

SERI/TR-234-2907

ANNUAL REPORT

LIQUID FUELS FROM LIGNINS

Task: 5216.29

WPA: 516

Helena Li Chum

and

David K. Johnson

Editors

January, 1986

PREFACE OF THE DRAFT ANNUAL REPORT ON LIQUID FUELS FROM LIGNIN

This task was initiated on March 15, 1985 to assess the conversion of lignins into liquid fuels, primarily of lignins relevant to biomass-to-ethanol conversion processes. The task was composed of a literature review of this area and an experimental part to obtain pertinent data on the conversion of lignins germane to biomass-to-ethanol conversion processes. We engaged the advice of Dr. David Goheen, who worked at Crown Zellerbach Corp. and was heavily involved with their development of a phenols from lignins process, and is now with E. Seidell Associates, Inc. Dr. Goheen helped us review the literature of the area and provided extremely helpful suggestions for the experimental work, which started in late April of 1985. In order to quickly set-up experiments and start to assess the area, we engaged the cooperation of Professors Robert Baldwin and Scott Cowley from Colorado School of Mines. Much of the lignin hydrodeoxygenation reported here was performed by SERI staff at Colorado School of Mines. The bulk of the analytical work was carried out at the SERI laboratories. The cooperation of Dr. Cowley, an expert in heterogeneous catalysis, included a course on this subject, tailored to deoxygenation reactions and the areas of relevance to our work; and discussions on mechanisms and general guidance. Dr. Baldwin, an expert chemical engineer, with considerable experience in coal processing, helped us to obtain the first measurements and redesign his equipment, such that we could perform experiments sweeping volatile products as they were formed in the reactor, and thus avoiding excessive condensation reactions. We believe that this approach was very cost-effective and benefited from the experience of three independent researchers, with expertise in various fields necessary to this research. The experimental work reported here has been carried out in less than six months, and it is, therefore, preliminary. During this time, we evaluated reactors and analytical methodology. We also prepared the present draft report, with partial input from our coworkers.

At this point, the report will be reviewed by Drs. Goheen, Cowley, and Baldwin. After these reviews, it will be peer reviewed. We'll select a number of researchers in the field and solicit their input and suggestions. Among the peer reviewers, Professor K. V. Sarkanen, (University of Washington), Dr. John Hyatt (Eastman, Chemical Division), and Professor I. S. Goldstein (University of North Carolina) will be asked to review this document

prior to its more general distribution. The report will also be reviewed by SERI management and the U.S. Department of Energy program monitor, Mr. Richard Moorer.

We hope this document will be useful to the research community and to the U.S. Department of Energy in assessing the role of lignins coproduced with ethanol, or other fuels, in the biomass-to-fuels scenario.

Helena Li Chum  
January 30, 1986

## TABLE OF CONTENTS

|   | <u>Page</u> |
|---|-------------|
| I.0 EXECUTIVE SUMMARY.....  | 1           |
| II.0 INTRODUCTION.....  | 3           |
| II.1 Lignins and Their Preparation.....   | 4           |
| II.2 Methods of Conversion of Lignins Into Low-Molecular-Weight<br>Phenolic Compounds.....                                    | 10          |
| II.3 Summary of Petroleum Processing Technology Terminology.....  | 17          |
| III.0 LIGNIN CONVERSION TO LOW MOLECULAR WEIGHT COMPOUNDS - LIQUID FUELS<br>AND FUEL PRECURSORS.....                          | 25          |
| by:   |             |
| H. L. Chum, D. K. Johnson, S. Black, M. Ratcliff  |             |
| Solar Energy Research Institute   |             |
| 1617 Cole Boulevard   |             |
| Golden, CO 80401  |             |
| and   |             |
| D. W. Goheen  |             |
| E. Seidel Associates, Inc.  |             |
| 5545 East Evergreen Boulevard   |             |
| Vancouver, WA 98661   |             |
| III.1 Introduction.....   | 25          |
| III.2 Review of Hydrotreating of Lignins.....   | 26          |
| III.2.1 References from Eastern Europe.....   | 26          |
| III.2.1.1 General Hydrotreating Conditions.....   | 26          |
| III.2.1.2 Effect of the Nature of the Lignin and<br>of the Presence of Phenol.....  | 28          |
| III.2.1.3 Other Inhibitors and Other Catalysts.....   | 36          |
| III.2.1.4 Comparison Between Alkaline Hydrogenolysis<br>and Alkaline Solvolysis in the Presence<br>and Absence of Phenol..... | 38          |
| III.2.1.5 Other Work.....   | 38          |
| III.2.1.6 Applications of Hydrotreated Acid Hydrolysis<br>Lignins.....  | 43          |
| III.2.2 References from North America, Western Europe and Asia.....   | 44          |
| III.2.2.1 Summary of Hydrotreating of Lignin and<br>Wood in Organic/Aqueous Solvents under Mild<br>Reducing Conditions.....   | 44          |
| III.2.2.2 Hydrotreating in Organic Solvents Under<br>More Drastic Reducing Conditions.....                                    | 48          |
| III.2.2.3 Hydrotreating of Sweetgum Lignin from<br>Superconcentrated HCl Treatment of the Wood.....                           | 51          |
| III.2.2.4 Hydrogen-Donor Solvents.....  | 57          |

|           |  |     |
|-----------|--|-----|
| III.3     | Review of Petrochemical/Coal Techniques Applied to Lignin<br>Hydrotreating.....      | 61  |
| III.3.1   | Inventa A.-G. für Forschung und Patentverwertung.....                                | 61  |
| III.3.2   | Noguchi Institute of Japan and Crown-Zellerbach, Corp.....                           | 63  |
| III.3.3   | Hydrocarbon Research, Inc. (HRI).....  | 71  |
| III.3.3.1 | Description of Patents.....  | 71  |
| III.3.3.2 | Economic Evaluations of the Lignol <sup>TM</sup><br>Process.....                     | 77  |
| III.3.3.3 | Comparison of Hydrocracking/ Hydrodealkylation<br>with Fluidized-Bed Pyrolysis.....  | 85  |
| III.3.4   | Other Processes - Lignin as Catalyst for Coal or Oil<br>Residue Hydroprocessing..... | 87  |
| III.4     | Review of Selected Model Compound Hydrotreating.....                                 | 88  |
| III.4.1   | Thermolysis.....   | 88  |
| III.4.2   | Comparison of Thermal and Catalytic Hydrotreatments.....                             | 89  |
| III.4.3   | Catalytic Hydrocracking.....   | 92  |
| III.4.4   | Catalytic Hydrocracking Studies by Other Researchers.....                            | 96  |
| III.5     | Summary and Recommendations for Future R & D.....                                    | 103 |
| IV.0      | EXPERIMENTAL HYDROTREATING OF LIGNIN AND MODEL COMPOUNDS.....                        | 117 |
|           | By:  |     |
|           | D. K. Johnson, M. Ratcliff, F. Posey, H. L. Chum                                     |     |
|           | Solar Energy Research Institute  |     |
|           | 1617 Cole Boulevard  |     |
|           | Golden, Colorado 80401   |     |
| and       |  |     |
|           | R. Baldwin and S. Cowley   |     |
|           | Colorado School of Mines   |     |
|           | Golden, Colorado 80401   |     |
| IV.1      | Introduction.....  | 117 |
| IV.2      | Experimental.....  | 119 |
| IV.2.1    | Lignin Hydrotreatment Set-up.....  | 119 |
| IV.2.2    | Model Compound Hydrotreatment Set-up.....  | 122 |
| IV.2.3    | HPLC and GPC Analysis Conditions.....  | 124 |
| IV.2.4    | GC and GC/MS Analysis Conditions.....  | 125 |

|        |   |     |
|--------|---|-----|
| IV.3   | Results and Discussion.....                     | 131 |
| IV.3.1 | Lignin Hydrotreating Experiments.....           | 131 |
| IV.3.2 | 4-Propylguaiacol Hydrotreating Experiments..... | 141 |
| IV.4   | Conclusions and Future Work.....                | 145 |
| V.0    | BIBLIOGRAPHY.....                               | 147 |

SECTION I.0

EXECUTIVE SUMMARY

Will be prepared with input from the outside coworkers and reviewers to be included in the final report.

See Section III.5 for a Summary and Recommendations for future R&D.

## SECTION II.0

### INTRODUCTION

Over the past eighty years lignin researchers have focused their attention on the production of phenolic compounds from lignins. In addition to this synthetic goal, the elucidation of the structure of lignins was the driving force for much of the work carried out throughout these years. Whereas the elucidation of the composition and structure of lignin materials through degradative routes was more successful, the production of useful phenolics from waste lignins has not achieved commercial practice. One major reason for the lack of a viable commercial process has been the fact that lignin processing yields a complex mixture of products. Product separation costs are high and contribute to the difficulty of designing an economic process based on one or a few products. In addition, the cost of petroleum-derived phenol, the major envisioned competitive product throughout this research, went down from about \$0.20/lb in the 1950s to \$0.08/lb in the 1970s and is now about \$0.35/lb. The first price decrease was due to the introduction of new synthetic phenol capacity through the cumene process. The subsequent price increase was due to the increase in petroleum costs and shortages which followed the oil embargo. Now, in the mid 1980s, the price of petroleum has decreased substantially because of free market forces, conservation and a slow down in world economic activity. However, petroleum is a depletable resource, decreasing at a finite rate. Replacements of fuels derived from petroleum, primarily the liquid fuels employed in transportation, which account for about one-quarter of the use of petroleum today in the U.S.A., are needed for the future. Biomass is a renewable resource which can contribute to the liquid fuels pool.

This report addresses the desirability of conversion of the lignin fraction of biomass into a mixture of compounds that are higher value octane enhancers and fuel additives. It makes use of the mixture of phenolics generated in the conversion of lignin into phenolic compounds, and transforms them into a mixture of methyl ethers, which are suitable non-metallic octane enhancers, similar in properties to benzene, toluene, and xylene. Similar mixtures of ethers from coal liquids have been successfully tested with gasoline (Singerman 1980). These octane enhancers are fully compatible with gasoline. This report addresses the first stage - the production of low-molecular-weight



phenolic compounds, precursors of liquid fuels.

The economics of biomass-to-ethanol conversion processes can profit from the utilization of the lignin fraction for a higher value application than just furnishing process heat. In cooperation with Virginia Polytechnic Institute and State University researchers, "The Economic Contribution of Lignins to Ethanol Production from Biomass", has been assessed (Chum et al. 1985a). Markets for use of the lignin polymers and derived fuels have been identified and projections of intensity of demand were made for the year 2000 for various applications. The report showed that if fuel alcohol production in the billions of gallons scale was achieved in the future, lignin markets would not be saturated provided several polymeric applications were developed or that the conversion of lignins into liquid fuels was successfully achieved.

The coproduct credit can be calculated as follows:

$$\text{coproduct credit} = \frac{\sum_i^N (\text{wt lignin/wt ethanol}) \times (\text{lignin market value})}{\text{x (alcohol density)}}$$

The coproduct credit is given in \$/gallon of ethanol; wt lignin/wt ethanol represents the lignin recovery factor; the alcohol density is 6.6 lb/gallon. The symbol *i* represents the different lignin-derived products produced. In general, 7-10 lb of lignin can be coproduced with one gallon of alcohol. The economic impact can be felt even if only a fraction of the lignin was converted into higher value products. Figure 2-1 displays the coproduct credit as a function of the lignin value. The largest market for lignin-derived products is, in fact, the liquid transportation fuels. This report assesses one of the possible routes to convert lignins into higher value octane enhancers which can be used in lieu of benzene, toluene, and xylene. Contrary to ethanol or methanol usage, these enhancers would not increase the gasoline vapor pressure appreciably. They would allow the use of n-butane and light isoparaffins without adding appreciably to the vapor pressure of the resulting gasoline (see Section II.3).

## II.1 LIGNINS AND THEIR PREPARATION

Wood and its processing wastes represent a major source of renewable feedstocks for the production of fuels. Wood has a complex structure composed primarily of three interpenetrating biopolymers--cellulose, hemicelluloses (the carbohydrates), and lignin (the amorphous polyaromatic matrix around the

cellulosic fibers). Table 2-1 compares the composition of wood species with that of other forms of biomass, such as agricultural residues. Lignins are very abundant biopolymers, second only in availability to the natural polysaccharides. The separation of lignins from biomass is not a straightforward process; the isolation of lignin is generally integrated with the production of cellulosic fibers (Sarkanen 1979). Examples of the commercial processes that produce technical lignins are listed in Table 2-2 together with the most common preparations of lignins for structural determination investigations. The potential availability of industrial lignins produced by all these processes, but primarily by the kraft process in the United States, is very large. About 20 million tons of kraft lignins are used annually, almost exclusively as a fuel in recovery boilers. Lignosulfonates are produced at a much smaller scale, and are sold today primarily as inexpensive surfactants. The 1984 market of lignosulfonates and sulfonated kraft lignins was about 1 billion lb [see Chum et al. 1985a and references therein; Lin 1983].

