acids Production Model

1. Program Flow Sheet



2. Program

```

1 | -----
31 | PROGRAM ORGANIC ACID MODEL
61 | -----
91 | CALCULATES AND DRAWS THE
    | CURVE OF CONVERSION VS
    | TIME
121 |
151 |
181 | Initialize The Variables
211 | GOSUB 871
241 |
271 | Set The Variables
301 | GOSUB 4771
331 |
361 | Draw The Graph Axis
391 | GOSUB 5551
421 |
451 | Plot The Data Points
481 | GOSUB 6421
511 |
541 | Compute And Draw The Curve
571 | GOSUB 2161
580 |
582 | Print graph and variables
585 | GOSUB 6940
601 |
631 | END
721 |
751 |
781 |
911 | -----

841 |
871 | SUBROUTINE Initializes the
    | Variables
901 |
931 |
961 | T1=20
991 | T2=180
1041 | H1= 1
1051 | E1=14000
1081 | E2=30000
1111 | K1=2.5*10^7
1141 | K2= .35*10^-13
1190 | C1=-.061
1201 | A9= .1
1231 |
1261 | RETURN
1291 |
1321 |
1351 |
1381 | -----

1411 |
1441 | SUBROUTINE Initializes T,
1471 | X And Defines The
1501 | Time-Temp FUNCTION

1591 |
1621 | T=20
1651 | X=0
1681 | Y=.16
1741 |
1801 |
1831 | Define The Time-Temp Func
    | tion.
1861 | DEF FNT(N) = 300-EXP(5.6348
    | +01*N)+273.15
1891 |
1981 |
2011 | RETURN
2041 |
2071 |
2101 |
2131 | -----

2161 |
2191 | SUBROUTINE To Compute And
    | Draw The Curve
2221 |
2251 |
2281 | Initialize T and X and
2282 | define the time-Temp
2284 | function.
2341 | GOSUB 1411
2371 |
2401 | MOVE 0,0
2431 |
2461 | DO LOOP TO CALCULATE THE
    | CURVE.
2491 |
2521 | FOR I=A9 TO 100 STEP A9
2531 | IF T=T2+273.15 THEN GOTO 25
    | 61 ! T2 is the max temp.
2541 | T=FNT(I)
2551 | IF T>T2+273.15 THEN T=T2+27
    | 3.15
2561 | H=H1-Y*X
2571 | IF H<0 THEN H=0
2581 | X1=A9*(K1*EXP(-E1/(1.987*T))
    | )*H+K2*EXP(-E2/(1.987*T))*X
    | ^ .5)*(1-X)
2591 | X=X1+X
2595 |
2597 | DRAW I,X
2601 |
2610 | NEXT I
2620 |
2611 | RETURN
2640 |
2641 |
2671 |
2691 | -----

4500 |
4510 | SUBROUTINE to set the
4511 | variables.
4520 |

```

```

4741 |
4751 | DISP "THE VALUES OF THE CON
START: ARE:"
4801 DISP "T1=";T1
4831 DISP "T2=";T2
4861 DISP "E1=";E1
4891 DISP "E2=";E2
4951 DISP "K1=";K1
4961 DISP "K2=";K2
5000 DISP "H1=";H1
5041 DISP "A9=";A9
5071 DISP
5101 DISP
5131 DISP "ARE YOU GOING TO CHAN
GE ANY OF THE VARIABLES? A
NSWER EITHER YES OR NO."
|
5161 |
5191 INPUT J1#
5221 |
5251 IF NUM(J1#)=NUM("N") THEN R
ETURN
5281 IF NUM(J1#)=NUM("Y") THEN G
OTO 5341 ELSE GOTO 5131
5311 |
5341 DISP "AFTER EACH VARIABLE A
ND ITS VALUE ARE ENTERED, P
RESS ENDLINE."
5371 DISP "AFTER ALL OF THE CHAN
GES ARE MADE, PRESS CONT."
5401 PAUSE
5420 |
5431 GOTO 4771
5461 |
5491 |
5521 |
5525 | -----

5551 REM SUBROUTINE DRAWS AXIS
5581 |
5611 |
5641 GOCLEAR
5671 SCALE -10,110,-.1,1
5701 XAXIS 0,5,0,110
5731 YAXIS 0, .05,0,1
5761 |
5791 REM * LABEL X-AXIS *
5821 |
5851 LDIR 0
5881 FOR X=0 TO 100 STEP 20
5911 MOVE X-2.5,-.1
5941 LABEL VAL$(X)
5971 NEXT X
6001 |
6031 REM * LABEL Y-AXIS *
6061 |
6091 LDIR 0
6121 FOR Y=0 TO 1 STEP .1
6151 MOVE -10,Y-.03
6181 LABEL VAL$(Y)
6211 NEXT Y

6241 MOVE 0,0
6271 |
6301 RETURN
6331 |
6361 |
6391 |
6400 | -----

6421 | SUBROUTINE PLOTS THE DATA
POINTS
|
6451 |
6481 |
6511 READ N
6541 FOR I=1 TO N
6571 READ X,Y
6601 |
6631 GOSUB 6811 ! GRAPH POINTS
6661 |
6691 NEXT I
6721 |
6725 RETURN
6730 |
6735 |
6751 DATA 7,13,1,47,15,7,58,21
4,64,28,9,64,36,4,71,43
9,74,73,9,78 ! DATA AT
1%@180c

6781 |
6785 |
6790 |
6795 | -----

6811 REM * PLOT CROSS *
6820 |
6824 |
6841 MOVE X,Y
6871 IMOVE 0, .025 @ IDRAW 0,-.05
6901 IMOVE 1.5, .025 @ IDRAW -3,0
6920 |
6931 RETURN
6932 |
6933 |
6934 |
6937 | -----

6940 | SUBROUTINE to Print
6941 | graph and variables.
6942 |
6943 |
6945 COPY
6950 PRINT "T1=";T1,"T2=";T2,
"E1=";E1,"E2=";E2,"K1=";
K1,"K2=";K2," Y=";Y," H=
";H
6955 PRINT "A1=";A1,"A9=";A9
6960 |
6965 RETURN
6966 |
6968 |

```


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