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**ENERGY & ENVIRONMENT
DIVISION**LIQUID FUELS FROM BIOMASS:
CATALYSTS AND REACTION CONDITIONS

Manu Seth, Sabri Ergun, Ted Vermeulen and Roger Djafar

April 1980

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CATALYSTS AND REACTION CONDITIONS

Manu Seth, Sabri Ergun,
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April 1980

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ABSTRACT

The use of α -phellandrene as a hydrogen transfer agent in wood liquefaction was studied at 200°C. No significant thermally promoted hydrogen transfer occurred under these conditions. Dilute sulfuric acid was added to test the possibility of hydride transfer from α -phellandrene to wood. Extensive solvent alkylation of the wood occurred in the presence of up to 2 wt-% of sulfuric acid. Addition of palladium as a hydrogenation catalyst resulted in lower overall conversion based on the toluene-insoluble residue obtained, and in lowered levels of solvent alkylation.

Several inorganic salts were tested as catalytic additives for wood liquefaction at 250°C in the presence of tetralin as a possible hydrogen donor. No hydrogen transfer from the solvent was observed. About 50% by weight of the wood was converted to gases and toluene and water extractable materials in the absence of an additive. Of the additives tested, nickel chloride, sodium carbonate and ferric chloride resulted in wood conversions greater than or equal to those obtained in the absence of an additive. Toluene extraction was used as a measure of oil yield. Of the additives tested, ferric chloride resulted in the highest yield of toluene solubles with about 28 wt.% of the wood being converted to oil. Atomic H/C ratios of the toluene extracts ranged from 1.51 to 0.85 compared to 1.21 for untreated wood. The O/C ratios of the toluene extracts ranged from 0.18 to 0.44 compared to an O/C ratio of 0.57 for untreated wood. Nuclear magnetic resonance spectroscopy indicated that the toluene soluble fraction of the products

contained benzylic, phenolic and alcoholic protons. Ultraviolet spectra indicated the presence of carbonylic and aldehydic groups.

I. INTRODUCTION

The depletion of conventional fuels has led to increasing emphasis on developing alternate sources of clean energy. Renewable energy resources are the preferred long-term solution for supplying the energy needs of industrial economies. The conversion of biomass to fuels is an important route to energy supply, and is receiving increased government funding. It is estimated that crop, forestry, and manure residues amount to 430 million dry tons within the continental United States (1). Of this amount, crop wastes constitute 280 million tons, livestock and poultry manure 30 million tons, and logging residues about 120 million tons.

Wood and forest residues are readily available and have been selected for major developmental programs. Gasification, direct combustion, and the production of liquid fuels are some of the energy-conversion methods being developed for wood utilization.

This study is aimed at screening various biomass liquefaction techniques. Sawdust from Douglas fir wood flour was selected as an abundant softwood. Several catalysts were compared for their effectiveness in wood liquefaction. Products from these treatments were characterized and compared.

A. Chemical Structure of Wood

The chemistry of wood can for the most part be described by the chemistry of its constituents. Wood is composed of carbohydrates, phenolic materials, terpenes, aliphatic acids, proteins, and inorganic constituents. Of these the chief carbohydrate is the polysaccharide, cellulose, which accounts for about 50% by weight of dry wood. Hemicelluloses are related polysaccharides comprise about 10 to 30% of the wood. The phenolic substance, lignin, amounts to about 15 to 35% of wood, and is generally higher in softwoods than in hardwoods (2).

Cellulose is formed from D-glucose blocks joined by α -1,4-glucosidic bonds. Wood cellulose occurs as polymeric molecules with molecular weights generally in the range of 80,000 to 340,000, corresponding to degrees of polymerization of 500 to 2,100 (3). If one considers conformational analysis in which anhydroglucopyranose units are in chair form, the structure of cellulose is as shown in Fig. 1.

Hemicelluloses are complex molecular chains formed of xylose or arabinose backbones. Xylans combined with substantial amounts of uranoic acids are the most important hemicelluloses in wood (4). Other important species are arabinose-glucose-uranoic acid polymers and glucose-mannose polymers.

Lignin is a polymeric substance whose complexity results from the variety of ways in which the multitude of monomeric units can be linked. Freudenberg (5) has considered that the biogenesis of lignin results from the action of enzymes on coniferyl alcohol radicals, with subsequent random combination of these radicals. A wide range of analytical information consistent with the biogenesis scheme led

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Figure 1. Structure of Cellulose

Freudenberg to propose a schematic model of the constitution of spruce lignin, shown in Fig. 2. The model accounts adequately for the elemental analysis, aromaticity, and hydroxyl, carbonylic, phenolic, etheric, and methoxy groups.

Little is known about linkages between lignin and carbohydrate molecules. Grion (6) has proposed that linkages of carbohydrate p-hydroxybenzyl ether types are probably the main way in which lignin is grafted onto carbohydrates.

Differences between the chemistry of wood and that of its separated components are introduced by factors such as the macro- and micro-structures and the chemical links between the components.

B. Chemistry of Wood and Wood Components

1. Overview

The hydrolysis of wood, as reviewed by Harris (10), has been studied by several investigators. Typical hydrolysis conditions range from 70% acid at 20°C for 2 hours, to 0.4% acid at 190°C for 20 minutes (12). At ordinary temperatures, relatively concentrated acids (e.g. 60% sulfuric acid or 37% hydrochloric acid) attack wood rapidly with hydrolysis of the polysaccharides. Above 100°C, hemicellulose is rapidly attacked with dilute mineral acids (2 to 3% sulfuric or hydrochloric acid). The cellulose itself is attacked more slowly, probably because of its partly crystalline nature. Some loss of sugars during hydrolysis occurs because of reversion reactions (11) and degradation to furan-type compounds. The hydrolysis kinetics of wood and polysaccharides is first-order in acid concentration (8).

XBL 795-1648

Figure 2. Structure of Lignin

Wood is essentially unattacked at ordinary temperatures by neutral organic solvents, cold water, or dilute acids. As extraction temperature is increased, dissolution of progressively higher amounts of wood into water occurs by hydrolysis of acetyl groups, and of the other groups linking the saccharides and lignin. Extracts with pH as low as 3.5 have been obtained (7). At temperatures of 150 to 175°C, 20 to 30% of the wood may be dissolved in a few hours (8). Up to about 100°C neutral organic solvents are ineffective, while alcohols result in considerable dissolution. The latter is attributed to alkylation of lignin catalyzed by acids generated from the wood (9).

Solutions of strong bases dissolve a considerable fraction wood at room temperature; the major attack is on carbohydrates, but a portion of the lignin is also dissolved at 80°C. Solutions of sodium hydroxide remove about 80% of the pentosans from hardwoods (13). At about 100°C, similar treatment yields a number of simple aromatic substances, including vanillin, hydroxybenzaldehyde, and hydroxybenzoic, coumaric, ferullic, vanillic, and syringic acids (14). Alkaline reactions involved in wood pulping are discussed later.

Wood is generally reactive towards strong oxidizing agents such as potassium permanganate, chromic acid, chloric acid, hydrogen peroxide, and sodium peroxide. Cellulose and lignin are both attacked to produce carbonyl and carboxylic groups, progressively simpler compounds result with increasing severity of reaction conditions (8,15). Oxidation reactions occur in both acidic and basic solutions, between 100 and 200°C, with reaction times of 1 to 5 hours, and usually produce complex mixtures of organic acids.

Nitration of wood leads to the formation of nitrate esters, mainly with lignin (16,17,25,27). The hydroxyl groups of wood can also be esterified with organic acids, notably glacial acetic acid, acetic anhydride, and mixtures of acetic anhydride and sulfuric acid (19,20).

Alkyl ethers are formed by alkylation of hydroxyl groups, usually with dimethyl sulfate or acid alcohol (18). Alcoholysis of wood adds new alkoxy groups to lignin, forming ethers which retain the original structure of wood and are relatively insoluble in organic solvents; this alkylated lignin can be isolated by hydrolysis (30).

2. Hydrogenation and Hydrogenolysis

Hydrogenation and hydrogenolysis of wood and its components have been extensively studied, and are most important in the production of liquid products from wood. Hydrogen treatment is normally applied to wood hydrolysates, acidic or more often basic.

Credit for having carried out the first hydrogenation of wood and lignin goes to the Swedish chemist, Lindblad (22). Sawdust impregnated with nickel hydroxide and heated to 250°C absorbed 5% hydrogen and formed a heavy tar. When cobalt hydroxide was used instead, methane generation became significant. Wood impregnated with 7.5% cobaltous sulfide absorbed 6.6% hydrogen (based on wood) giving 40.5% oils of which 67% distilled below 180°C. At higher temperatures, lighter tars were obtained with nickel hydroxide; above 400°C large amounts of methane were formed. Nickel sulfide suppressed gasification of tar above 400°C. Ferrous sulfide was an effective catalyst producing higher amounts of carbon dioxide. Cupric hydroxide, zinc chloride, and molybdic acid were also found to be effective catalysts.