Additional sources of lignins as co-products of biomass conversion processes may become available in the future, primarily if wood-to-ethanol processes are commercialized. Wood saccharification is practiced today on an industrial scale in the Soviet Union (Bungay 1981). The acid hydrolysis process yields a solid lignin byproduct. Table 2-2 presents examples of such lignins. The large lignin residue from wood saccharification plants in the USSR has been the driving force for the numerous research and development activities trying to convert these residues into more useful polymers of low-molecular-weight or into chemicals. Thus far, a viable commercial process has not emerged.

There is renewed interest in wood acid hydrolysis processes to produce high concentration sugar solutions for subsequent fermentation to ethanol. Both concentrated and dilute acid approaches are under investigation. These processes would produce solid lignins as residue. With the probable exception of those produced by hydrolysis with superconcentrated hydrochloric acid, the bulk of these acid hydrolysis lignins will be of high molecular weight and heavily condensed.

A different strategy can be employed, which does not use acids as hydrolysis catalysts for depolymerization of cellulose. [Acids catalyze the degradation reactions of carbohydrates into furfural derivatives and mixtures of carboxylic acids, and thus reduce the ultimate yields of fermentable sugars.] This

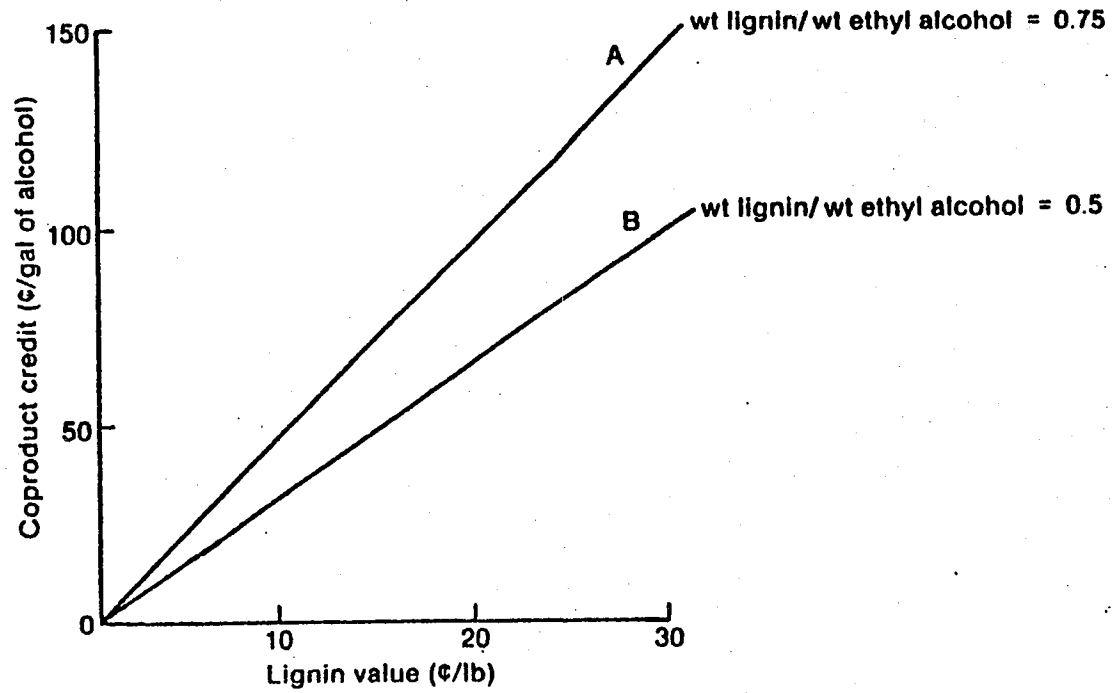


Figure 2-1. Lignin Coproduct Credit

Table 2-1 Composition of Various Types of Biomass (% dry weight)\*

| Material                         | Cellulose | Hemicelluloses | Pentosan | Lignin | Extractives |
|----------------------------------|-----------|----------------|----------|--------|-------------|
| Temperate hardwoods <sup>a</sup> | 43-45     | 23-35          | 12-24    | 16-24  | 2-8         |
| Softwoods <sup>a</sup>           | 41-43     | 24-33          | 8-14     | 24-33  | 1-7         |
| Grasses <sup>b</sup>             | 25-40     | 25-50          | 25-29    | 10-30  | ---         |
| Corn cobs                        | 41        | 36             | ---      | 6      | 14          |
| Corn stalks                      | 29        | 28             | ---      | 3      | ---         |
| Wheat straw                      | 40        | 29             | ---      | 14     | ---         |
| Bagasse <sup>c</sup>             | 37        | (29)           | 29       | 21     | 4.0         |

\*Adapted from Goldstein (1981), Chum et al. (1985a)

<sup>a</sup>Normal wood; the not-normal reaction wood for softwoods (compression wood) will have higher content of lignin and lower content of cellulose; for hardwoods tension wood will have higher contents of cellulose and lower content of lignin.

<sup>b</sup>Includes palms, bamboo, etc.

<sup>c</sup>Ash content 3%.

approach employs the enzymatic hydrolysis of the polysaccharides to fermentable sugars. This strategy requires that the biomass structure, and thus the carbohydrates, be made accessible to enzymes. Steam explosion of hardwoods or of agricultural residues can make the cellulosic structure accessible to enzymes [Iotech Corp., Ltd. 1980 and 1982, Chum et al. 1985b, and references therein]. Lignins can be isolated by dissolution (or extraction) from the exploded material by bases or other solvents. Table 2-2 lists some common preparations of these materials.

Another approach consists of simultaneously hydrolyzing and dissolving the lignin in an aqueous alcoholic medium in the temperature range of 180°-210°C or at lower temperatures (140°-160°C) in the presence of catalysts. This method of delignification is commonly called the organosolv pulping process and it has been reviewed by Sarkanen (1980). Table 2-2 also lists organosolv lignin preparations. Both steam explosion and organosolv delignification processes produce soluble low-molecular-weight lignin feedstocks. A comparison between organosolv lignins and steam exploded materials has been made on the basis of their chemical composition and molecular weight distribution (Chum et al. 1985c,d).

Thus, a variety of lignin products will be available for potential use as a chemical feedstock or as a source of heat, the lowest value application possible (-2¢/lb compared to coal, based on 11,300 BTU/dry lb higher heating value). The isolation costs of the lignins from biomass-to-ethanol processes are smaller than those from conventional kraft pulping because of the absence of large amounts of pulping chemicals that need to be recovered. Estimates of marginal costs to recover these lignins are -1-2¢/lb, depending on the process. It should be noted that lignins produced from different biomass sources (softwoods, hardwoods, bagasse, and straw) and by different processes will vary extensively in terms of chemical structure and molecular weight. Those produced by enzymatic hydrolysis (see Table 2-2, e.g. cellulolytic enzyme lignin) may differ little from the original plant lignins. Next, the milled wood lignin samples will not have been modified to a significant extent by reactions between the lignins and the solvents employed in their preparation. Lignins from acid-catalyzed saccharification processes will be more extensively modified by condensation reactions (except probably for concentrated HCl). Lignosulfonates are of high molecular weight (~25,000) but

Table 2-2. Lignin Isolation Methods and Resulting Preparations.

| Remark   | Treatment  | Preparation  |
|--|--|--|
| <u>Lignin isolated as derivatives by inorganic reagents</u>  |  |  |
| Technical pulping processes  | sulfite/bisulfite  | Lignin sulfonates (lignosulfonates)                                      |
|  | NaOH   | Alkali lignin (soda lignin)  |
|  | Na <sub>2</sub> S/NaHS   | Thiolignin   |
|  | NaOH/Na <sub>2</sub> S   | Kraft lignin (sulfate lignin)  |
| <u>Lignin as solid residue</u>   |  |  |
| Acid hydrolysis of polysaccharides   | H <sub>2</sub> SO <sub>4</sub>   | Sulfuric acid lignin (Klason lignin)                                     |
|  | HCl  | Hydrochloric acid lignin (Willstätter lignin)                            |
|  | HF   | Hydrofluoric acid lignin   |
| Oxidation of polysaccharides   | Na <sub>3</sub> H <sub>2</sub> IO <sub>6</sub>   | Periodate lignin (Purves lignin)   |
| Hydrolysis/dissolution of polysaccharides  | NaOH/H <sub>2</sub> SO <sub>4</sub> /<br>Cu(NH <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> | Cuoxam lignin, cuproxam lignin, cuprammonium lignin (Freudenberg lignin) |
| <u>Lignin by dissolution or extraction</u>   |  |  |
| Steam explosion (hydrolysis of polysaccharides and of lignins with steam followed by solvent extraction) | NaOH   | Alkaline-extracted steam-exploded lignin                                 |
|  | Alcohol:Water  | Methanol-(or ethanol)-extracted steam-exploded lignin                    |
|  | Dioxane:Water  | Dioxane-extracted steam-exploded lignin                                  |
| No appreciable reactions between lignin and solvent. (Treatment of wood)                                 | Alcohol extraction   | Native lignin (Brauns lignin)  |
|  | Vibratory milling dioxane-water extraction   | Milled wood lignin (MWL)<br>Björkman lignin                              |
|  | Brown-rot fungi treatment  | Enzymically liberated lignin (ELL)                                       |
|  | Milling/enzymatic treatment/solvent extraction   | Cellulolytic enzyme lignin (CEL)   |
| <u>Organosolv lignins</u>  |  |  |
| Hydrolysis of lignins (reactions between lignin and solvent)   | Alcohol/HCl  | Alcohol lignin   |
|  | Dioxane/HCl  | Dioxane acidolysis lignin  |
|  | Phenol/HCl   | Phenol lignin  |

Adapted from Fengel and Wegener, 1984.

See: Rydholm 1965, Brauns and Brauns 1952, Browning 1967, Sjöström 1981, Lai and Sarkanen 1971.

only a small fraction (~20%) of the aromatic rings carry a free phenolic hydroxyl group. Hardwood kraft, organosolv, and steam exploded lignins have a low average molecular weight ( $\leq 5000$ ) and the content of free phenolic hydroxyl groups is high (near 0.7 phenolic units per aromatic structure for hardwoods), particularly in kraft lignins.

## II.2 METHODS OF CONVERSION OF LIGNINS INTO LOW-MOLECULAR-WEIGHT PHENOLIC COMPOUNDS

Several methods have been used for lignin conversion into low-molecular-weight compounds. These methods are:

1. Destructive distillation at atmospheric or reduced pressure in air or reducing atmosphere to produce a mixture of gaseous and liquid products;
2. Pyrolysis of lignins under various conditions to produce a mixture of gaseous and liquid products, which contain phenolic compounds;
3. Fusion with salts or alkalies to yield phenolic acids and catechol;
4. Hydrotreating with a variety of catalysts, temperature ranges, hydrogen pressures, and reaction media to produce phenol, cresols and substituted mononuclear phenols;
5. Hydrolysis under acid, alkaline or neutral conditions to yield various types of phenolic compounds;
6. Oxidative degradation to vanillin, syringaldehyde and other compounds, and reductive degradation to low-molecular-weight phenols; and
7. Enzymatic degradation to mixtures of phenolic compounds.

Whereas the first six methods mentioned have been carried out on a preparative scale, the enzymatic processes have not been reported under those conditions and therefore will not be reported here. Reviews of these methods (all or partial) have been made by Chudakov (1968), Coughlin et al. (1984), Fischer (1980), Goheen (1971), Goldstein (1975), Hrutfiord (1971), Kringstad (1980), Osuskii and Kubin (1965), Sarkanen (1979), Schweers (1971) Seidel (1967), Soltes (1983), and Wienhaus et al. (1976).

Table 2-3 assembles selected references for the production of phenols from lignin using examples of the first six methods mentioned above. It contains some information on yields and qualitative composition. The more quantitative composition of the products will be given in Section III for the various hydrotreating and pyrolytic processes described in detail in that Section.