Copper chromite and Raney nickel have both been widely tested as catalysts for hydrogenation of wood and lignins. Harris and co-workers (24) tested copper chromite with three lignins between 250-290°C, using dioxane as solvents for reaction times of 12 to 15 hours, and obtaining up to 30-wt% of distillable products. Hubbert et al (26,31) also investigated copper-chromite under similar conditions, and obtained up to 70 wt-% of distillable products. Other tests with copper chromite were made by Hachihama (32) and Purues (33). When Raney nickel was used as a catalyst for lignin conversion at 250°C, 24 wt-% of distillable products were obtained by treatment for 5 hours at 300 psig hydrogen pressure.

Kraft spent liquor, hydrogenated with bog iron ore as catalyst at 450-480°C, gave oil and tar yields of 38 to 45% (39). Molybdenum sulfide was tested as hydrogenation catalyst at 400 to 450°C (40); with phenol as solvent, 44% tar and 56% gaseous products were formed. Bogiar (41) obtained good tar yields on treating cotton beechwood at 460°C with molybdenum oxide as catalyst and cresol as solvent; addition of small amounts of sulfur increased the tar yields.

Lautsch and others (34,38) have reported extensive investigations of lignin hydrogenation in 1 to 4% sodium hydroxide solutions; reaction temperatures ranged from 250 to 265°C and from 8 to 12 hours, using various nickel, cobalt and copper catalysts. Products ranged from 10 to 30% in ether solubility, and 7 to 27% distillable oils were obtained. Less active catalysts gave phenolic products, whereas more active catalysts resulted in cyclohexanol derivatives.

Lautch and Piazzolo (36) hydrogenated lignin by treating it in sodium hydroxide solution at 355°C for 12 hours. The products contained 45% neutral oils and 15% phenol (based on lignin charged). In a similar way, they hydrogenated sulfite and sulfate spent liquors with nickel catalysts at 350°C to yield up to 84% ether-soluble products. When carbon monoxide was used instead of hydrogen, 42% of ether-solubles were obtained in 9 hours at 350°C. Lautsch suggested that below 310°C hydrogenolysis involves side-chains cracking with low hydrogen consumption. Although lower hydrogen pressures could be used when catalyst was present, the course of hydrogenation was not greatly affected by the catalyst.

When sodium hydroxide-ethanol-water mixtures were used at 350°C for 9 to 11 hours, up to 77% of the lignin charged was converted to ether-soluble material (36). Hydrogenation of lignin, using ethanol solutions of sodium hydroxide with Raney nickel as catalyst, gave products containing 48% neutral oils at 350°C in 9 hours.

Hachihama and co-workers (56-63) also investigated the hydrogenation of wood and of lignin in alkali media, both with and without added catalysts. They hydrogenations were conducted for 1 to 20 hours at 270°C, using 1 to 5% NaOH solutions. Catalytic activity of certain tested catalysts increased in the order: nickel oxide, copper - chromium-oxide, cobalt sulfide and Raney nickel. When 10 to 12% nickel oxide (based on wood) was used as catalyst, hydrogenation was completed in 22 to 25 hours and gave an oily tar soluble in ether. In order to find possible structural differences in lignins from different sources, Hachihama and Jyodi (59,61) compared the behavior of

hydrochloric-acid lignins from Ezomatsu wood, Beech, and bagasse, when hydrogenated in dioxane in the presence of nickel oxide on kieselguhr at 270°C. Phenolic reaction products were isolated and separated by distillation at up to 280°C/5 mm of mercury; from the results, these workers concluded that softwood lignins contain guaiacyl propane structures, and hard woods contain guaiacylpropane and syringylpropane structures.

On the acid side, Hallonquist (64) carried out numerous hydrogenations with Douglas fir in aqueous suspensions at pH 4-5, 250°C and 3700-4500 psi maximum pressure, chiefly with Raney nickel as catalyst. Up to 50% distillable liquids were obtained, and the hydrogen absorbed ranged from 0.6 to 10.6%.

Iodine and hydrogen iodide at hydrogen pressures of 2800 psig have been used as catalysts for liquefaction of wood, cellulose, and lignin (91). By using temperatures between 300 and 325°C, 75% of the carbon in wood was converted in 2 hours to oils rich in ring structures. When a mixture of iodine and hydrogen was used, hydrogen iodide was recovered in the water phase.

Two pilot-scale hydrogenation experiments with methanol lignin were carried out by Harris and co-workers (65). Copper chromite was used as a catalyst at 325°C for one experiment, and tin sulfide and tin iodide at 400°C for the other [see Stroch et al. (66)]. In both experiments the lignin absorbed about 5% by weight of hydrogen, with about 70% conversion to volatile products and 28% to heavy oils; the products included substituted phenols and catechols. Similarly, Kashima

and Osada (67-70) studied the cracking of lignin, using phenol, cyclohexanol, and tetralin as solvents with an iron hydroxide-sulfur catalyst mixture and producing mainly phenolic materials.

Goheen (71) discussed a process developed by the Noguchi Institute of Japan for the conversion of lignin into a relatively few mono-phenols. Partial results were disclosed in several papers and patents (72-77). The catalysts comprised mixtures of iron sulfide with cupric hydroxide, nickel hydroxide or sulfide, or zinc sulfide. Crown Zellerbach Corporation further optimized the process (71) using a preferred temperature of 450°C and a 15-minute residence time, and obtaining 55-wt% conversion of lignin to materials boiling under 240°C, along with water and gases. In one experiment with wood flour, high yields of water, gas and "neutral oils" were reported.

The hydrogenation of lignin obtained from acid hydrolysis of wood was studied by Sakakibarer et al. (78-80). Copper chromite and cobalt, molybdenum, and nickel carbonyls were found to be effective catalysts between 400 and 450°C, but phenol yields were lower than those obtained from alkali lignin under the same conditions. Other workers who tested the hydrogenation of alkali lignin include Vasyernina (81-82) and Sergeeva (83). Ruthenium in alkali medium and iron and molybdenum compounds were found to be effective catalysts.

Gaslini (84) described a combined hydrogenation and pulping operation in which wood was suspended in a solvent that also contained a dissolved metal carbonyl as catalyst, and the suspension was treated with carbon monoxide and hydrogen at elevated temperature and pressure; the products obtained were predominantly phenols.

Several hydrogen-donating solvents have been studied for their effectiveness in liquefaction of wood lignin and cellulose. Edwards and co-workers (85) heated cotton cellulose and fir sawdust, with tetralin as a hydrogen donor, at 300 to 350°C with an initial hydrogen pressure of 1000 psig; they found that both cellulose and wood were completely converted into oils, with simultaneous dehydrogenation of a part of the tetralin to naphthalene.

Bobrov and Kolotova (86) hydrogenated sulfite spent liquor, suspended in hydrogenated oil. Hydrogen consumption became significant at 340 to 350°C where high yields of a heavy oil were obtained. When the temperature was raised to above 400°C, a light oil boiling at 150°C was formed.

Suida and Prey (87,88) hydrogenated spruce lignin with decalin for 12 hours at 440°C. Products were 40% liquid (98% neutral and 2% phenolic), 15 % tar, 30% residue, and 15% water and gases. Kleinert (89,90) treated spruce lignin with cyclohexanol as a hydrogen donor for 3 hours at 300°C. α -Pinene also served as a hydrogen donor for lignin hydrogenation, in the presence of strong acids at 120 to 150°C, and was thereby converted to p-cymene.

Selective hydrogenation of cellulose and sugars has also been well studied. Tanteuschlager (41) found that carbohydrates and other polyhydroxy compounds are cleaved when treated with hydrogen under pressure at 190 to 300°C over catalysts from the iron and platinum groups; simple reduction or reduction and decomposition may result. Glucose yields sorbitol, glycerol and other hydroxy compounds; cellulose yields glycerol, 1,2, dihydroxypropane, and other products, but no

cyclohexanol derivatives (42). Zartman and Adkins found that simple sugars in ethanol solution undergo rapid hydrogenolysis over copper chromite at 250°C; methanol ethanol, substituted furals, and polyhydroxy alcohols are produced (43). At 140 to 160°C, with the pH of the solution below 7 and nickel as the catalysts, glucose is converted to sorbitol (44).

In other early carbohydrate research, Willstatter and Kalb (45) heated cotton cellulose samples to 250°C in the presence of hydroiodic acid and red phosphorus, and found the products to contain solid and liquid hydrocarbons. Bowen, Shatwell, and Nash (46), heating cotton samples in hydrogen at 420-440°C, obtained coke, carbon dioxide, water, light oils, and tar. When nickel oxide was added as catalyst, the yield of oil and tar increased, as did the hydrogen consumption.

Rantala (47) reported that copper, iron, and cobalt hydroxides, nickel formate, ammonium molybdate, and ammonium chromate each catalyzed the liquefaction of sawdust, giving oil yields as high as 35%. Berl and Biebesheuner (54) and Berl and Schmidt (55) reacted cotton pretreated with sodium hydroxide, and recovered gases and tars at 310 to 330°C; further hydrogenation of the tar at 420°C yielded hydrocarbon oils. Several other investigators have studied alkali-treatment of cellulose (48,51) between 200 and 300°C, with formation of alcohols, aldehydes, acids, and ketones. More recent studies of cellulose and glucose chemistry (52,53) have shown that when carbohydrates and sodium hydroxide are reacted at temperatures between 150 and 350°C, coke and bitumen are formed.

C. Sodium Carbonate Catalyzed Liquefaction

Appel and co-workers at the Bureau of Mines (92-97) developed a process for the production of oils from wood, cellulose, and urban refuse. The process involves the production of heavy oil from cellulosic matter by treatment with carbon monoxide and water in the presence of sodium carbonate as catalyst. Studies done initially with cellulose and then municipal refuse as substrates were later extended to include newsprint, pine needles, and sewage sludge (94). Two sets of conditions were tested. At 250°C and 1-hour of reaction time, the resulting product was a soft bitumen-like solid high in oxygen content sparingly soluble in benzene; oil production consumed almost no carbon monoxide under these conditions. In high-severity experiments at temperatures between 350 and 380°C, for reaction times ranging from 20 minutes to 1 hour, oils of low oxygen content (about 9 wt-%) were obtained in yields as high as 40%.

In its second phase, this work was extended to include wood and bovine manure as substrates (97). The effects of water addition, catalyst concentration, reaction time, reaction temperature, and carbon monoxide pressure were studied in batch autoclave experiments. Several alkaline salts were tested for catalytic activity, and the effect of a carrier oil was also determined. Sodium carbonate was found to be the best catalyst, and the presence of liquid water at reaction conditions was also found to be essential. Apart from its possible generation of hydrogen by water-gas shift, water may be needed to activate the sodium carbonate and may serve to dissolve polyhydroxyl compounds formed by the reaction. Carbon monoxide pressure was also found to be an important

variable in cellulose conversion; at 250°C conversion increased from 78 wt-% of substrate fed without carbon monoxide, to 90 wt-% for an initial CO pressure of 600 psi, with respective oil yields of 24% and 40%. As organic solvents, both anthracene oil and isoquinoline were tested with soft pine at 380°C for 15 minutes. Without these solvents, oil yields amounted to 22%, and with them, 51%.

The Bureau of Mines work was later extended to obtain greater insight into chemical reactions involved in liquefaction of cellulose. When cresol was used as solvent at 275°C for 1 hour, up to 60% of benzene-soluble material was obtained. Sodium formate and sodium carbonate were both effective as catalysts, and no carbon monoxide was consumed. With n-butanol and sodium carbonate at 250 to 300°C in 1 hour, 60% conversion to oil resulted. Diphenyl ether and alkyl naphthalenes were found to be poor solvents, but gave higher oil yields than for no solvent whatever. The effects of heating rate of reactants were also studied; for a hardwood as substrate, slower heating over a longer period gave a product of lower softening point.

Reaction mechanism studies were carried out with simple model compounds. Methyl ethyl ketone, n-butyraldehyde, benzaldehyde, and acetophenone were tested with Na₂CO₃ and carbon monoxide at 250°C. Based on these studies, and earlier work with carbohydrates (97), the following reaction mechanism was proposed:

1. Production of sodium formate:

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

3. Reduction of this carbonyl group by formate ion and water

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

A pilot plant for processing 3 tons/day of wood by this process has been designed and installed at the Bureau of Mines facility in Albany, Oregon. The plant has experienced several start-up problems which are presently being worked on.

D. Reactions in Wood Pulping

The objective of all pulping processes is to remove the lignin part of the wood and leave the cellulosic part unaltered. Production of paper from cellulose obtained by pulping was developed in the early eighteenth century. Mechanical pulping was the first process for isolating the cellulose; wood blocks were pressed against a rotating grindstone to reduce the wood to a fibrous mass, in a flow of water which kept the stone cool and washed away the pulp (cellulose).

Mechanical pulping gave way to sulfiting later in the same century. In this process, wood chips are treated with calcium bisulfite solution to 130 to 150°C and 60 to 160 psig for 7 to 25 hours. Lignin is converted to water-soluble sulfite salts, and the cellulose is recovered by filtration.

In the so-called alkali process, wood is treated with sodium hydroxide, or a mixture of sodium hydroxide and sodium sulfide. Typical reaction times range from 7 to 12 hours, and the temperature is 170 to 180°C.

The Kraft process is most widely used for pulping. In chemical pulping process, lignin solubilization occurs by the chemical cleavage of weak links - specifically, carbon-oxygen linkages among which the β - aryl ether group (shown below) is the major center.

Sodium sulfide in the cooking liquor hydrolyzes to form sodium hydroxide and sodium hydrosulfide:

The HS^- ion, a strong nucleophile, attacks the β -aroxyl group, introducing a $-\text{SNa}$ group and a proton to achieve lignin depolymerization. Methylenequinone intermediates formed during lignin degradation tend to condense, and hydrosulfide ion has the advantage of protecting the methylenequinone structures so as to prevent condensation. An undesirable side reaction of cellulose in the Kraft process involves group attack at the terminal reducing groups of the polysaccharides, resulting in the formation of saccharinic acids.

Waste liquor containing the soluble lignin salts is usually concentrated in multieffect evaporators, and burned to recover the sodium hydroxide and sodium sulfide and to provide process heat. As indicated, several catalysts have been tested for hydrogenation of sulfite spent liquor and of lignin, with the aim of recovering useful chemicals or

fuels. The sulfur content of the lignin and the high dilution of the liquor by water pose sizeable barriers to the economy of such steps.

E. Liquefaction Prospects

In retrospect, the chemical structures of major wood components involve a large number of functional groups containing oxygen. Two essential elements for wood liquefaction are depolymerization of high-molecular-weight structures (especially by carbon-oxygen scission) and the removal of nearly all the chemically bound oxygen, which together can lead to formation of liquid product with a high heating value.

The conversion of wood is complicated by the fact that it is a solid. Improved mass transfer and selectivity can be expected if the wood can be solubilized in a carrier solvent during the early stage of defunctionalization. At this stage a polar reaction medium could be expected to be beneficial because the oxygen-containing groups are quite polar. As the treatment proceeds, wood-derived molecules of lower molecular weight and reduced oxygen functionality are produced, which should be protected from degradative attack by the reagents, and from condensation with the highly functional species and their reaction intermediates. In principal, such protection of the conversion products could be achieved by extracting them in a less polar reactive medium. Thus, a slurring medium consisting of two partially immiscible liquid phases appears to hold promise for wood liquefaction; the unreacted wood and high molecular weight products would be dissolved or suspended in the polar phase, and the low-molecular weight products would transfer to the less polar phase.

Oxygen removed from wood as waste would exit any processing scheme as water, carbon dioxide, or carbon monoxide. Removal of water from an organic molecule results in little net change in the molar heating value, as indicated by Dulong formula for estimation of heating value. Carbon dioxide is a more efficient oxygen carrier than carbon monoxide in terms of heating value of the desired product. The amount of carbon dioxide generated in any processing scheme is therefore an important criterion in wood conversion.

If hydrogenation is used as a means of stabilizing reaction intermediates and eliminating oxygen from wood, the hydrogen can be supplied as dissolved gas in the reaction medium, from inorganic intermediates (such as sodium formate), or from organic molecules (such as hydrogen donor solvents which involve lower reaction pressures). Hydrogen and carbon monoxide must ultimately be generated from raw wood or wood residues by gasification, and the extent of hydrogenation thus effects the total consumption of wood.

F. Scope of Experimental Investigation

Two liquid-phase slurry systems have been evaluated in this study. In each case, a polar water phase and a hydrogen-donor solvent were both present. The first system studied utilized dilute sulfuric acid as the inorganic phase and α -phellendrene as the H-donating liquid. The objective of these experiments was to see if hydrogenation and acid hydrolysis could be made to occur simultaneously. The second system studied used tetralin as the hydrogen donating solvent. The aqueous phase contained

either soluble or insoluble, or both, additives as potential hydrogenation catalysts. Several hydrogenation catalysts were tested in this system.

The structure and reactions of wood and its constituents have been well studied as the earlier review of literature suggests. The task ahead appears to be in building on this base of knowledge so as to develop economic wood liquefaction processes. Homogeneous and heterogeneous catalysts, organic and aqueous carrier solvents and separation methods that could be combined into integrated processes must be developed, tested, and evaluated. The inherent chemical susceptibility of biomass offers a wide variety of possibilities and a large scope for creative process development.