From the data of Table 2-3, the yields of soluble products from lignin range

Table 2-3. Summary of Methods for Production of Low Molecular Weight Compounds from Lignins - continuation

| Reference  | Lignin Type                             | Soluble Tars % | Phenols %       | Neutral Oils % |
|--|---|----------------|-----------------|----------------|
| <u>Hydrolysis Under Acid, Alkaline or Neutral Conditions</u> |   |                |                 |                |
| Clark, Green 1968  | Indulin AT                              | 70             | 11 <sup>b</sup> |                |
| Enkist et al. 1962   | Kraft                                   | 50             | 38              |                |
| Kirshbaums, Domburga 1970                                    | Alkali (aspen)                          |                | 12 <sup>b</sup> |                |
| Tegai et al.   | Lignin/<br>supercritical<br>isopropanol | 90             | 60 <sup>a</sup> |                |
| Zarubin, Tishchenko 1959                                     | Hydrolytic lignin                       | 108            | 20              |                |

| Reference                    | Lignin Type          | Phenols %        | Oxidizing Agent, Base    |
|------------------------------|----------------------|------------------|--------------------------|
| <u>Oxidative Degradation</u> |                      |                  |                          |
| Fisher, et al. 1951          | Lignosulfonates      | 6-8 <sup>d</sup> | O <sub>2</sub> , lime    |
| Freudenberg, Lautsch 1939    | Spent sulfite liquor | 12 <sup>d</sup>  |                          |
| Leger, Hibbert 1938          | Lignofulfonate       | 7 <sup>d</sup>   | none, NaOH               |
| Leopold 1952                 | Spruce wood lignin   | 27 <sup>d</sup>  | nitrobenzene, NaOH       |
| Monsanto Chemical Co. 1953   | Spent sulfite liquor | 10 <sup>d</sup>  |                          |
| Pearl 1942                   | Lignosulfonate       | 22 <sup>d</sup>  | CuSO <sub>4</sub> , NaOH |
| Pearl 1944                   | Lignin sulfonates    | 23 <sup>d</sup>  |                          |
| Pearl 1949                   | Lignosulfonate       | 28 <sup>e</sup>  | Ag <sub>2</sub> O, NaOH  |
| Pearl 1950                   | Lignin sulfonates    | 22 <sup>d</sup>  |                          |
| Schultz 1940                 | Spent sulfite liquor | 20 <sup>d</sup>  |                          |



Table 2-3. Summary of Methods for Production of Low Molecular Weight Compounds from Lignins - continuation

| Reference  | Lignin Type         | Phenols %          | Oxidizing Agent, Base                    |
|--|---------------------|--------------------|--|
| <u>Oxidative Degradation continued</u>                     |                     |                    |  |
| Sorensen, Mehlum 1956                                      | Lignosulfonate      | 32 <sup>d</sup>    | Na <sub>2</sub> S, O <sub>2</sub> , NaOH |
| Tomlinson, Hibbert 1936                                    | Lignosulfonates     | 6-8.5 <sup>d</sup> |  |
| <u>Reductive Degradation (Na in Liquid NH<sub>3</sub>)</u> |                     |                    |  |
| Shorygina, et al. 1949                                     | cuprammonium lignin | 21                 |  |

from 10-100% of the starting material. The higher yields of phenolic compounds are usually associated with the hydrotreating processes and pyrolysis. In general, the yield of single products in the mixture is low. The Hydrocarbon Research, Inc. (HRI) process described in detail in Section III.3.3., combines hydrocracking with hydrodealkylation and could produce 24.4 wt % phenol, 13.1 wt % benzene, 22.5 wt % light hydrocarbons (mostly gas), and 22.0 wt % heavy liquid used to provide process heat. The first step of that process produces a mixture of phenolic compounds. Detailed composition of this fraction is given in Table 3-18. In view of the higher yields of the hydrotreating processes, and of selected pyrolysis routes, the bulk of the report will deal with these processes. Fast pyrolysis, coupled with low pressures and short residence times, is another potential route to make phenolic compounds (Evans et al. 1986).

The production of low-molecular-weight chemicals from lignin involves the breaking of carbon-oxygen and carbon-carbon bonds which are common linkages of the lignin macromolecule. Such reductive cleavages are endothermic processes. It is common to allow the endothermic cleavage to occur in an atmosphere of hydrogen such that after cleavage, the fragments can react with hydrogen; the bond making with hydrogen will release energy. If reactive reactants such as hydrogen are not provided, secondary reactions, such as radical recombination (the main competing reaction even in the presence of hydrogen) reactions, will lead to the formation of higher molecular weight compounds (chars, heavy tars). Overhydrogenation (perhydrogenation) can occur in the presence of hydrogen and catalysts, leading to the formation of neutral compounds, such as cyclohexane and derivatives, thus destroying the aromatic rings and consuming too much hydrogen. To achieve the best yield of phenolic compounds, while minimizing the yield of the neutral fraction, with the minimum consumption of hydrogen is one of the goals of the R&D activities described in Section IV.

### II.3 SUMMARY OF PETROLEUM PROCESSING TECHNOLOGY TERMINOLOGY

The terminology used in petroleum processing (also applicable to coal) will be briefly reviewed because of its relevance to lignin processing. A summary of the common types of heterogeneous catalysts, their chemical class, their function in the various processes, and selected examples are given in Table 2-4. References to detailed discussions are Bond (1974), Cowley (1985), Gates

Table 2-4. Examples of common types of heterogeneous catalysts, their chemical class, their function and selected examples. (Adapted from Cowley, 1985)

| Class          | Function  | Examples   |
|----------------|---|--|
| Metals         | Hydrogenation<br>Dehydrogenation<br>Hydrogenolysis                        | Fe, Co, Ni<br>Pt, Pd, Ir   |
| Acids          | Polymerization<br>Isomerization<br>Cracking<br>Alkylation<br>Dealkylation | H <sub>3</sub> PO <sub>4</sub><br>H <sub>2</sub> SO <sub>4</sub><br>Silica-Alumina<br>Zeolites |
| Metal Sulfides | HDO, HDS, HDN <sup>a</sup><br>Hydrotreating                               | Co-MoS <sub>2</sub><br>Ni-WS <sub>2</sub>  |
| Metal Oxides   | Oxidation<br>Dehydrogenation  | NiO, ZnO<br>MoO <sub>3</sub>   |
| Metal Oxides   | Dehydration   | Al <sub>2</sub> O <sub>3</sub><br>SiO <sub>2</sub>   |

<sup>a</sup> HDO = hydrodeoxygenation, HDS = hydrodesulfurization, and HDN = hydrodenitrogenation.

et al. (1979), Emmett (1965), Pines (1981), and Satterfield (1980).

The term hydrogenation is nonspecific, but it often refers to saturation of multiple (double or triple) bonds or saturation of aromatic entities. In processes carried out at higher temperatures, significant cleavage of carbon-carbon bonds can occur with subsequent reaction of the fragments with hydrogen. The term hydrogenolysis implies the cleavage of C-C and C-O bonds in the presence of hydrogen. It is used whether metallic catalysts (usually unsupported) are present or not. Common types of catalysts are Fe, Co, and Ni.

The metallic catalyst can be supported on a material that contains acid sites, such as silica-alumina, that can carry out cracking reactions. The term hydrocracking is then used to indicate that the reactions with hydrogen are carried out on a catalyst that contains both metallic and acid sites.

Metal sulfides are often employed as catalysts for the removal of oxygen, nitrogen, or sulfur in processes known as hydrodeoxygenation (HDO), hydrodenitrogenation (HDN), and hydrodesulfurization (HDS). These catalysts provide a much milder treatment than metallic catalysts, and do not lead to excessive saturation of multiple bonds (perhydrogenation).

Catalytic reforming is another important process in the petroleum industry. It involves various reactions such as dehydrogenation and isomerization plus some hydrocracking.

The term hydrotreating (hydroprocessing) is used in a general way to include a variety of catalytic hydrogenation processes used in fuels refining and for the purification of products such as industrial solvents. The term can refer to producing a final product (e.g. special oils or lubricants) or to improve the quality of a feedstock stream for further processing.

We will use the term hydrotreating (hydroprocessing) in this report in general to indicate a process producing an intermediate feedstock for further processing. Whenever the processes utilized are well defined in terms of catalysts or processes, the appropriate name will be used.

In addition to these catalysts and processes which involve hydrogen reactions, other important processes in the petroleum industry that involve heterogeneous catalysts are polymerization, isomerization, cracking, and alkylation. Table 2-4 gives examples of catalysts employed in some of these processes. For the

chemical industry in general other catalysts are also important such as metal oxides on which dehydration reactions can occur (e.g. the synthesis of ethers), oxidation and dehydrogenation.

Heterogeneous catalysts are often employed because, among other advantages, it is easy to separate the reaction products from reactants. The catalysts can be made stable at the temperatures of operation, and are inexpensive. Unfortunately, some disadvantages of heterogeneous processes include less selectivity than, for instance, the corresponding homogeneous catalysts, and a very complex chemistry. Often catalysts are developed by trial and error. However, the powerful experimental techniques available today, and increased knowledge of the field of heterogeneous catalysis, make the selection or design of catalysts a much simpler task.

Also of interest to this report are thermal processes, carried out in the absence of hydrogen, referred to as pyrolysis, thermal cracking or thermolysis. An additional process of interest to this report is steam reforming. It is somewhat of a misnomer since it refers to a catalytic reaction on supported nickel (for example). For instance, while steam cracking and catalytic cracking which are not catalyzed processes, steam reforming converts naphtha to substitute natural gas, town gas, synthesis gas or hydrogen.

Many of these catalytic and non-catalytic processes are commonly employed in the petroleum industry. Scheme 2-1 shows an example of the catalytic refining picture for a crude oil (Wyoming sour). The refining scenarios will vary from one refiner to another. The representative fractions from petroleum distillation are assembled in Table 2-5. Usually, gasoline is blended from streams from several sources in the refinery, including portions of the products of suitable volatility from catalytic cracking, catalytic reforming, hydrocracking, alkylation and straight run gasoline. In addition, light isoparaffins and n-butane may be added in amounts that vary according to the season.

Aromatic compounds such as benzene, xylene and toluene (BTX) have among the highest octane numbers. They are produced primarily by the catalytic reforming (dehydrogenation) of naphthenes. Typical aromatic composition is benzene (10%), toluene (47%), xylenes (32%), other aromatics (e.g. ethylbenzene) 11%. The lignin-derived compounds, primarily the methyl aryl

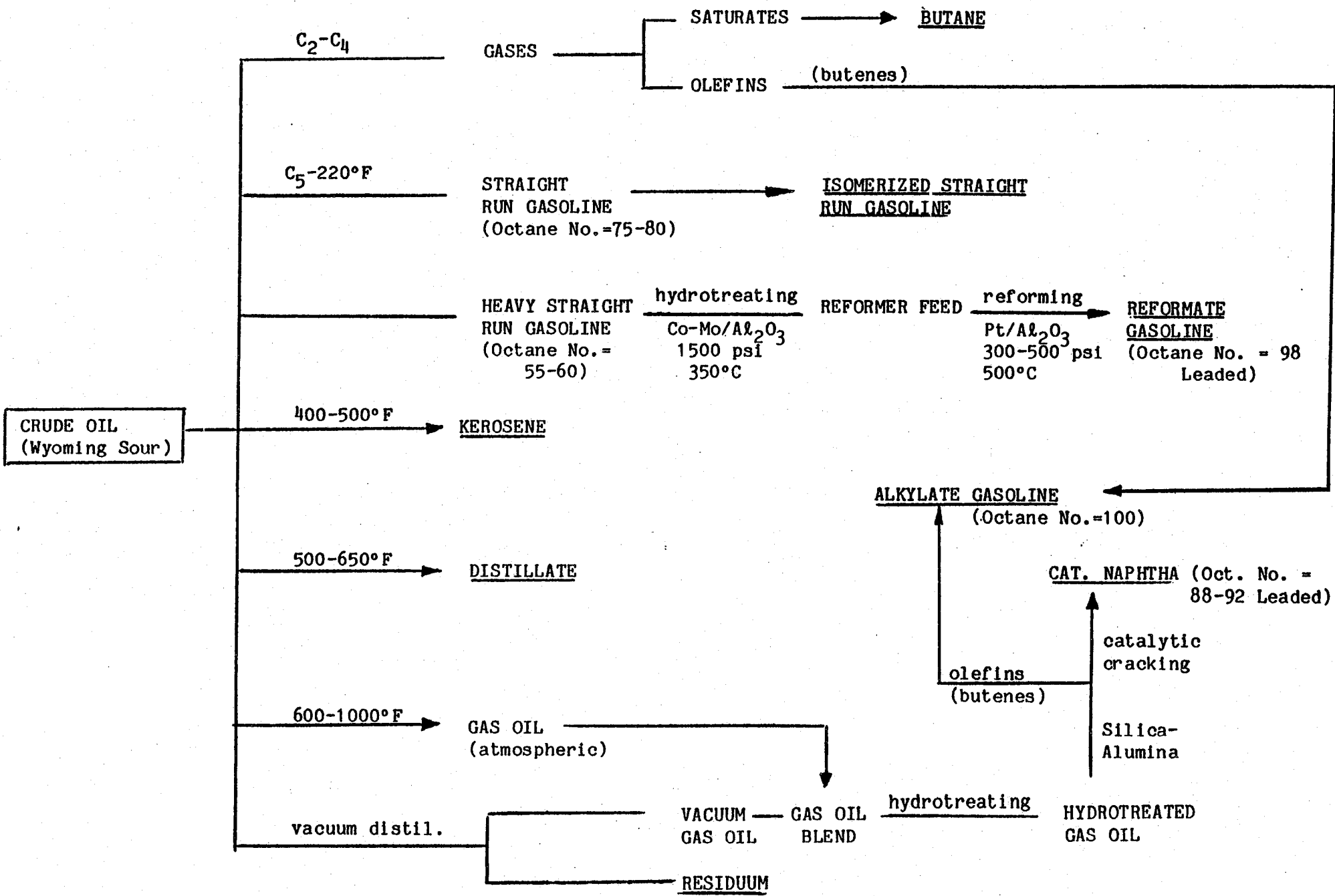


Table 2-5. Representative fractions from distillation of petroleum. (from Satterfield, 1980)