II. EXPERIMENTS AND PROCEDURES

A. Wood Procurement and Analysis

The wood selected for this study was Douglas Fir, from Oregon. The wood was ground to flour and dried to a moisture content of 8 wt-%, at the Albany, Oregon DOE facility operated by Rust Engineering Company. The wood flour was used as received.

A sample of the flour was analyzed by the University's Microanalytic Laboratory. To determine its moisture content, a 10-g sample was weighed before and after drying at 110°C in a vacuum oven at 10^{-2} torr for 18 hours. Another small sample was subjected to ultimate analysis, results are shown in Table 1.

B. Equipment and Procedure

1. Experimental Apparatus

Reactions were run in a 300 ml autoclave, supplied by Parr Instrument Company, constructed of 316-type stainless steel. Glass liners fitting snugly into the vessel were used for all experiments. The reactor contents were agitated by a three-paddle stainless-steel stirrer driven by a constant-speed motor. There were two openings in the reactor head, one of these openings being used to feed in gaseous reactants after the reactor had been loaded with reaction materials, and the other being connected to a vent line and used for discharging gases at the end of the run.

The reaction-vessel temperature was maintained by an on-off controller, which was activated by an iron-constantine thermocouple. The controller supplied electric power to a cylindrical furnace

Table 1: Ultimate Analysis of Douglas Fir Wood (wt-%)

	Dry Basis
Carbon	53.17
Hydrogen	5.61
Nitrogen	0.13
Sulfur	0.05
Ash	0.50
Oxygen (by difference)	40.54

surrounding the reactor. As cooling fluid, white oil was circulated from a reservoir through a cooling loop in the reactor, using a 1/4 hp. centrifugal pump. The cooling fluid flow was activated whenever the vessel temperature exceeded the set-point temperature. In this way the reactor contents were maintained within 2°C of the desired reaction temperature.

The pressure in the reaction vessel was measured by a 2500 psig pressure gauge attached to a sidearm of the gas outlet port.

2. Reaction Procedure

The method described here was used for all experiments. Twelve grams of wood flour and 48 g of organic solvent were weighed into a glass liner. Water-insoluble catalysts were weighed into the liner, followed by addition of water. Water-soluble catalysts were first dissolved in a glass beaker, and the required amount of catalyst solution was then added to the liner.

After weighing in all the reactants, the liner was placed in the reactor vessel, and the reactor was sealed and mounted into its stand. The reactor was flushed several times with hydrogen (or carbon monoxide) to remove the air present. The reactor was then loaded with hydrogen (or carbon monoxide) to an initial pressure of 200 psig, and tested for leaks.

To facilitate rapid heat-up to reaction temperature (200 or 250°C) the power to the furnace was turned on until the heating element was red-hot. The heated furnace was slipped over the reactor vessel and fastened into place, and the reactor stirrer was turned on. Temperature and pressure were recorded every two minutes during the heat-up

period. The reactor contents required 14 to 16 minutes to reach 200°C, and between 17 to 20 minutes to reach 250°C. In two experiments run with carbon monoxide instead of hydrogen, reactor heat-up proceeded normally to about 140°C, but then became quite slow so that the heating rate was the total time to reach 250°C was about 32 minutes. It appears likely that hydrogen begins to react exothermically at a lower temperature than carbon monoxide.

In all experiments an exthermic reaction occurred between 180 and 200°C, as indicated by a rapid rise in temperature.

The pressure in the reaction vessel rose gradually up to 180°C, reaching about 300 psig. A sharp rise in pressure was observed between 180 and 200°C, accompanying the exothermic reaction, so that it reached 420 to 425 psig. When heating was continued to 250°C, a further increase in pressure occurred to a value between 700 and 820 psig. When carbon monoxide was used as the gaseous reactant, reaction pressure rose from 580 psig at 220°C to 800 psig at 250°C.

After heat-up, the reactor and its contents were held at reaction temperature for the desired time. Pressure was recorded after 2 minutes and 5 minutes, and then every five minutes until the end of the run.

At the end, the heater was removed and cooling oil turned on. The temperature dropped to 150°C in about 5 to 7 minutes, after which the reactor was immersed in cold water to speed the cooling. Reactor temperature and pressure were recorded every 2 minutes during cool-down to 50°C, which usually required between 14 and 17 minutes. The temperature history of two typical runs is shown in Fig. 3, and the corresponding pressure history is shown in Fig. 4.

XBL 80I-88

Figure 3. Temperature History for Two Typical Experiments

XBL80I-89

Figure 4. Pressure History for Two Typical Experiments

After the reactor reached 50°C, and stirring was stopped, the reactor and its contents were allowed to cool to room temperature. Reaction gases were then vented, and the reactor was opened to recover and separate the products.

C. Product Separation and Characterization

1. Acid Hydrogen-Donor Experiments

The contents of the reactor were passed through a pre-weighed dry extraction thimble. The liner and reactor internals were washed with toluene, and the wash was also passed through the thimble. Liquid products were quantitatively transferred to a 500-ml round-bottom flask and diluted to about 300 ml with additional toluene. The thimble containing the insoluble residue was placed in a Soxhlet extraction apparatus and extracted with the toluene solution by the procedure described in Section D.

The insoluble residue and the toluene-soluble extract were each dried at 110°C in a vacuum oven at 10^{-2} torr for 18 hours. An Ultimate analysis of the toluene soluble material was made by the University's Microanalytical Laboratory.

2. Metal-Salt Catalysis

For experiments with salts as catalysts, the contents of the reactor were passed through a pre-weighed thimble as before. The reactor internals and glass liner were then washed with about 30 ml of acetone, the resulting slurry was transferred to a test tube and allowed to stand for about 15 minutes, in which time all the solids settled to the bottom. Acetone was then carefully removed with a

disposable pipette, and the settled residue was transferred to the thimble by spatula. Also, the acetone was evaporated, and the acetone-soluble materials (usually 0.2 to 0.4 g) were transferred to the thimble in about 10 ml of toluene. The thimble was placed in a Soxhlet extraction apparatus and extracted with toluene as described in Section D.

At the end of the toluene extraction, all the solvent was removed from the apparatus, and the thimble was extracted with demineralized water at 100°C. The water-extraction procedure is also described in Section D. The toluene- and water-insoluble material remaining in the thimble was then dried in a vacuum oven at 110°C for 18 hours at 10^{-2} torr.

Toluene was removed from the Soxhlet extract in a Buchi rotating vacuum evaporator at about 40°C. The extract and tetralin remaining were transferred to a preweighed 100-ml round-bottom flask using about 20 ml of acetone as a wash. The acetone was first removed on the rotary evaporator at room temperature. The tetralin was evaporated under vacuum (at about 100°C), collected and weighed. Next, the toluene-soluble fraction was dried 18 hours in a vacuum oven at 110°C and 10^{-2} torr, and weighed.

In selected experiments (Runs 20 through 24), the water-soluble products were collected. About 200 ml of water was first removed on the rotary evaporator. The remaining solution was then transferred to a pre-weighed 100-ml round-bottom flask. About 20 ml acetone was used for washing the flask. The remaining water and acetone were then evaporated, and the water-soluble, toluene-insoluble materials were dried in a vacuum oven.

Four fractions were thus obtained from the reaction products.

Each fraction was further characterized as follows:

- a) Solvent-Boiling-Range Materials: The tetralin recovered by evaporation was analyzed by gas chromatography. Samples of tetralin from Experiments 12, 13 and 17 were analyzed.
- b) Toluene-Solubles: Ultimate analysis was made by the University's Microanalytical Laboratory. All extracts were analyzed on a T-60 Varian NMR Spectrometer using deuterated pyridine as the solvent. Extracts from Experiments 12, 13 and 17 were dissolved in chloroform and analyzed using a Cary ultraviolet-visible spectrophotometer.
- c) Toluene-Insoluble Water-Soluble Fractins: Ultimate analysis of this fraction was done by the University's Microanalytical Laboratory.
- d) Toluene- and Water-Insoluble Fraction: Ultimate analysis of this fraction was also done by the University's Microanalytical Laboratory.

By determining the elemental composition of the three major fractions (toluene-soluble, water-soluble, and residue), a mass balance and an elemental balance could be made. Proton NMR of the toluene soluble materials gave an approximate indication of the nature of the low-molecular-weight toluene-soluble products.

D. Extractions

Products from the acid hydrogen-donor experiments were extracted with toluene in a Soxhlet extraction apparatus, at the atmospheric boiling point of the solvent (110°C). Extraction was continued until the toluene returning to the flask became colorless, indicating complete removal of soluble material. The extraction time was different for each experiment, and ranged from 4 to 26 hours.

Toluene extraction of products from the metal-salt catalyst experiments was done in the same manner as that for the acid hydrogen-donor experiments. When toluene-extraction was complete, the flask containing the toluene-solubles was replaced by another 500 ml flask containing about 300 ml demineralized water. The sample was then extracted for 18 hours with water.

Toluene-soluble and water-soluble materials were recovered by evaporation using a Buchi rotating vacuum evaporator.

E. Experiments Performed

1. Acid Hydrogen-Donor Experiments

Hydrogen-donor solvents have been found to be effective in the liquefaction of wood and of wood components (85-90) at temperatures above 300°C . These solvents donate hydrogen to thermally cleaved bonds in wood. To study the effectiveness of lower-temperature hydrogen donation, experiments were run using wood and α -phellandrene (5-isopropyl-2-methyl-1,3 cyclohexadiene) in an acidic medium. α -phellandrene is a major constituent of wood-derived terpinols, and has been shown to be an effective hydrogen donor at 200°C (98). Sulfuric acid (1 to 98 wt-%

aqueous solution) was added in an attempt to promote hydrolytic bond cleavage at reaction temperature. In certain runs, small quantities of palladium supported on carbon were added to the acid hydrogen-donor mixture to study the effect of improved hydrogen transfer. The usual reaction conditions were a reaction temperature of 200°C, an initial hydrogen pressure of 200 psig and a reaction time of 20 minutes. A wood-to- α -phellandrene ratio of 1:4 by weight was used for all experiments.

To begin, wood was treated with α -phellandrene, both with and without palladium as catalyst. 0.5 gram of 10% Pd on carbon was used for 48 g of α -phellandrene. Two experiments were run to characterize the effectiveness of sulfuric acid and α -phellandrene with wood. In the first, 12 g of wood, 48 g of α -phellandrene, and 2 g of 98 wt-% sulfuric acid were used. In the second, with identical amounts of wood and solvent, 20 g of 2 wt-% acid was used. The role of palladium as a catalyst in acidic media was tested in two experiments, both using 0.5 g of 10 wt-% palladium on carbon. In one experiment, 25 g of 2 wt-% sulfuric acid was used, and in the other 20 g of 1 wt-% sulfuric acid. Finally, decalin was used as the hydrogen-donor solvent with 20 g of 2% sulfuric acid. Experimental conditions and catalysts are listed in Table 2.

2. Metal-Salt Catalysis Experiments

Eight potential catalysts were tested for the liquefaction of wood flour at 250°C and 1 hour of residence time. In the pilot-scale sodium carbonate process at Albany, the standard reaction temperature is 340°C. Catalyst screening at a lower temperature enabled us to

minimize thermal reactions, and provided larger observable differences in catalyst effectiveness. Tetralin was selected as an organic solvent to encourage liquefaction because of its potential hydrogen-donor capability. Also, any low-boiling wood-derived products could be distilled with tetralin and collected in the solvent fraction. Furthermore, toluene-soluble reaction products would be soluble in tetralin at reaction temperature, and so be separated from the untreated wood. Reaction conditions and catalysts tested are shown in Table 2.

In each experiment 12 g of wood was treated with 48 g tetralin and 20 g of a 5% solution (or slurry) of catalyst, resulting in a slurry containing 15 wt-% of wood solids. An initial hydrogen (or carbon monoxide) pressure of 200 psig was used.

Reaction products were extracted successively with toluene and with water. Product fractions were characterized by ultimate analysis and by nuclear magnetic and ultraviolet spectroscopy.

Table 2: Experimental conditions and Catalytic Additives

Douglas Fir Wood Flour: 12 g
Initial Hydrogen Pressure: 200 psig

Experiment No.	Organic Solvent	Amount (g)	Catalytic Additive	Water (g)	Residence Time (min.)	Reaction Temperature (°C)
1	α -Phellandrene	48	None	None	20	200
2	α -Phellandrene	48	10% Pd on Carbon	0.5	20	200
3	α -Phellandrene	48	98% H ₂ SO ₄	2	20	200
4	α -Phellandrene	48	Sulfuric Acid	0.4	20	200
5	α -Phellandrene	48	Sulfuric Acid	0.5	20	200
6	α -Phellandrene	48	10% Pd on Carbon	0.5		
			Sulfuric Acid	0.2	20	200
7	Decalin	48	Sulfuric Acid	0.4	20	200
8	Tetralin	48	Molybdic Acid	1	60	250
9	Tetralin	48	Zinc Chloride	1	60	250
10	Tetralin	48	Antimony Tribromide	1	60	250
11	Tetralin	48	Nickel Chloride	1	60	250
12	Tetralin	48	Ferric Chloride	1	60	250
13	Tetralin	48	Sodium Carbonate*	1	60	250
14	Tetralin	48	Copper Chromite	1	60	250
15	Tetralin	48	Ferric Sulfate	1	60	250
16	Tetralin	48	Ferric Chloride*	1	60	250
17	Tetralin	48	None	20	60	250

*Under carbon monoxide instead of hydrogen.

III. RESULTS AND DISCUSSION

A. Acid-Hydrogen Donor Treatment

1. Rationale and Approach

Simultaneous depolymerization and hydrogenation of wood could result in liquid products of high heating value. Hydrogenation of wood by the transfer of hydrogen from hydrogen-rich (or donor) solvents at temperatures above 300°C has been accomplished in several earlier investigations (85-88). At these temperatures depolymerization occurs by the thermal cleavage of carbon-oxygen and carbon-carbon bonds.

An integrated liquefaction process based on donor solvent hydrogenation of wood would include a solvent separation and a solvent hydrogenation step. If petroleum-derived donor solvents were used, any solvent losses (e.g., into the product) would need to be replenished, and the process economics would depend on the separation efficiency and cost of the solvent. Considerable savings in both separation and replenishment costs may be possible if a hydrogen donor solvent could be produced by hydrogenating a fraction of the products of wood liquefaction.

Since lignin is composed of phenyl propane units, it is likely that significant amounts of phenyl propane derivatives would be formed during the hydrogenation of wood. Adequate hydrogen-donor solvents could be produced by the partial hydrogenation of such phenyl propanes.

α -phellandrene (5 isopropyl-2-methyl-1,3 cyclohexadiene) was selected for testing as a representative partially hydrogenated phenyl propane, because it is known to be a major constituent of wood-derived terpinols

and because Breiger and Nestruck (98) found it to be a good hydrogen transfer solvent.

The reaction temperature of the liquefaction step is another important consideration in wood liquefaction. High temperatures could result in lower residence times and hence in smaller reactor volumes. However, high pressures are usually required to keep solvents (and water) as liquids at high temperatures. In order to feed wood slurries into high pressure reactors the wood must be ground to fine powder, which could be an energy intensive (and expensive) step. In the pulp and paper industry wood chips (1 to 1-1/2" pieces) are fed into reactors, called digestors, at 200 to 400 psig. Crushing and grinding of wood chips could be avoided if liquefaction could occur at temperatures between 150 and 250°C, so that chips could be fed with the reactor using existing feeders. Acid-catalyzed hydrogen transfer was tested to allow hydrogenation at temperatures below 300°C, the lower limit of thermal hydrogen transfer. Acid catalyzed hydrogen donation occurs by the transfer of a hydrogen atom with its pair of electrons from one center to another and is commonly referred to as hydride transfer. Deno et al. (99) have reviewed the use of hydrocarbons, alcohols and aldehydes as hydride transfer agents. A large number of reactions of this type are known and hydride transfer can occur at temperatures as low as 25°C. (99) An additional advantage of using an acid catalyst is the simultaneous depolymerization of wood by hydrolysis of the cellulose and hemicellulose fractions resulting in greater accessibility of the substrate.

2. Chemical Conversions and Product Yields

To study the effectiveness of hydrogen-donor solvents in low temperature hydride transfer liquefaction, wood flour was treated with mixtures of α -phellandrene and sulfuric acid. Palladium (as 10% Pd on C) was added in some runs to improve the rate of hydrogenation. Reaction products were extracted with toluene to obtain a toluene-soluble and insoluble fraction. Reaction conditions, product yields and total mass recovered are shown in Table 3. Ultimate analysis on all insoluble residues and selected toluene extracts were determined by the University's Microanalytical Laboratory. The Ultimate analysis of the insoluble residues and the corresponding atomic H/C and O/C ratios are shown in Table 4.

Wood flour was first treated with α -phellandrene (at 200°C for 20 min) to determine the extent of thermally induced depolymerization and hydrogenation. Only about 1% of the products were soluble in toluene. Next, palladium was added as a catalyst to see if improved hydrogenation occurred. In the presence of the catalyst about 8% of the wood was converted to toluene-soluble material. These results indicate that little depolymerization of wood occurs at 200°C in 20 min. The donation of hydrogen from the solvent was probably restricted by diffusion limitations. The presence of a solid hydrogenation catalyst improves the conversion levels probably due to surface hydrogenation of the wood. In each case the insoluble solids from these treatments had atomic H/C ratios of about 1.4 compared to 1.3 for the starting wood indicating a small degree of hydrogenation. The O/C ratios remained essentially unchanged.

Table 3: Reaction Conditions and Product Yields from Acid-Donor Solvent Treatment of Wood.