| Fraction                             | Component range and/or boiling point range, °C(°F) | Use   |
|--------------------------------------|--|---|
| 1. Gas                               | Up to C <sub>4</sub>                               | Burned as fuel. Ethane may be thermally cracked to produce ethylene. Propane or a mixture of propane and butane may be sold as liquified petroleum gas (LPG). |
| 2. Straight-run gasoline             | C <sub>4</sub> -C <sub>5</sub>                     | Blended into gasoline.  |
| 3. Virgin naphtha (light distillate) | 150 (300)<br>(C <sub>5</sub> )                     | Used as a feed for catalytic reforming or blended into gasoline.  |
| 4. Heavy naphtha (kerosene)          | 120-200 (250-400)<br>(Up to -C <sub>15</sub> )     | Jet fuel, kerosene.   |
| 5. Light gas oil                     | 200-310 (400-600)<br>(Up to -C <sub>20</sub> )     | Used as No. 2 distillate fuel oil, or blending stock for jet fuel and/or diesel fuel.   |
| 6. Gas oil (heavy distillate)        | -350 (650)<br>(Up to -C <sub>25</sub> )            | Used as a feed to catalytic cracker or sold as heavy fuel oil.  |
| 7. Atmospheric residual              | -350+(650+)  | Various uses. May be distilled under vacuum to produce vacuum-gas oil, coked, or burned as fuel.  |
| 8. Vacuum residual                   | -560+(1050+)<br>equivalent boiling point           |   |

ethers we are investigating, could enter the gasoline blending system by replacing the high octane number aromatic fraction.



## SECTION III.0

LIGNIN CONVERSION TO LOW MOLECULAR WEIGHT COMPOUNDS - LIQUID FUELS AND  
FUEL PRECURSORS

by

H. L. Chum, D. K. Johnson, S. Black, M. Ratcliff  
Solar Energy Research Institute  
1617 Cole Boulevard  
Golden, CO 80401

and

D. W. Goheen  
E. Seidel Associates, Inc.  
5545 East Evergreen Boulevard  
Vancouver, WA 98661

## III.1 INTRODUCTION

This section presents a review of the lignin hydrotreating literature, primarily, the references that have not been reviewed in a systematic manner before. Thus, Section III.2 contains a review of lignin hydrotreating, in which references are grouped geographically. One part of the section details the references from Eastern Europe. A second part assembles references from North America, Western Europe and Asia. Since the latter part has been reviewed before, up to the early eighties, the coverage of recent citations is more complete.

Some complete processes for lignin conversion to low-molecular weight phenolics, or to phenol and benzene, have been developed over the years. These processes employ techniques developed and used in petroleum processing. These references are discussed and assembled in Section III.3. The co-processing of lignins and coal or heavy petroleum residues is also presented. For comparison, a few thermal processes are also reviewed in this Section.

The past five years have seen some studies of lignin model compound hydroprocessing. Examples of these reactions are discussed in Section III.4. The aim of these studies is to guide catalyst selection, and through the understanding of the reactions involved, to allow the design of better processes (higher selectivity for desired reactions).

A summary of the reported results and some recommendations for further R&D are made in Section III.5.

The references cited in this Section are included in Section V, the Bibliography. This Section contains, in addition to all references cited, additional references which were obtained as a result of computer searches of both Chemical Abstracts and the Institute of Paper Chemistry Abstracts using key words germane to this Section. We feel that providing all references can be helpful to researchers in the field, since all citations contain full titles of the papers. References from manual searches of Chemical Abstracts prior to 1969 have also been included.

### III.2 REVIEW OF HYDROTREATING OF LIGNINS

#### III.2.1 References from Eastern Europe

The present review is based on available translations of the work plus additional translations of other papers, either in full, or of the relevant parts for the preparation of this report, such as experimental sections, tables, discussions and conclusions. This review incorporates as much of the primary data as possible, such that readers can have access to most of the data we have at hand.

The order in which the papers are reported was selected to represent as clear a picture of the work as possible. At the end of the section, we will also present summaries of the papers and patents dealing with the envisioned application for the hydrotreated products. The concept of converting the low molecular weight phenolics into fuel additives (octane enhancers) was not explored in the Soviet Union literature we analyzed.

##### III.2.1.1 General Hydrotreating Conditions

The bulk of the Russian literature reviewed utilized the following conditions for hydrotreating:

Lignin: Acid hydrolysis.

Medium: 5% by weight aqueous sodium hydroxide solutions; in general, 15 g of base were employed for 100 g of lignin and a 1:3 ratio of lignin to base solution.

Catalyst: Sulfides of cobalt, copper, nickel, molybdenum, and iron at 2 g for 100 g of lignin were investigated. Most of the papers that detail product composition employed sulfides of either

cobalt, molybdenum or iron, as preferred catalysts.

Temperature: 360° - 380°C.

Reactor: Described as a rotating autoclave in most papers.

Reaction Time: 2 hours at temperature. No details relative to heating up time are given.

Initial Hydrogen Pressure: 100 atm.

Hydrogen Consumption: About 0.026 m<sup>3</sup> (or about 2.3 g) per 100 g lignin, or 23 kg/ton lignin.

Inhibitors: A number of substances were found to inhibit the formation of condensation products and, therefore, increase the the yield of low molecular weight products. The most successful inhibitor was phenol, although phenol could be replaced by the phenolic fraction generated during hydrotreating. Typical experiments employed 20 g of phenol added to 100 g of lignin.

Product separation after hydrotreating: The contents of the autoclave were discharged to a beaker; water was used to rinse the autoclave. After filtration of the solids, followed by ether washes of the solid residue, the combined ether washes and aqueous solution containing the hydrotreated products, were exhaustively extracted with ether. After drying the ethyl ether solution with anhydrous sodium sulfate, filtering the solids and evaporating the ether, the total products of hydrotreating were isolated.

Separation of Fractions: The organic product was extracted with aqueous solutions at various pH's to give three fractions: acids (extracted from 10% sodium bicarbonate), phenolics (extracted from 10% sodium hydroxide), and neutrals (remained in petroleum ether after the previous extractions).

Typical Example: To 100 g cotton hull hydrolysis lignin, 300 ml of 5% sodium hydroxide solution, 20 g of phenol, and 2 g of a catalyst were added. The mixture was charged to the autoclave with an initial hydrogen pressure of 100 atm. The mixture was heated, the autoclave rotated, and the reaction was allowed to proceed for two hours at 360° - 380°C. The typical yield of product was 90 g (as described in work-up above). After subtraction of the amount of phenol added, the yield of hydrotreated products is 70 g. From these, 24.5 g phenolics, 35.0 g neutrals, and 10.5 g acids were obtained. Weight percent of phenolics, neutrals, and acids: 50, 35, and 15%

respectively (Bronovitskii, Cheremukhin, Volochkovich, and Kalinskaya 1967).

### III.2.1.2 Effect of the Nature of the Lignin and of the Presence of Phenol

Five acid hydrolyses lignins listed in Table 3-1 were the feedstocks for the hydrotreating studies, as described in Section III.2.1.1, in the presence and absence of phenol with CoS as catalyst (Bronovitskii, Kalinskaya, and Ikramova 1971a). The composition of these lignins, in terms of their  $C_9$  formulae and monomer molecular weight are also given in Table 3-1. The effect of phenol on the distribution of products from hydrotreating these five lignins can be seen in Figure 3.1. The left bars correspond to yields in the absence of phenol, while the right bars indicate the yields in the presence of 20 g phenol per 100 g of lignin investigated. The yields of residue, resins, and total liquid products are displayed in this figure. The liquid products and the residue were influenced by the presence of phenol more than the yields of resins. Within the various feedstocks, the presence of phenol most influenced the results from cotton hull lignins, followed by the various types of acid hydrolyses lignins from spruce; the least influenced were the data from sunflower hull lignins. The ether-soluble fraction contained the following weight % of phenolics, acids and neutral substances: 45.7, 14, and 40.3 and 47, 27, and 26 respectively for cotton hull and spruce (sulfuric acid) lignins. The average molecular weights of the neutral products and of the phenolics obtained without phenol were 332 and 204, respectively. In the presence of phenol, the corresponding molecular weights were 130 and 120, supporting their suggestion that phenols inhibit radical chain reactions. The monohydric phenolic fraction yields from cotton hull and spruce lignins were respectively 27 and 34%. Table 3-2 compares the amounts and types of phenolic compounds as determined by gas-liquid chromatography and shows that the two samples had a high content of cresols. The higher yield of phenol from cotton hull lignin is due to the importance of cinnamyl alcohol as precursor of this lignin. The authors suggest that this process could be a source of cresols.

The composition of the neutral fraction, which remains in ether solution after extraction with 10% aqueous sodium bicarbonate and 10% aqueous sodium hydroxide, was described by Bronovitskii, Kalinskaya, and Ikramova (1971b). In this mixture there are true neutral substances, which do not contain groups that react with base. Ketones, alcohols and hydrocarbons are present in this fraction (see Table 3-3). In addition to neutral substances, this fraction

Table 3-1. Examples of Lignins Investigated (Bronovitskii, Kalinskaya, and Ikramova 1971a)

| LIGNIN                         | ASH % | KLASON<br>LIGNIN<br>CONTENT % | $C_9$<br>x | FORMULA <sup>a</sup><br>y | z   | m    | MONOMER<br>MOL. WEIGHT |
|--------------------------------|-------|-------------------------------|------------|---------------------------|-----|------|------------------------|
| Spruce <sup>b,c</sup>          | 1.7   | 81.6                          | 7.7        | 2.0                       | 1.0 | 0.94 | 194                    |
| Spruce <sup>c,d</sup>          | 1.5   | 82.3                          | 8.8        | 2.5                       | 1.3 | 0.84 | 205                    |
| Sunflower hulls <sup>b,e</sup> | 5.4   | 74.0                          | 8.3        | 2.7                       | 1.0 | 0.72 | 200                    |
| Spruce <sup>b,f</sup>          | 1.1   | 80.5                          | 8.7        | 2.3                       | 1.1 | 0.72 | 194                    |
| Cotton hulls <sup>b</sup>      | 3.7   | 78.0                          | 9.7        | 3.6                       | 0.6 | 0.32 | 195                    |

<sup>a</sup>  $C_9H_xO_y$  (OH total)  $z$   $(OCH_3)_m$ ; <sup>b</sup>  $H_2SO_4$ ; <sup>c</sup> HCl; <sup>d</sup> located in Kanskii;

<sup>e</sup> located in Krasnodar; <sup>f</sup> located in Leningrad; <sup>g</sup> located in Ferganski;

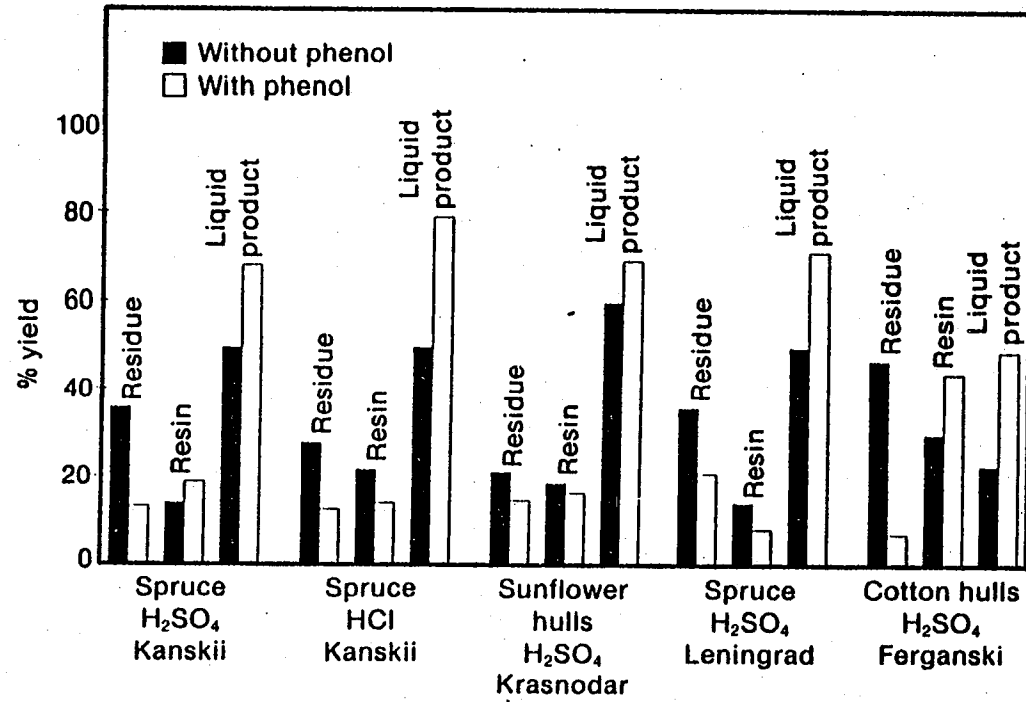


Figure 3-1. Effect of Phenol on Lignin Hydrotreating Product Distribution. (Bronovitskii, Kalinskaya, and Ikramova 1971a)