Conditions: Reaction Temperature: 200°C
 Reaction Time: 20 min.
 Wood Flour: 12 g
 Organic Solvent: 4 g
 Gas: H₂
 Initial Pressure: 200 psig.

Experiment No.	Solvent	Sulfuric Acid		Palladium (10% Pd on C)	Yields (Z rel. to dry wood)		Mass Recovered (Z rel. to dry wood)
		Amount (g)	Concentration		Toluene Solubles	Insoluble Residue	
1	α -Phellandrene	None	--	None	1.2	98	99.2
2	α -Phellandrene	None	--	0.5	8.2	92.9	101.1
3	α -Phellandrene	2	98	None	196.5	41.5	238.0
4	α -Phellandrene	20	2	None	118.0	34.4	152.4
5	α -Phellandrene	25	2	0.5	50.8	41.5	92.3
6	α -Phellandrene	20	1	0.5	31.2	43.5	74.7
7	Decalin	20	2	None	17.7	43.8	6.2

Table 4: Ultimate analysis of toluene-insoluble material from acid and hydrogen-donor solvent treated wood.

Conditions: Reaction Temperature: 200°C
 Reaction time: 20 min
 Initial Pressure: 200 psig.
 Wood Flour: 12 g
 Organic Solvent: 48 g
 Gas: H₂

Experiment No.	Solvent	Sulfuric acid		Palladium Amount	Analysis, wt. % (Rel. to dry wood)					H/C (atomic)	O/C (atomic)
		Amount	Concentration		C	H	O	N	S	Ash	
1	α-Phellandrene	None	--	None	51.24	6.20	41.97	0.02	0.03	0.5	0.614
2	"	None	--	0.5	50.99	5.86	41.91	0.05	0.09	1.1	0.616
3	"	2	98	None	68.35	6.33	20.73	0.47	4.12	6.0	0.227
4	"	20	2	"	65.26	6.07	25.86	0.13	2.68	3.9	0.252
5	"	25	2	0.5	65.77	5.20	23.92	0.01	1.20	3.9	0.273
6	"	* 20	1	0.5	67.22	5.34	24.9	0.24	--	2.3	0.278
7	Decalin	20	2	None	65.83	5.04	27.8	0.05	--	1.3	0.317
Untreated Wood					53.17	5.61	40.54	0.13	0.05	0.50	0.572

The effect of acid catalyzed hydrogen transfer was tested in two experiments (Runs 3 and 4, Table 3). In one run 2 g of 98% sulfuric acid was added to α -phellandrene and wood flour. Extensive alkylation occurred and the toluene soluble and insoluble fraction of the product added up to over two times the weight of the starting wood. The acid concentration was reduced to 2 wt-% and the amount of acid increased to 20 g. A great deal of alkylation occurred on treatment at 200°C for 20 min, and the products recovered were 142% by weight of the starting wood.

In order to determine the effect of an added hydrogenation catalyst two runs were done with palladium added to the α -phellandrene and acid mixtures. In the first run (Experiment No. 5) 25 g of 2% by weight sulfuric acid and 0.5 g of 10% palladium on carbon were used as catalysts with 12 g wood flour and 48 g α -phellandrene. After treatment for 20 min at 200°C about 51% of the wood flour was converted to toluene-soluble material. About 40% of the wood was recovered as toluene-insolubles resulting in mass recovery of about 92%. In the second run (Experiment No. 6) both the acid concentration and the amount of acid used were lowered to study the effect of the acidic catalyst activity. The only change from the previous run was that 20 g of 1% by weight sulfuric acid were used (instead of 25 g of 2% acid). Under these conditions both the toluene-soluble and toluene-insoluble materials formed declined to 31 and 44% respectively, resulting in a total mass recovery of about 75% of the starting wood flour.

Decalin was used as an alternate hydrogen source in an acidic medium. When 12 g wood flour became treated with 48 g of decalin and 20 g of 2 wt-% sulfuric acid at 200°C for 20 min, about 18% of the treated wood was soluble in toluene, and about 44% was recovered as toluene-insolubles.

Ultimate analysis were determined for the toluene-insoluble residues obtained from all of the acid catalyzed hydrogen-donor experiments. These are shown in Table 4. Atomic H/C ratios O/C of all residue fractions were lower than those of the starting wood. The toluene-insoluble fractions had the H/C ratios ranging from about 1.1 to 0.9 compared to 1.27 for the starting wood. The O/C ratios of these fractions varied from 0.23 to 0.32 compared to 0.57 for untreated wood. These results indicate considerable dehydration of the wood resulting in products of lowered H/C and O/C ratios.

Two runs (experiments 5 and 6) where α -phellandrene acid and palladium were used for the treatment of wood flour, resulted in mass recoveries of less than 100% of the starting wood. To determine if there was any solvent incorporation in the product, the ultimate analysis was done for the toluene-soluble and insoluble fractions and a net carbon recovery was calculated. The carbon recovered in the two products were 120 and 114% of the carbon in the starting wood for experiments 5 and 6 respectively. These carbon recoveries indicate considerable alkylation of the solvent even at mild acid concentration and in the presence of a hydrogenation catalyst.

3. Conclusion

The use of α -phellandrene as a hydrogen transfer agent in wood liquefaction was studied at 200°C for a reaction time of 20 min. No significant thermally promoted hydrogen transfer occurred under these conditions even when palladium was used as a catalyst.

In the presence of small quantities of concentrated sulfuric acid extensive alkylation (or condensation) of the solvent occurred. When dilute (2 wt-%) acid was used, the extent of alkylation was still high. Addition of palladium as a hydrogenation catalyst resulted in lower overall conversion (based on the insoluble residue obtained) and much lower levels of alkylations. Products obtained from experiments run with palladium amounted to less than the mass of the starting wood, however carbon recoveries exceeded 100%, indicating some alkylation. Decalin was significantly less effective than α -phellandrene based on the insoluble residue obtained.

A major drawback of the hydrogen transfer solvent selected for this study was that considerable fractions of the solvent alkylated (or condensed) to higher molecular weight materials. A systematic search for other hydride donors could lead to acceptable solvents which could result in high wood conversion levels without solvent condensation.

B. Metal Salt Treatment

1. Rationale and Approach

Several potential hydrogenation catalysts were screened to evaluate their effectiveness for wood liquefaction. As discussed earlier, a slurring medium consisting of two partially immiscible liquid phases was used, so that the untreated wood and high molecular weight products would be dissolved or suspended in the polar phase, and the low-molecular-weight products would transfer to the less polar phase. Water was used as the polar solvent because of its ability to dissolve sugars, polyhydric alcohols and other highly polar compounds. The non-polar phase comprised of tetralin which could dissolve non-polar, low-molecular-weight products and could also be a potential source of hydrogen.

Molybdic acid, zinc chloride, antimony tribromide, nickel chloride, ferric chloride, sodium carbonate, copper chromite and ferric sulfate were tested at 250°C for reaction times of 1 hr. Results of these screening experiments are discussed below.

2. Chemical Conversions and Product Yields

To study the effectiveness of various inorganic salts as low temperature liquefaction catalysts, wood flour was treated with a mixture of tetralin and an aqueous solution of the salt at 250°C for 1 hr. Reaction products were separated into toluene-soluble, water-soluble and insoluble fractions by procedures described in Chapter 2. The conversion of wood was calculated on the basis of insoluble residue obtained. Conversions resulting from the use of various additives are shown in Table 5. Yields of toluene and water-soluble products based on the starting wood, are shown in Table 6. The total mass

Table 5: Conversion of wood treated with Tetralin and inorganic additives.

Conditions: Temperature: 250°C
 Residence time: 1 hr
 Initial hydrogen pressure: 200 psig
 Wood: 12 g
 Tetralin: 48 g
 Water: 19 g
 Additive: 1 g

Experiment No.	Additive	Conversion wt. % of dry wood
8	Molybdcic Acid	36.6
9	Zinc Chloride	43.8
10	Antimony Tribromide	36.9
11	Nickel Chloride	52.3
12	Ferric Chloride	60.3
13	Sodium Carbonate*	52.0
14	Copper Chromite	42.3
15	Ferric Sulfate	44.0
16	Ferric Chloride*	51.1
17	None	50.2

*Under carbon monoxide instead of hydrogen.

Table 6: Yield of Toluene-extractables and water-extractables in treated wood: Effect of additives.

Conditions: Temperature: 250°C
 Residence time: 1 hr.
 Initial hydrogen pressure: 200 psig
 Wood: 12 g Tetralin: 48 g
 Water: 19 g
 Additive: 1 g

Experiment No.	Additive	Yield (relative to dry wood)			
		Toluene extractables		Water extractables	
		% of wood	% Initial Carbon	% of wood	% Initial Carbon
8	Molybdic Acid	8.9	11.32	not determined	
9	Zinc Chloride	11.9	15.55	"	
10	Antimony Tribromide	5.7	7.94	"	
11	Nickel Chloride	19.3	13.18	"	
12	Ferric Chloride	28.4	27.83	"	
13	Sodium Carbonate*	15.8	19.62	6.6	5.71
14	Copper Chromite	10.8	14.53	5.4	3.90
15	Ferric Sulfate	8.7	7.82	8.4	5.36
16	Ferric Chloride*	18.39	17.86	4.5	3.23
17	None	10.3	14.02	7.5	9.73

*Under carbon monoxide instead of hydrogen.

recovered in various fractions is given in Table 7 as a weight percent of the starting wood.

When treated at 250°C for 1 hr. with tetralin and water about 50 wt-% of the wood was converted to gases and products soluble in toluene and water. Of the additives tested, only nickel chloride, sodium carbonate and ferric chloride resulted in wood conversions greater than or equal to those obtained in the absence of an additive. Ferric chloride was found to give a substantially higher conversion (about 60 wt-% of wood) than any of the other effective additives when hydrogen gas was used. This difference in conversion however, was reduced when carbon monoxide was the reducing gas with ferric chloride.

Reaction products were successively extracted with toluene and water. Toluene, a relatively non-polar solvent, could be expected to dissolve products of lower polarity. Sugars and other highly polar substances could be expected to dissolve in a highly polar solvent such as water. Since polar functional groups in wood and wood-derived products result primarily from carbon-oxygen linkages, the toluene-soluble fraction of the products probably contains compounds relatively free of carbon-oxygen links and hence of greater value as liquid fuels. The water-soluble products, on the other hand, would probably be composed of depolymerized compounds containing a larger fraction of carbon-oxygen bonds.

Table 7: Total mass recovery of products from wood treated
with additives and tetralin.

Conditions: Temperature: 250°C
Residence time: 1 hr.
Initial hydrogen pressure: 200 psig
Wood: 12 g
Tetralin: 48 g
Water: 19 g
Additive: 1 g

Experiment No.	Additive	Recovery (wt % of dry wood)	
		Total mass	% of Initial Carbon
8	Molybdic Acid	72.2 ⁺	83.74
9	Zinc Chloride	68.1 ⁺	75.60
10	Antimony Tribromide	68.8 ⁺	81.30
11	Nickel Chloride	67.0 ⁺	74.64
12	Ferric Chloride	68.2 ⁺	79.34
13	Sodium Carbonate*	70.4	85.94
14	Copper Chromite	74.1	84.26
15	Ferric Sulfate	73.1	85.94
16	Ferric Chloride*	71.8	84.67
17	None	67.6	88.20

*Under carbon monoxide instead of hydrogen.

⁺ Does not include the mass of water-extractables.

When wood flour was treated with water and tetralin alone (at 250°C for 1 hr), about 10% by weight of the wood was converted to products soluble in toluene. Of the additives tested, ferric chloride, copper chromite, sodium carbonate, nickel chloride and zinc chloride resulted in toluene soluble yields greater than or equal to those obtained in the absence of an additive.

About 7.5 wt-% of the wood was converted to water extractable material when no additives were present. Of the additives tested, only ferric sulfate gave a greater yield of water extractable material. Water extracts of experiments 8 through 12 were clear indicating little or no extractable materials had been obtained, and the extracts were, therefore, not evaporated.

The total mass recovered as toluene extractables, water extractables and insoluble residue for each additive is shown in Table 7. Between 67 and 72 by weight of the starting wood was recovered, with the rest being converted to water and gases. The carbon content of the three fractions was determined by ultimate analysis and the net carbon recovered was also calculated. Between 74 and 88% of the carbon in the starting wood was recovered with the rest probably present as carbon dioxide and carbon monoxide.

Tetralin was evaporated and collected from each reaction product by the procedure described in Section II-C-2. In each case, between 95 and 98% by weight of the starting tetralin was recovered. Distilled tetralin from Experiments 12, 13 and 17 were analyzed by gas chromatography and mass spectrometry by Dr. Amos Newton of the Lawrence Berkeley Laboratory. A sample of the starting tetralin was also analyzed for comparison. No wood derived materials were identified in any of the recovered tetralin, indicating that no low-boiling materials were formed by these treatments. No significant amounts of naphthalene or dihydronaphthalene were produced suggesting the absence of hydrogen transfer from the solvent. The tetralin behaved only as an organic solvent with no hydrogen donation and little, if any, alkylation from the solvent to the wood.

3. Characteristics of Extracts

a. Ultimate Analysis

Ultimate analysis of toluene and water extracts and insoluble residue were determined for all experiments in the University's micro-analytical laboratory. The ultimate analysis of toluene extractables, water extractables and insoluble material are given in Tables 8, 9 and 10, respectively.

In general, the toluene extractable materials had atomic H/C ratios which were about the same as those of the starting wood. The presence of nickel chloride as additive resulted in a toluene soluble material of highest H/C ratio (1.51) compared to that of starting wood (1.21), whereas zinc chloride treated extract had the lowest H/C ratio (0.85). The atomic O/C ratios of toluene extractables ranged

Table 8: Ultimate analysis of toluene-extractables from wood treated with additives and tetralin.

Conditions: Temperature: 250°C
 Residence time: 1 hr.
 Initial hydrogen pressure: 200 psig
 Wood: 12 g
 Tetralin: 48 g
 Water: 19 g
 Additive: 1 g

Experiment No.	Additive	Analysis, wt. % (Ref. to dry wood)				H/C (atomic)	O/C (atomic)
		C	H	O	Ash		
8	Molybdic Acid	67.93	6.45	24.48	0.7	1.14	0.27
9	Zinc Chloride	69.37	4.94	24.30	1.3	0.85	0.26
10	Antimony Tribromide	73.60	7.13	17.75	1.5	1.16	0.18
11	Nickel Chloride	36.22	4.57	34.43	24.6	1.51	0.71
12	Ferric Chloride	52.02	5.60	23.83	10.9	1.29	0.34
13	Sodium Carbonate	66.20	7.01	18.57	7.7	1.27	0.21
14	Copper Chromite	71.48	6.46	21.86	0.0	1.08	0.23
15	Ferric Sulfate	47.84	4.74	26.62	15.5	1.19	0.42
16	Ferric Chloride*	51.63	5.34	29.99	12.8	1.24	0.44
17	None	72.58	6.53	20.58	0.1	1.07	0.21

*Under carbon monoxide instead of hydrogen

Table 9: Ultimate analysis of water-extractables from wood treated with additives and tetralin.

Conditions: Temperature: 250°C
 Residence time: 1 hr.
 Initial hydrogen pressure: 200 psig
 Wood: 12 g
 Tetralin: 48 g
 Water: 19 g
 Additive: 1 g

Experiment No.	Additive	Analysis, wt. % (Ref. to dry wood)				H/C (atomic)	O/C (atomic)
		C	H	O	Ash		
8	Molybdic Acid						
9	Zinc Chloride						
10	Antimony Tribromide				not recovered		
11	Nickel Chloride						
12	Ferric Chloride						
13	Sodium Carbonate*	45.97	5.67	24.72	23.5	1.48	0.40
14	Copper Chromite	38.14	4.55	37.5	19.7	1.43	0.74
15	Ferric Sulfate	34.16	4.18	38.38	23.1	1.46	0.84
16	Ferric Chloride*	38.38	5.21	39.96	16.1	1.63	0.78
17	None	68.56	5.29	21.97	2.5		

*Under carbon monoxide instead of hydrogen

Table 10: Ultimate analysis of insoluble material from wood treated with additives and tetralin.

Conditions: Temperature: 250°C
 Residence time: 1 hr.
 Initial hydrogen pressure: 200 psig
 Wood: 12 g
 Tetralin: 48 g
 Water: 19 g
 Additive: 1 g

Experiment No.	Additive	Analysis, wt. % (Ref. to dry wood)				H/C (atomic)	O/C (atomic)
		C	H	O	Ash		
8	Molybdic Acid	60.78	4.71	18.95	14.5	0.93	0.23
9	Zinc Chloride	56.83	5.59	29.66	7.9	1.18	0.39
10	Antimony Tribromide	61.81	4.35	25.67	8.10	0.85	0.31
11	Nickel Chloride	68.57	4.75	23.74	2.7	0.83	0.26
12	Ferric Chloride	68.90	4.75	24.25	1.8	0.83	0.26
13	Sodium Carbonate*	67.10	5.88	27.77	0.0	1.05	0.31
14	Copper Chromite	60.65	4.79	33.39	0.9	0.95	0.41
15	Ferric Sulfate	69.04	5.09	28.38	1.80	0.88	0.31
16	Ferric Chloride*	69.11	5.50	23.17	2.4	0.88	0.25
17	None	68.81	5.22	22.10	3.7	0.91	0.24
Untreated wood (dry)		53.17	5.61	40.54	0.50	1.27	0.57

*Under carbon monoxide instead of hydrogen

from 0.18 when antimony tribromide was used as an additive to 0.44 when ferric chloride was used as an additive. Untreated wood had an O/C of 0.57.