Table 3-2. Yields (wt %) of Monohydric Phenolic Compounds from Hydrotreating of sulfuric acid cotton hull and spruce lignins (Bronovitskii and Kalinskaya 1967b).

| Phenolics*                  | Cotton Hull | Spruce |
|-----------------------------|-------------|--------|
| phenol                      | 38          | 3.8    |
| o-cresol                    | 13.8        | 12.5   |
| m, p-cresol                 | 11.9        | 35     |
| 2,6-xyleneol                | 1.3         | --     |
| unidentified                | 5.2         | 10.6   |
| o-ethylphenol               | 12.5        | 10     |
| p-ethylphenol               | 11.2        | 14.9   |
| unidentified                | 3.2         | 5.2    |
| p-propylphenol/3,4-xyleneol | 2.9         | 5.2    |
| 3-methyl-4-ethylphenol      | --          | 1.6    |
| unidentified                | --          | 1.2    |

\*Unidentified compounds listed in the order they appeared in the gas-chromatographic determination on a polyether of diethylene glycol and adipic (and succinic) acid and Apiezon L stationary liquid phase. Identification based on comparison of retention times of methylated mixture with that of authentic methylated compounds.

Table 3-3. Gas-liquid Chromatograms of True Neutral Compounds in the Neutrals Fraction on Apiezon L (Bronovitskii, Kalinskaya, and Ikramova 1971b).

| RETENTION TIME<br>MIN | COMPOUND            | WT%  |
|-----------------------|---------------------|------|
| 1.8                   | methyl ethyl ketone | 2.1  |
| 1.9                   | unidentified        | 3.3  |
| 2.5                   | cyclohexane         | 1.1  |
| 3.4                   | unidentified        | 2    |
| 4.0                   | unidentified        | 2.9  |
| 7.7                   | cyclopentanone      | 8.4  |
| 8.2                   | cyclopentanol       | 28.1 |
| 10.3                  | unidentified        | 11.0 |
| 12.5                  | unidentified        | 36.5 |
| 17.7                  | cyclohexanol        | 2.6  |
| 19.3                  | cyclohexanone       | 4.0  |

also includes sterically hindered phenols and complex phenolic compounds, which cannot be extracted from 10% aqueous sodium hydroxide, as well as quinol-ether substances. In order to unravel the composition of this complex fraction, a very strong base (sodium alkoxide - commonly referred to by the Russian authors as Claisen base) was added to the petroleum ether solution of the neutrals. This base decomposes the complex phenolics and quinol-ethers, thus allowing the identification of possible precursor compounds, most of which are phenolic compounds. The true neutral fraction does not dissolve in the strong base. Table 3-4 summarizes the compounds determined by gas-liquid chromatography soluble in strong base for two acid hydrolyses lignins [spruce 80%) and cotton hull (80%)] compared to the hydrotreating under identical conditions of two model compounds [1-(4-hydroxy-3-methoxyphenyl)-propanone-1 and dehydrodivanillin]. The nature of the neutrals fraction is quite complex and uncertain; however, it is clear that under the influence of strong bases simple phenolic compounds, alcohols, ketones and hydrocarbons are isolated.

The acids fraction from the acid hydrolysis cotton hull lignin hydrotreatment (14%) was composed of 5.1% of hydroxyaromatic acids, 3.9% of saturated carboxylic acids and 5% of alicyclic aromatic acids. From spruce lignin, the corresponding amounts of hydroxyaromatic, saturated carboxylic, and alicyclic aromatic acids were respectively 10.8, 6.0, and 10.2%. The hydroxyaromatic acids fraction was analyzed by distillation and decarboxylation, which converts the hydroxyacids into the corresponding phenolic compounds. Table 3-5 presents the compounds identified after distillation and decarboxylation, and their proportions.

The content of saturated carboxylic acids of low molecular weight was 5.6% of ether-soluble fraction, and included formic acid (10.5%), acetic acid (32.5%), and propionic acid (19.7%) for the acid hydrolysis cotton hull lignin. The corresponding data for the acid hydrolysis spruce lignin are: 10.3% of ether soluble with formic, acetic, and propionic acid contents, respectively, of 10, 26.8, and 26.6% (see also Bronovitskii, Kalinskaya, and Ikramova 1968).

The yield of neutrals was found to increase with increased reaction time with concomitant decrease of both phenolics and acids fractions. For cotton hull acid hydrolysis lignins the yields of phenols, acids, and neutrals for 2 and 3 hour processes are compared in Fig. 3-2. Data for the 2 hour process with hydrolyzed spruce lignin is also included in the figure.



Table 3-4. Gas-liquid chromatograms of the phenolic compounds obtained after strong base treatment of the Neutrals fraction (Bronovitskii, Kalinskaya, and Ikramova 1971b).

| Comparative Retention Times | Substance Identification | % identified substance on polyethyleneglycol 6000 from: |                                       |                     | Comparative Retention Time | % identified substance on Apiezon L from: |                    |
|-----------------------------|--------------------------|---|---------------------------------------|---------------------|----------------------------|---|--------------------|
|                             |                          | Spruce Lignin   | 1 (4-oxy-3-methoxyphenyl propanone-1) | Dehydro-di-vanillin |                            | Substance Identification                  | Cotton Hull Lignin |
| ≤1                          | Not identified           | 1.3   | 16.3                                  | 0.6                 |                            |   |                    |
| 1.00                        | phenol                   | 2.9   | 4.5                                   | 0.8                 |                            |   |                    |
| 1.43                        | o-cresol                 | 2.0   | 3.1                                   | 1.9                 | 1.00                       | phenol                                    | 1.7                |
| 1.53                        | m,p-cresol               | 2.9   | 4.9                                   | 1.7                 | 1.33                       | Not identified                            | 4.5                |
| 1.73                        | o-ethylphenol            | 3.5   | 6.1                                   | 6.1                 | 1.53                       | m-cresol                                  | 6.2                |
| 1.96                        | 2,5-xyleneol             | 11.3  | 4.6                                   | 4.4                 | 1.80                       | Not identified                            | 9.7                |
| 2.35                        | p-ethylphenol            | 12.1  | 2.3                                   | 4.0                 | 2.2                        | o-ethylphenol                             | 12.9               |
| 2.78                        | p-propylphenol           | 13  | 22.8                                  | 4.9                 | 2.68                       | p-ethylphenol                             | 7.7                |
| 3.20                        | 3,4-xyleneol             | 11.9  | 12.7                                  | 2.1                 | 2.86                       | 3,4-xyleneol                              | 8.5                |
| 3.72                        | 3-methyl-4-ethylphenol   | 8.2   | 1.8                                   | 1.7                 | 3.20                       | hydroquinone                              | 9.1                |
| 4.5                         | Not determined           | 5.2   | 2.2                                   | 2.1                 | 3.30                       | p-propylphenol                            | 9.5                |
| 5.1                         | Not determined           | --  | 2.8                                   | --                  | 4.0                        | p-methylguaiacol                          | 8.7                |
| 5.6                         | hydroquinone             | 2.7   | 8.7                                   | 3.6                 |                            |   |                    |
| 6.6                         | p-methylguaiacol         | 2.2   | --                                    | --                  | 4.60                       | Not identified                            | 4.9                |
| 7.0                         | Not identified           | --  | 1.5                                   | 4.7                 | 5.4                        | Not identified                            | 5.8                |
| 7.7                         | Not identified           | 3.3   | 2.3                                   | 7.5                 | 6.8                        | Not identified                            | 3.2                |
| 8.6                         | Not identified           | --  | --                                    | 8.2                 | 8.30                       | p-propylguaiacol                          | 3                  |
| 10.3                        | p-propylguaiacol         | 5.6   | 5.4                                   | 7.4                 | 10                         | Not identified                            | 4.6                |
| 11.6                        | Not determined           | --  | --                                    | 12.3                |                            |   |                    |
| 13.3                        | Not determined           | 5.8   | --                                    | 11.3                |                            |   |                    |
| 15.7                        | Not determined           | 3.5   | --                                    | 12.8                |                            |   |                    |

Table 3-5. Phenols from gas-liquid chromatography of distillate of hydroxyaromatic fraction on Apiezon L 15% on INZ-600 (Bronovitskii, Volochkovich, Kalinskaya, and Nam 1968).

| Phenolics              | Cotton Hull | Spruce |
|------------------------|-------------|--------|
| phenol                 | 42.3        | 78.2   |
| o-cresol               | 19.2        | 4.5    |
| p-cresol               | 4.1         | --     |
| guaiacol               | 10.3        | --     |
| o-ethylphenol          | 8.0         | --     |
| p-ethylphenol          | 5.2         | 3.5    |
| p-ethylguaiacol        | --          | 2.0    |
| 3,4-xylenol            | 2.1         | 2.1    |
| hydroquinone           | 5.0         | --     |
| propylguaiacol         | 0.3         | 2.5    |
| 3-methyl-4-ethylphenol | --          | 1.5    |
| unidentified           | 3.5         | 5.7    |

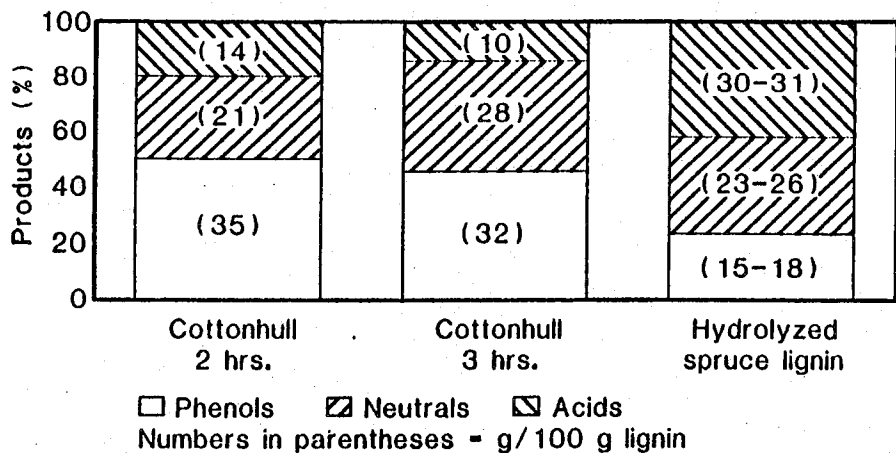


Figure 3-2. Products from Lignin Hydrogenolysis (Phenol Added) (Bronovitskii, Volochkovich, Kalinskaya, and Nam 1968)

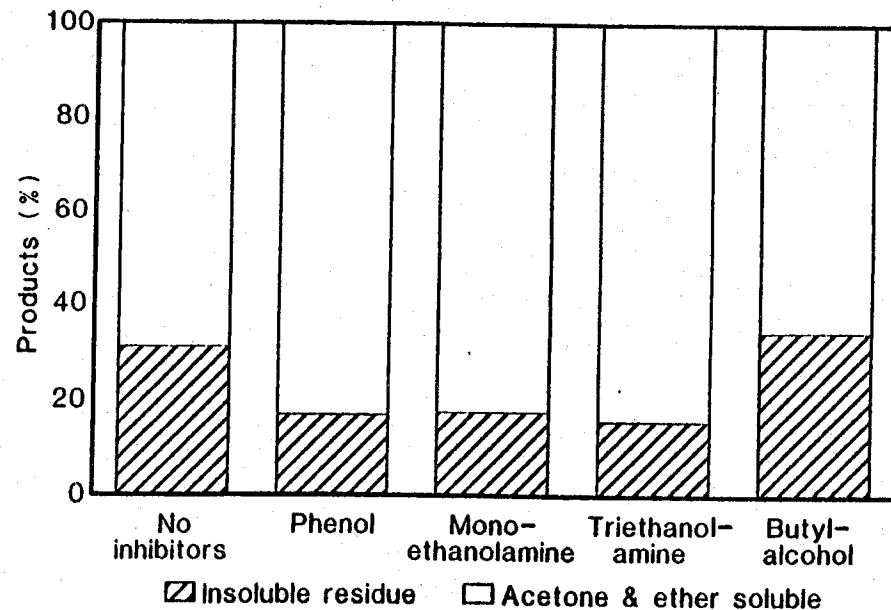


Figure 3-3. Products from Cotton Hull Lignin Hydrogenolyses for 2 Hours at 360°C on CoS. Yield of Soluble and Insoluble Products as a Function of the Nature of the Inhibitor. (Bronovitskii, Volochkovich, Kalinskaya, and Nam 1968)

In addition, Bronovitskii and Kalinskaya (1972) investigated the hydrogenolysis of spruce lignin prepared according to Willstätter (HCl). After hydrogenolyses under the conditions described in Section III.2.1.1, up to 80% of the Willstätter lignin was transformed into low-molecular weight ether-soluble products. Yields of phenolics, neutrals and acid fraction in the ether soluble fraction were 43.7%, 43.7% and 12.7%, respectively. About 47% of the phenolic fraction consisted of simple phenols such as o-, m-, and p-cresol. The neutral fraction had a similar chemical composition to the corresponding fraction described before. Treatment of the neutrals with strong (Claisen) base gave a soluble (25%) and an insoluble (75%) fraction. Among the soluble products, hydroquinone, phenol, o-, and p-cresol, o- and p-ethyl phenol were present. The total amount of neutral fraction was 1.7 times higher for the spruce Willstätter lignin than for spruce acid hydrolyses ( $H_2SO_4$ ) lignin.

### III.2.1.3 Other Inhibitors and Other Catalysts

The quantity of insoluble residue formed in the hydrotreating process is a function of the catalyst and of the nature of inhibitor used. For instance, for acid hydrolysis cotton hull lignin hydrotreating, CoS was found to be the best catalyst, and the effect of the added inhibitor is shown in Figure 3-3. While phenol, monoethanolamine and triethanolamine gave about half of the insoluble residue of the process with no inhibitor, butyl alcohol gave even more insoluble residue than in the absence of inhibitor. Copper sulfide was considered an unsatisfactory catalyst but iron sulfide gave results similar to cobalt sulfide (26% insoluble residue in the presence of phenol and 40% in its absence).

A more detailed investigation of the hydrogenolyses of cotton hull lignin and model compounds in the presence of monoethanolamine (MEA) was made by Bronovitskii, Ikramova, and Kalinskaya (1973). The model compounds selected for this study were dehydrodiguaiacol (I), 1-(4-hydroxyphenyl)-propanone-1 (II), and 1-(4-hydroxy-3-methoxyphenyl)-propanone-1 (III). The model compound or lignin (12 g based on organic content), monoethanolamine (8 g) and CoS catalyst were investigated under the conditions described in Section III.2.1.1. The products were extracted in ether and the ether-soluble fraction was separated into three portions: acidic, phenolic, and neutrals. Table 3-6 shows the yields from the above model compounds and cotton hull

Table 3-b. Yield of Extractable materials and composition of products after hydrogenolyses in the presence of monoethanol amine (MEA) inhibitor compared to phenol as inhibitor. (Bronovitskii, Ikramova and Kalinskaya 1973)

| Compounds<br>Hydrogenated | Yield of Ether<br>Extractables |       | Phenols (%) |       | % Total<br>Phenols | Neutrals (%) |       | % Phenols<br>Isolated      | Acids (%) |       | Elemental Analysis<br>of Neutral Products<br>w/ethanolamine (%) |       |      |
|---------------------------|--------------------------------|-------|-------------|-------|--------------------|--------------|-------|----------------------------|-----------|-------|---|-------|------|
|                           | w/phenol                       | w/MEA | w/Phenol    | w/MEA | w/MEA <sup>a</sup> | w/phenol     | w/MEA | from neutrals <sup>b</sup> | w/phenol  | w/MEA | C   | H     | N    |
| I.                        | --                             | 116.6 | --          | 33.2  | 69.0               | --           | 57.3  | 35.8                       | --        | 12.3  | 80.5  | 10.9  | 1.20 |
| II                        | 91                             | 123   | 83.7        | 66.3  | 83.5               | --           | 28.7  | 17.2                       | 16.3      | 5.0   | 80.75   | 10.33 | 1.19 |
| III                       | 80                             | 91.6  | 7.9         | 9.5   | 54.2               | 36.6         | 74.5  | 44.7                       | 55.1      | 16.5  | 78.3  | 10.4  | 1.1  |
| Cotton Hull<br>Lignin     | 58.6                           | 70.8  | 45.7        | 32.5  | 66.6               | 40.3         | 58.8  | 34.1                       | 14.0      | 17.6  | 81.07   | 10.80 | 3.27 |

I. Dehydrodiguaiacol

II. 1-(4-hydroxyphenyl)-propanone-1

III. 1-(4-hydroxy-3-methoxyphenyl)-propanone-1

a. Includes phenols isolated from the neutrals fraction.

b. Expressed as % phenols in ether extractables.

lignin. In all cases, the addition of monoethanolamine (MEA) caused an increase in the yield of the ether extractable materials due to the addition of MEA to the products. The use of MEA also caused an increase in the amount of neutrals fraction obtained at the expense of the phenolic and acidic fractions. Similarly to the treatment of the neutrals fractions obtained in phenol, the neutrals fraction obtained in the presence of MEA when treated with strong base and extracted, also yielded phenolic structures. Tables 3-7 and 3-8 show the yield of phenols and "true" neutrals after treatment with base as well as the identity of the compounds that were obtained.

Table 3-9 shows the effect of MEA on the types of phenols obtained when compared to the phenols obtained using phenol as the inhibitor. As can be seen, when phenol is used as the inhibitor, the reaction is more selective toward phenol and substituted phenols with shorter side chains. On the other hand, using MEA as the inhibitor gives a much more complex product slate in which substituted phenols with longer side chains predominate.

#### III.2.1.4 Comparison between alkaline hydrogenolysis and alkaline solvolysis in the presence and absence of phenol

Bronovitskii and Kalinskaya (1970) compared the behavior of lignins in aqueous alkaline solutions in the presence and absence of phenol by comparing the products of these reactions. The base treatment of lignins in the presence of phenol, and the base treatment under the reducing conditions described in Section III.2.1.2 were also compared. The authors found that, whereas the base hydrolysis of cotton hull lignin led to about 16% of hydroquinone, the presence of phenol reduced the content of hydroquinone to 2% with concomitant increase of pyrocatechol in the phenolic fraction. Under hydrotreating conditions, no dihydroxyphenols were observed. The authors concluded that since hydroquinone is not a structural unit of lignin, its presence in the products of the first two types of reactions must result from hydroxylation reactions by hydroxy radicals.

Additional data on alkaline hydrolyses of acid hydrolysis lignins in the presence and absence of phenol was given by Bronovitskii and Nam (1973).

#### III.2.1.5 Other work

The destructive hydrogenation of corncob hydrolysis lignin in anthracene oil in the presence of limonite (a natural mineral composed of hydrated iron

Table 3-7. GC of Phenolics from Neutral Fraction (w/MEA) after treatment with base. (Bronovitskii, Ikramova, and Kalinskaya 1973)

| Compound   | % in Mixture |      |      | Cotton<br>Hull<br>Lignin |
|--|--------------|------|------|--------------------------|
|  | I            | II   | III  |                          |
| phenol   | 11.8         | 1.0  | 5.5  | 5.9                      |
| o-cresol   | 13.6         | 0.8  | 13.6 | 10.5                     |
| m,p-cresol   | 12.5         | 0.7  | 7.5  | 7.2                      |
| guaicol/o-ethylphenol  | 11.9         | 0.7  | 5.4  | 2.5                      |
| 2,5-xylenol  | 8.8          | 0.5  | 3.2  | 26.4                     |
| 3,5-xylenol  | --           | 8.8  | --   | --                       |
| p-propylphenol   | --           | 28.5 | 5.6  | --                       |
| hydroquinone   | 7.7          | 6.2  | 6.7  | 4.9                      |
| Not identified   | 33.7         | 53.3 | 52.5 | 23.5                     |
| % of Neutrals<br>Converted to Phenols<br>by Treatment with<br>Base | 62.5         | 60   | 60   | 58                       |

- I. Dehydrodiguaiacol
- II. 1-(4-hydroxyphenyl)-propanone-1
- III. 1-(4-hydroxy-3-methoxyphenyl)-propanone-1

Table 3-8. GC of Neutrals After Treatment of Neutral Fraction (w/MEA) with Base. (Bronovitskii, Ikramova, and Kalinskaya 1973)

| Compound  | % in Mixture |      |      | Cotton<br>Hull<br>Lignin |
|---|--------------|------|------|--------------------------|
|   | I            | II   | III  |                          |
| Cyclohexane   | --           | --   | --   | 16.6                     |
| Cyclopentanone  | --           | 12.1 | --   | --                       |
| Cyclopentanol   | 6.8          | 10.2 | 4.2  | 18.3                     |
| Cyclohexanone   | 25.9         | 13.4 | 9.0  | 13.0                     |
| Cyclohexanol  | 11.4         | 19.3 | 2.3  | 12.9                     |
| Methylcyclohexanol  | --           | 12.1 | 7.8  | 17.1                     |
| Not identified  | 55.9         | 32.9 | 67.2 | --                       |
| % Remaining in the<br>Neutral Fraction After<br>Treatment with Base | 37.5         | 40   | 40   | 42                       |

I. Dehydrodiguaiacol

II. 1-(4-hydroxyphenyl)-propanone-1

III. 1-(4-hydroxy-3-methoxyphenyl)-propanone-1



Table 3-9. Composition of Phenolic Fraction Using MEA and Phenol. (Bronovitskii, Ikramova, and Kalinskaya 1973)

| Compound       | Phenol Content (%) |        |      |        |      |        |                    |        |
|----------------|--------------------|--------|------|--------|------|--------|--------------------|--------|
|                | I                  |        | II   |        | III  |        | Cotton Hull Lignin |        |
|                | MEA                | Phenol | MEA  | Phenol | MEA  | Phenol | MEA                | Phenol |
| phenol         | 8.5                | --     | 40.6 | 80     | 9.1  | 64     | 12.7               | 38.0   |
| 2,6-xyleneol   | --                 | --     | --   | --     | --   | --     | --                 | 1.3    |
| o-cresol       | --                 | --     | 5.6  | 8.5    | --   | 7.0    | --                 | 13.8   |
| p,m-cresol     | 13.2               | --     | 1.4  | 10.0   | 14.6 | 8.5    | 17.9               | 11.9   |
| guaiacol       | 7.4                | --     | --   | --     | 4.2  | --     | 7.9                | --     |
| o-ethylphenol  | --                 | --     | 3.3  | --     | 6.2  | --     | --                 | 12.5   |
| p-ethylphenol  | 25.1               | --     | --   | --     | 3.2  | 3.5    | 24.4               | 11.2   |
| 3,5-xyleneol   | --                 | --     | 4.5  | --     | --   | --     | --                 | --     |
| xyleneol       | --                 | --     | 2.8  | --     | 6.3  | --     | 8.1                | --     |
| p-propylphenol | 16.6               | --     | 41.6 | 1.2    | 22.1 | 11.0   | 10.2               | 2.9    |
| pyrocatechol   | 0.3                | --     | 0.3  | --     | 0.6  | 0.3    | 0.3                | --     |
| hydroquinone   | 11.1               | --     | 0.5  | --     | 5.7  | --     | 3.5                | --     |
| Not identified | 17.8               | --     | --   | --     | 23.0 | --     | 16.0               | 8.4    |

I. Dehydrodiguaiacol

II. 1-(4-hydroxyphenyl)-propanone-1

III. 1-(4-hydroxy-3-methoxyphenyl)-propanone-1

oxide, possibly containing sulfides) as catalyst was investigated. The hydrogenation conditions of the Bulgarian work are similar to that described in Section III.2.1.1 but the hydrogen pressure was higher (240 atm). The total yield of phenols was 46.2 g per 100 g of lignin charge. In addition, neutral and acid fractions were also isolated. In the phenolic fraction, phenol, cresols, methylphenols, propylphenols and xylenes were identified. The most important phenolic compound was p-cresol (54% of total phenols) (John and Dobrev 1973).