Water extractables from products of wood treatment with various salts were found to have higher H/C and O/C ratios than the starting wood. Atomic H/C ratios ranged from 1.43 to 1.63 compared to 1.27 for untreated wood flour. The O/C ratios were usually between 0.7 and 0.85 compared to 0.57 for untreated wood. The water extractable materials appeared to contain a greater fraction of oxygen-carbon linkages than the toluene extractable as indicated by the high O/C ratios.

In all experiments the insoluble residues obtained had lower H/C and O/C ratios than the starting wood. Residue obtained by treatment with zinc chloride had the highest H/C ratio (1.18) whereas ferric chloride and nickel chloride gave residues of the lowest H/C ratio (0.83). The insoluble residue from treatment with copper chromite had the highest O/C ratio (0.41) and molybdic acid gave a residue with the lowest O/C ratio (0.23). Dry untreated wood in comparison had an H/C ratio of 1.27 and an O/C ratio of 0.57.

b. Nuclear Magnetic Resonance Spectroscopy

Since the toluene extracts were probably a set of related compounds, an attempt was made to elucidate their characteristic structure. Nuclear magnetic resonance data for deuterated pyridine solutions of toluene extracts were obtained for all experiments. Tetramethyl silane was used as reference. Peaks obtained for various products are given in Table 11. These peaks were compared to standards given in

Table 11: Proton NMR of toluene extracts from wood treated with additives and tetralin.

Conditions: Temperature: 250°C

Residence time: 1 hr.

Initial hydrogen pressure: 200 psig

Wood: 12 g

Tetralin: 48 g

Water: 19 g

Additive: 1 g

Experiment No.	Additive	Resonance Shifts (δ) ppm (measured in deuterated pyridine)													
8	Molybdic Acid	7.9- 3.53	4- 2.33	2.83- 2.13	2.33- 1.9	2.13- 1.4	1.73- 1.1	1.4- 0.73	1.0- 0.16	0.53- 0.16	6.66				
9	Zinc Chloride	7.9- 6.93	6.86- 6.36	6.26- 5.93	5.53- 5.26	5.2- 4.86	4.23- 3.26	3.2- 2.4	2.6- 1.96	1.83- 1.43	1.4- 1.16	1.06- 0.73			
10	Antimony Tribromide	8.0- 6.86	3.96- 3.4	3.16- 2.3	2.3- 1.86	1.76- 1.30	1.36- 1.06	1.06- 0.73							
11	Nickel Chloride	8.43- 8.0	7.46- 6.90	5.8- 4.93	4.0- 3.33	3.0- 2.33	2.16- 1.93	1.43- 0.83	0.46- 0.33						
12	Ferric Chloride	8.13- 7.20	7.20- 6.73	6.73- 6.56	5.83- 4.8	3.86- 3.0	2.23- 2.0	0.73- 0.5	0.4- 0.2						
13	Sodium Carbonate*	7.63- 6.5	4.23- 3.56	3.23- 1.96	1.96- 1.63	1.36- 1.03	1.03- 0.6								
14	Copper Chromite	7.86- 6.5	6.5- 6.03	3.96- 3.46	2.93- 2.33	2.33- 1.73	1.73- 1.36	1.36- 1.16	1.0- 0.66	0.5- 0.36					
15	Ferric Sulfate	8.03- 7.03	6.1- 5.8	4.13- 3.73	3.6- 2.46	2.46- 2.1	1.96- 1.56	1.56- 1.36	1.2- 0.9	0.9- 0.7					
16	Ferric Chloride*	Not determined													
17	None	7.9- 6.76	4.1- 3.46	2.9- 2.37	2.4- 2.0	1.76- 1.45	1.46- 1.23	1.06- 0.83							

*Under carbon monoxide instead of hydrogen.

the literature (100). Product peaks spanned the entire spectrum. Major peaks were observed between $\delta = 7$ and 8 ppm and between $\delta = 3$ and 4 ppm. The first group corresponds to aromatic and phenolic protons and the second to alcohol and $-O-CH_3$ groups. Lower peaks were observed in the $\delta = 6$ to 7 ppm which correspond to acyclic $\begin{array}{c} H \\ \diagup \\ C = C \\ \diagdown \\ H \end{array}$ and phenolic and benzylic protons. These results suggest the formation of phenols, substituted phenols, and alcohols similar to products reported in earlier studies of the hydrogenation of lignin and cellulose.

c. Ultraviolet Spectroscopy

Ultraviolet spectra were obtained of dilute carbon tetrachloride solutions of toluene extracts of Experiments 12, 13 and 17. In each case two broad peaks were obtained; one at 2900 and the other at 3200 wavelength. The first could be caused by the double bond in carbonyl groups and the second by aldehyde groups.

4. Conclusion

Several inorganic salts were tested as catalytic additives for wood liquefaction at $250^\circ C$ for 1 hr. in the presence of tetralin as a possible hydrogen donor. No hydrogen transfer from the solvent was observed. About 50% by weight of the wood was converted to gases and toluene and water extractable materials in the absence of an additive. Under these conditions about 10 wt-% of the wood was converted to toluene extractable products. Of the additives tested nickel chloride, sodium carbonate and ferric chloride resulted in wood conversions greater than or equal to those obtained in the absence of an additive. Ferric chloride was found to be the most effective catalyst resulting in an overall conversion of about 60%. Toluene soluble yields greater

than or equal to those obtained in the absence of an additive were obtained with ferric chloride, copper chromite, sodium carbonate, nickel chloride, and zinc chloride. Ferric chloride resulted in the highest toluene extractables yield of about 28%.

About 7.5 wt-% of the wood was converted to water extractables when no additives were present. The addition of ferrous sulfate alone gave a greater yield of water extractables.

Atomic H/C ratios of the toluene extracts ranged from 1.51 to 0.85 compared to 1.21 for untreated wood. The O/C ratios of the toluene extracts ranged from 0.18 to 0.44 compared to an O/C ratio of 0.57 for untreated wood. In all experiments the insoluble residue had lower H/C and O/C ratios than the starting wood. The H/C ratios of the residues ranged from 1.18 to 0.86 and the O/C ratios from 0.41 to 0.23.

Nuclear magnetic resonance spectroscopy indicated that the toluene-soluble fraction of the products containing benzylic, phenolic, and alcoholic protons. Smaller concentrations of $-O-CH_3$ and $\begin{matrix} H \\ \diagup \\ C \\ \diagdown \\ H \end{matrix} = C$ were also observed. Ultraviolet spectra indicated the presence of carbonyic and aldehydic groups.

The additives tested appear to catalyze the depolymerization of wood to lower-molecular weight products soluble in toluene and water. Ferric chloride was found to be most effective of the additives tested yielding the highest amount of toluene-soluble material and overall conversion.

IV. SUGGESTIONS FOR FUTURE WORK

A. General Considerations

The results of this study indicate two broad areas for future work: (i) Further evaluation of and hydrogen donor treatment of wood. (ii) Screening of other catalysts for wood liquefaction and testing of the additives used in this study at higher reaction temperatures.

B. Further Evaluation of Acid-Hydrogen Donor Treatment

α -phellandrene was the only hydrogen-donor solvent evaluated in this study. In future work the study should be extended to other wood-derived donor solvents. Other components of wood-extracted terpinols may prove to be more effective hydrogen donors. Cyclohexanols and cyclohexadienes which could be produced from the hydrogenation of lignin, should also be tested. The objective of future work in this area should reduce the extent of solvent alkylation and/or condensation. Once an adequate hydrogen donor has been identified, the extent of hydrogen donation from the solvent should be measured and correlated to reaction conditions.

C. Catalyst Screening

Screening of potential catalysts was limited to temperatures of 250°C in this study. The additives evaluated here should be tested at higher temperatures to see if wider differences in catalytic activity become apparent. Reaction temperatures between 300 and 350°C are suggested, so that results can be compared with the process being tested at the DOE facility in Albany, Oregon.

Screening experiments should also be extended to cover a wider range of potential catalysts. Oxides and sulfides of transition metals are known to be good catalysts for decarboxylation and hydrogenation reactions and appear to hold promise for wood liquefaction.

Most of the past work on the hydrogenation and hydrogenolysis of wood and its constituents has been done in alkaline medium. The objective of the earlier studies was to convert lignin sulfonic acids produced during the manufacture of paper pulp. These lignin derivatives are produced as alkaline solutions and should be hydrogenated in alkali. The liquefaction of wood, however, would not be limited to alkaline hydrogenation. Since acids hydrolyze the cellulose in wood it may be beneficial to use homogeneous catalysts effective in an acidic solution. Acidic hydrogenation catalysts should also be screened, and their products and yields compared with those obtained by hydrogenation in a basic medium.

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