Rieche et al. (1964, 1966) investigated hydrogenation of acid hydrolysis lignin and technical alkali lignin in phenol and diesel oil as solvents. A number of catalysts were screened:  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3\text{-CuO-S}$ ,  $\text{FeS-CuS}$  (1:0.05), and  $\text{NiS-WS}_2$  (35:65),  $\text{MoO}_3\text{-Fe}_2\text{O}_3$  (on 10%  $\text{Fe}_2\text{O}_3$ ), pyrophoric  $\text{Ni-Al}_2\text{O}_3$  (1:1). Lignin liquefaction yields ranged from 52-75%. One experiment gave 14% of p-alkylphenols but generally the yield of these phenols was 2-3%. An example given was the hydrogenolyses over  $\text{FeS-CuS}$  of alkali lignin (74 g) in 120 g of phenol at 350°C with 250 atm initial hydrogen pressure for two hours. In this example, 52% of the lignin was liquefied. Based on gas liquid chromatography, the following phenolic compounds were quantified: phenol and o-cresol (82.8 g); p- and m- cresol, 2,4- and 2,5-xyleneol (2 g); guaiacol (0.3 g); p-ethylphenol, 3,5-xyleneol (0.8); p-propylphenol (0.1 g). The neutral fraction (15.6 g) included benzene, cyclohexane, methanol and anisole. The aim of the work was the synthesis of p-alkylphenols. The yield for a one-product-only process was too low. The authors did successfully hydrogenate alkali lignin continuously in a "sumpphase" oven (300°-400°C) with a  $\text{MoO}_3$  catalyst.

In the thirties, sulfuric acid lignin was hydrogenated on  $\text{MoS}_2$  in a horizontally rotating autoclave, electrically heated to 400°-450°C, with hydrogen feed at 50-70 atm (gauge at ambient temperature). Experiments without solvents gave very small yields of solubilized tar. However, use of phenol or lignin tars as solvents resulted in 44% conversion of the lignin into soluble tar and 56% into gaseous products. The tar was fractionated according to boiling range into three fractions: 24.2% boiling below 200°C, 35.6% between 200°-300°C, 40.2% above 300°C (includes losses) (Moldavskii and Vainshtein 1935). The boiling range of phenols is 150°-240°C; catechols boil in the 240°-260°C range. Hydrocarbons boil under 150°C. Thus, the first two fractions contain the bulk of hydrocarbons, phenols and catechols.

In East Germany, hydrogenolysis of lignins from evaporated sulfite liquor or kraft lignins has been investigated (Wienhaus, Fischer and Schiene 1976). These authors have compared pyrolytic processes with hydrogenolyses of lignins for the production of phenolic compounds (Wienhaus, et al. 1980). The process and apparatus patented by Borchers et al. (1975) was described as a continuous pressure hydrogenator, a tube reactor, in contact with a copper-doped iron catalyst. The residence times were of 0.25-1.5 hours at temperatures in the 350°-550°C range with hydrogen pressures between 200 and 400 atm.

### III.2.1.6 Applications of Hydrotreated Acid Hydrolyses Lignins

Phenol substitute in phenol-formaldehyde thermosetting resins.

Bronovitskii, Volochkovich, Kalinskaya, and Nam (1968) have tested the acid hydrolysis hydrotreated lignin to form a resol<sup>1</sup> to manufacture "Getinaks" laminates. The quality of the product was considered comparable to that of phenol alone.

Cation exchange resin synthesis based on hydrotreated lignins.

Bronovitskii, Salyamova and Volochkovich (1967) investigated the production of cationic exchange resins from the hydrotreated lignins by two methods. In the first the hydrotreated product mixture of phenolics, acids and neutrals was sulfonated directly. The other method pre-condensed these materials with formaldehyde and furfuryl alcohol prior to sulfonation. The sulfonation was performed with 20% oleum at 180°C for 1 hour. The hydrotreatment involved molybdenum sulfide as catalyst. The resulting resin had an exchange capacity of 3.2 meq/g without pre-reaction with aldehydes.

---

<sup>1</sup> Resol = a formulation of phenol and formaldehyde containing an excess of the aldehyde, prepared under alkaline conditions. It consists primarily of single aromatic structures activated by CH<sub>2</sub>OH groups. If heated, the resol can be cured without further addition of aldehyde.

Condensation reactions did not improve the exchange capacity. Later, Salyamova and Bronovitskii (1970) were successful in forming novolaks<sup>2</sup> and resols between the spruce lignin (HCl and H<sub>2</sub>SO<sub>4</sub>) and formaldehyde and furfural in the presence of acids and bases. The products were sulfonated for 1 hour with 25% sulfuric acid. The best exchange resins were obtained by sulfonation (0.5 h) of the resin formed between formaldehyde and the low molecular weight products from hydrotreatment of sulfuric acid spruce lignin, which gave 83% of bound acid. The resulting colorless resin had 3.4 meq/g of exchange capacity and was stable under basic conditions. These results were patented by Bronovitskii, Salyamova, and Volochkovich in 1968.

Antioxidant properties.

Bronovitskii and Sharipdzhanov (1967) investigated the use of the phenolic and neutral fractions from Section III.2.1.2 as low-density polyethylene stabilizers. Full inhibition was found for the neutral fraction while the phenolic materials gave a strong inhibition as measured by comparing oxygen absorption at 170°C during 25 minutes. Such results were confirmed by viscosity and infrared data. Sufficient stabilization was obtained using 1-3% of the neutral fraction. The same authors demonstrated in 1970 that the neutral fraction serves as a thermostabilizer for polypropylene in addition to acting as an antioxidant.

### III.2.2 References from North America, Western Europe and Asia

#### III.2.2.1 Summary of hydrotreating of lignins and wood in organic/aqueous solvents under mild reducing conditions

This area has been reviewed in detail by Hrutfiord (1971), Schweers (1966, 1975), Goldstein (1975), Schultz (1981), and Goheen (1981). Therefore, only a summary will be presented here. For further details, the reviews and the primary references should be consulted.

---

<sup>2</sup> Novolak = a formulation of phenol and formaldehyde containing an excess of phenol, prepared under acidic conditions. The resulting prepolymer contains 4-6 aromatic rings linked by methylene bridges. Novolaks cannot be cured without further addition of aldehyde.

The studies of destructive hydrogenation of lignins have been carried out with two main purposes:

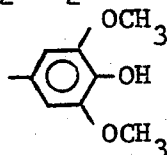
- 1) the determination of the chemical structure of lignin; and
- 2) the conversion of lignins into more useful, lower molecular weight organic chemicals.

Either acid or base catalyzed hydrolysis of lignin plays an important role in the overall hydrogenation reactions: acidic or alkaline hydrolysis provides the essential primary breakdown of the lignin macromolecule, while hydrogenolysis and hydrogenation provide further breakdown and stabilization of the depolymerization products. The interpretation of the results needs to take into account the past history of the lignin preparation prior to destructive treatment as well as the role of the solvolytic treatment.

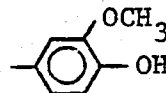
As an example of typical reaction conditions, maple woodmeal was hydrotreated in a 1:1 ethanol:water solvent system, using Raney nickel as catalyst and a temperature range of 160°C to 170°C (see, for instance, Bower, Cooke and Hibbert 1943).

Reaction products vary as a function of the pH and temperature. If the hydrogenations are carried out in neutral solvents (ethanol:water, dioxane:water) or in acidic environment, the major monomeric products isolated are phenylpropane ( $C_6C_3$ ) compounds such as:

S-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH, G-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>OH, and S-n-C<sub>3</sub>H<sub>7</sub> (where S=syringyl unit =



and G=guaiacyl unit =



).

Under alkaline conditions, the yield of low-molecular weight chloroform-soluble products is higher than under neutral conditions. The major monomeric products isolated are phenyl ethane ( $C_6C_2$ ) compounds:

G-C<sub>2</sub>H<sub>5</sub>; S-C<sub>2</sub>H<sub>5</sub>, and S-CH<sub>2</sub>-CH<sub>2</sub>OH.

Selected results from hydrogenolyses of hardwoods and softwoods are summarized in Table 3-10. A comparison of the major products of hydrogenolyses of a variety of hardwoods is given in Table 3-11. In addition to monomeric products, dimers have been isolated and identified, such as G-CH<sub>2</sub>-G, G-CH<sub>2</sub>CH<sub>2</sub>-G, S-CH<sub>2</sub>-S, S-CH<sub>2</sub>-CH<sub>2</sub>-S, and S-CH<sub>2</sub>-G. The remainder of the material is polymeric in nature. It is more heavily condensed than the starting lignin since upon oxidation, only about half of the yields of vanillin and syringaldehyde are obtained.

Table 3-10. Major monomeric products of hydrolytic treatment of hardwoods and softwoods. Yields given as % of Klason lignin.

| Compound   | Hardwoods         |          | Softwoods         |          |
|--|-------------------|----------|-------------------|----------|
|  | Neutral<br>(acid) | Alkaline | Neutral<br>(acid) | Alkaline |
| G-C <sub>2</sub> H <sub>5</sub>                      | --                | 2-5      | --                | 9.4      |
| G-n-C <sub>3</sub> H <sub>7</sub>                    | --                | --       | 1.2 (5.1)         | --       |
| G-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH | 6-11              | --       | 13.5              | --       |
| S-CH <sub>3</sub>                                    | 1.0               | 1.5      | --                | --       |
| S-C <sub>2</sub> H <sub>5</sub>                      | 2.0               | 9-15     | --                | --       |
| S-n-C <sub>3</sub> H <sub>7</sub>                    | (12)              | ≤1       | --                | --       |
| S-CH <sub>2</sub> CH <sub>2</sub> OH                 | --                | 4-6      | --                | --       |
| S-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH | 13                | 1.5      | --                | --       |

Adapted from Hrutfiord, 1971.

Condition: neutral = 1:1 dioxane:water solvent; acid = 0.1 M HCl added to the neutral solvent; alkaline = 3-5% NaOH added to the neutral solvent. Hydrogen initial pressure was 500 psig and the catalyst was Raney nickel.

Table 3-11. Major monomeric constituents of alkaline hydrogenolysis of some hardwoods. Yields are given as % of Klason lignin.

| Compound   | Aspen | Alder | Maple |
|--|-------|-------|-------|
| G-CH <sub>3</sub>                                    | 0.5   | 1.0   | trace |
| G-C <sub>2</sub> H <sub>5</sub>                      | 4.9   | 4.3   | 2     |
| G-n-C <sub>3</sub> H <sub>7</sub>                    | 1.3   | 1.9   | --    |
| S-CH <sub>3</sub>                                    | 1.5   | 0.7   | trace |
| S-C <sub>2</sub> H <sub>5</sub>                      | 9.1   | 10.7  | 15.4  |
| S-CH <sub>2</sub> CH <sub>2</sub> OH                 | 4.0   | 0.6   | 6.2   |
| S-n-C <sub>3</sub> H <sub>7</sub>                    | 0.6   | 1.4   | --    |
| S-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH | 1.7   | 3.0   | trace |

Adapted from Hrutfiord (1971); experimental conditions of Table 3-10.

Table 3-12. Monomeric Reaction Products of Non-Hydrolytic Hydrogenolysis of Milled Wood Lignins. Yields are given as % of the starting lignin weight.

| Compound   | Birch | Oak  | Blue Spruce | White Pine |
|--|-------|------|-------------|------------|
| G-H  | --    | --   | 0.3         | 0.3        |
| G-CH <sub>3</sub>                                    | 1.1   | 1.0  | 3.5         | 2.9        |
| G-C <sub>2</sub> H <sub>5</sub>                      | 0.9   | 0.6  | 2.1         | 2.9        |
| G-n-C <sub>3</sub> H <sub>7</sub>                    | 2.3   | 2.6  | 5.9         | 5.3        |
| G-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH | 2.0   | 0.6  | 8.1         | 7.3        |
| S-CH <sub>3</sub>                                    | 2.0   | 3.1  | --          | --         |
| S-C <sub>2</sub> H <sub>5</sub>                      | 1.1   | 0.7  | --          | --         |
| S-n-C <sub>3</sub> H <sub>7</sub>                    | 3.9   | 7.3  | --          | --         |
| S-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH | 7.9   | 0.8  | --          | --         |
| Totals   | 21.2  | 16.7 | 19.9        | 17.7       |

Conditions: Anhydrous dioxane solvent; temperature: 220°-250°C. From Coscia, Schubert and Nord, 1961, and Olcay, 1962.

A number of conditions have been tested. Reaction times of 4-5 hours for the low temperature reactions have been employed with about 500 psi of hydrogen as initial pressure. Many catalysts have been tested such as Raney nickel, copper chromite, and palladium, platinum or rhodium on charcoal.

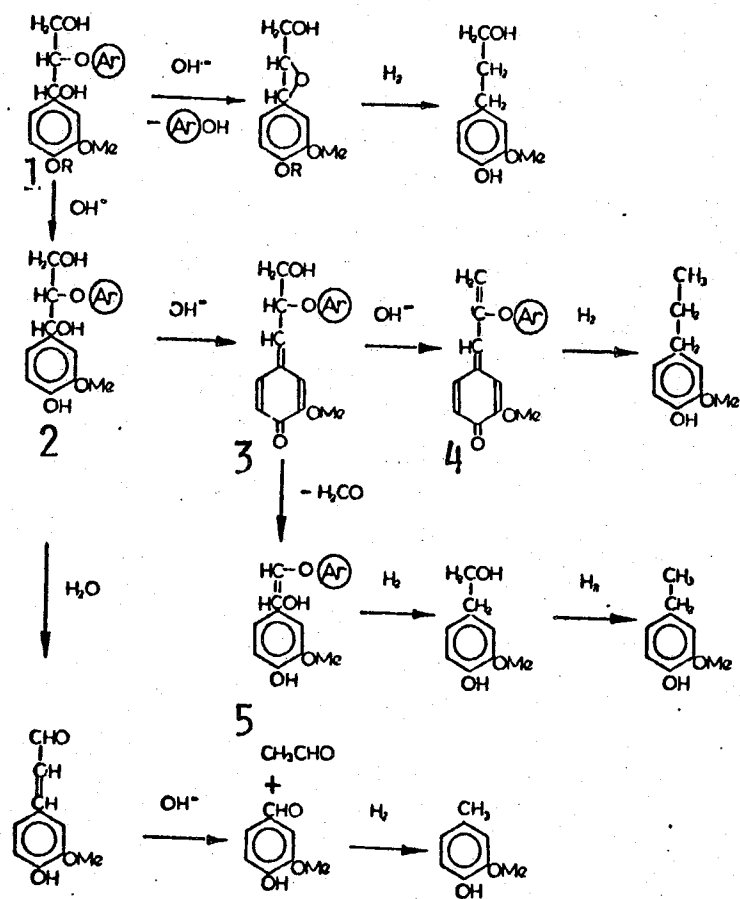
In order to successfully hydrogenate it is best to have water in the medium, which confirms the need for hydrolytic reactions to depolymerize the lignins. Successful hydrotreating in aqueous alkaline solutions has been described in Section III.2.1. The most common organic/aqueous solvents employed in these studies were ethanol:water and dioxane:water. Examples of hydrogenolyses products of milled wood lignins in anhydrous dioxane (without substantial hydrolytic contributions to the reaction products) are given in Table 3-12. Four moles of hydrogen reacted per phenylpropane unit. The products do not seem to have lost aromatic rings or methoxy content.

Hrutfiord (1971) summarizes the mechanistic studies carried out by many authors, including Pepper and co-workers, and Schuerch and co-workers. The proposed mechanism is compatible with lignin hydrolysis studies in base or acid medium, as well as the observed final monomeric products. Scheme 3-1 reproduces Hrutfiord's scheme involving the hydrolysis of  $\beta$ -O-4 alkyl aryl ether bonded structures followed by hydrogenation of the intermediates to a final stable product. The major source of guaiacylpropanol is the etherified unit (1), which can be converted to an epoxide through  $\beta$ -aryloxy elimination. The formation of guaiacylpropane invokes the intermediate formation of the phenolic unit (2) derived from hydrolysis of the phenol ether bonds. The most likely intermediate is the extended quinone-methide (4) formed from dehydration of the quinone-methide (3). The same quinone-methide can lead to the phenylethane products by the loss of the carbon as formaldehyde yielding intermediate (5). Phenylmethane products may arise from vanillin formed by reverse aldol condensation of coniferyl aldehyde.

#### III.2.2.2 Hydrotreating in Organic Solvents Under More Drastic Reducing Conditions

Above 200°C, in the 250°-260°C range, and with hydrogen pressures of 150-250 atm, and with reaction times of the order of a few hours to a day, perhydrogenation becomes more important leading to cyclohexane, other hydrocarbons, and neutral compounds.





Scheme 3-1. Proposed mechanisms of hydrolytic hydrogenolysis (after Hrutfiord, 1971).

The catalyst of choice was usually copper chromium oxide, although Raney nickel and tin sulfide were also used (Harris and Adkins 1938). Copper chromium oxide is prepared by numerous methods including decomposition of copper chromium nitrates, simple grinding of copper oxide and chromium oxide or, as is described by Adkins (1937), decomposition of copper ammonium chromate. Using aspen soda lignin and black gum soda lignin, Harris (1940) reported obtaining methanol (10.5%, 11.0%, respectively), n-propylcyclohexanol derivatives including propylcyclohexanediol (14.4%, 20.0%), water (9.0%, 10.5%), and a high boiling resin (66.0%, 60.0%). The patents by E. C. Sherrard and E. E. Harris (Forest Products Lab. 1940a, 1940b, 1942) describe a method by which lignin or raw pulping liquors could be hydrogenated over a variety of catalysts, i.e. Raney nickel or copper chromium oxide, to methanol, organic acid derivatives of propylcyclohexane and high boiling resins. An example of one of these preparations uses 1 liter of raw pulping liquor from the soda process in a 2 liter bomb with a nickel catalyst at 136 atm (initial H<sub>2</sub> pressure) heated to 300°C for 2 to 6 hours. An oily, water insoluble material was produced that contained n-propylcyclohexane derivatives, primarily propylcyclohexanols and diols as well as resins. Various aliphatic alcohols and glycols were also obtained from the carbohydrate degradation products which were present in the pulping liquor. Also investigated were acid hydrolysis and organosolv lignins.

Freudenberg et al. (1941) reported that S-containing waste liquors of softwoods could be hydrogenated at 340°C with or without a catalyst to give small amounts of phenolic compounds, cyclopentanols, and substituted cyclohexanols. It was also reported (Freudenberg, Lautsch, and Piazzolo, 1943) that 22% of the lignin in fermented sulfite waste liquor containing 1% ethanol could be converted to neutral hydrogenation products at 350°C with no added hydrogen. In the presence of hydrogen (140 atm) and Raney nickel catalyst, 48% of the lignin was converted to neutral hydrogenation products along with a small amount (7%) of phenols.

At higher temperatures in organic solvent systems (benzene, methanol or cyclohexane) near or at supercritical conditions, Schweers (1969) and Hoffmann and Schweers (1975 a,b,c) investigated the hydrogenolyses of a number of acid hydrolysis lignins, liginosulfonates, synthetic DHP lignins, and model

compounds, in the presence of transition metal complexes as catalysts. While the acetylacetonates of Fe, Co and Ni did not exhibit catalytic activity, the metallocenes, particularly the dicyclopentadienyl nickel (nickelocene) were found to be active. The best activity for the formation of phenolic compounds was achieved at 350°C, 100 atm starting hydrogen pressure, and 220 atm final pressure after about 20 hours of reaction. Typically, 2.5-10 g of lignin were placed in an autoclave system with 40-500 ml of solvent and 1 g of the organometallic catalyst. Typical product distributions of the phenolic fractions are given in Table 3-13. Yields of phenolic compounds as high as 36% of the starting lignin were obtained. The neutrals included cyclohexane, cyclopentane, and their alcohol derivatives. In addition, in the model compounds work, cycloheptane was also found (Hoffmann and Schweers 1975a). Blank experiments are not reported to assess whether under such extreme reducing conditions, the metallocene catalyst employed (in very large amounts) could undergo decomposition and thus increase the neutrals fraction. The resulting finely divided metallic nickel thus formed could certainly act as an excellent hydrogenation catalyst.

### III.2.2.3 Hydrotreating of Sweetgum Lignin from Superconcentrated HCl Treatment of the Wood

A number of conditions to degrade the lignin produced in the saccharification of sweetgum (Liquidambar styraciflua L.) wood meal with superconcentrated HCl (44-45%) into phenolic compounds were investigated (Schultz 1981; Schultz, Chen, and Goldstein 1982). This lignin is reported not to be as highly condensed as other acid hydrolysis lignins. Support for this statement can be found in the yield of total aldehydes (vanillin and syringaldehyde) produced in the nitrobenzene oxidation of this HCl lignin which is 31.4% whereas the yield of the aldehydes from milled wood sweetgum lignin is 33.7%. For comparison, the total yield of aldehydes from the Klason sweetgum lignin is only 4.8% (for detailed yields of these various nitrobenzene oxidation results, see Schultz 1981).

A comparison was made of the yields of phenolic compounds obtained under hydrolysis conditions in aqueous dioxane alkaline solutions or in aqueous alkaline solutions in the absence of hydrogen and heterogeneous catalyst, and in the presence of catalysts and hydrogen. The selected catalysts were

Table 3-13. Major monomeric constituents of hydrogenolysis of HCl lignins (2.5 g) in benzene, catalyzed by 1 g of nickelocene at 350°C. Starting pressure of 100 atm. Reaction time about 20 hours (Schweers, 1969).

| Compounds                                    | Spruce | Beech | Bamboo | Maize |
|--|--------|-------|--------|-------|
| P-H  | --     | 2.7   | 15.1   | 17.9  |
| P-CH <sub>3</sub>                            | --     | 1.4   | 6.5    | 8.9   |
| P-C <sub>2</sub> H <sub>5</sub>              | --     | 2.7   | 16.9   | 40.3  |
| P-n-C <sub>3</sub> H <sub>7</sub>            | --     | 2.7   | 4.5    | --    |
| G-H  | 13.8   | 6.1   | 10.9   | 6.3   |
| G-CH <sub>3</sub>                            | 20.4   | 5.3   | 4.0    | 3.0   |
| G-C <sub>2</sub> H <sub>5</sub>              | 35.1   | 15.1  | 8.8    | 8.0   |
| G-n-C <sub>3</sub> H <sub>7</sub>            | 30.8   | 12.1  | 20.6   | 1.3   |
| G-n-C <sub>3</sub> H <sub>6</sub> OH         | --     | 0.4   | --     | --    |
| S-H  | --     | 9.7   | 2.6    | 5.5   |
| S-CH <sub>3</sub>                            | --     | 4.9   | 2.8    | 2.3   |
| S-C <sub>2</sub> H <sub>5</sub>              | --     | 18.6  | 1.6    | 4.6   |
| S-n-C <sub>3</sub> H <sub>7</sub>            | --     | 19.0  | 5.7    | 1.9   |
| Total  | 100.0  | 100.0 | 100.0  | 100.0 |
| Phenolic Compounds<br>(% of starting lignin) | 32     | 36    | 24     | 16    |
| Neutral Compounds<br>(% of starting lignin)  | 32     | 40    | 24     | 36    |

primarily oxides of iron, cobalt and molybdenum ( $\text{CoOMoO}_3$ ), though a few preliminary experiments were performed with Raney nickel and Rh on carbon, typical hydrogenation catalysts. One experiment was performed with the iron oxide in the presence of sulfur in 5% aqueous NaOH, at 340°C, with hydrogen for one hour. (This experiment was the closest to the experimental conditions employed by the Russian workers, except that they employed the metal sulfides directly as catalysts and the preferred reaction time was two hours.) No phenolic compounds could be isolated from this particular experiment. The experimental work was performed in a batch 1 liter Parr rocking autoclave, heated at 5°C/minute, to a final temperature in the 250°-350°C range; reaction times varied from 0.5-5 hours, and most of the experiments were carried out at 1.5 hours. Typically, 5 grams of lignin were mixed with 0.5 g of catalyst and added to 200 ml of solvent (dioxane:3% aqueous NaOH in 1:1 proportion or 1.5% or 3% aqueous NaOH).<sup>1</sup> Under the conditions employed by Schultz et al. (1982), catalyst, temperature, time, and solvent, listed in Table 3-14, the nature of the catalyst was found to have very little, if any, apparent influence on the total yields of phenolic monomers. The composition of the phenolic fractions was investigated in detail. Analyses of the corresponding neutrals or gaseous fractions were not given. A very successful analytical procedure for the determination of the phenolic compounds produced in the reactions investigated involved acetylation of the phenolic compounds and analyses on a 6 foot, 1/8 inch o.d. stainless steel column packed with 3% OV-17 (10-120 mesh WHP support) (Schultz, Chen, Goldstein and Scaringelli 1981). Flame ionization detection was used. In the procedure developed, the phenolic mixture was added to acetic anhydride and pyridine. The mixture was heated to 60°C for two hours. The whole mixture was added to the column

---

<sup>1</sup> Note that these conditions involve much more dilute lignin solutions than those employed by the Russian workers, which were 100 g lignin, 300 ml 5% NaOH, 20 g phenol and 2 g of metal sulfides. The conditions are similar to those employed by Pepper and coworkers (1978) which were 10 g wood meal, 0.5 - 3 g catalyst, 150 ml of 1:1 dioxane: water; 195 ± 5°C and a heating rate of 120°C/h; an Aminco (chrome steel) continuously rocked autoclave or a stainless steel Parr pressure reactor were used. Different product distributions were obtained in the two autoclaves, which were assigned to the catalytic effects of chrome steel.

Table 3-14. Comparison between alkaline hydrolysis and alkaline hydrolysis under reducing conditions (in the presence of hydrogen and heterogeneous catalysts) of acid hydrolysis sweetgum lignin isolated from superconcentrated HCl wood saccharification treatment. (Schultz, Chen, Goldstein 1982)

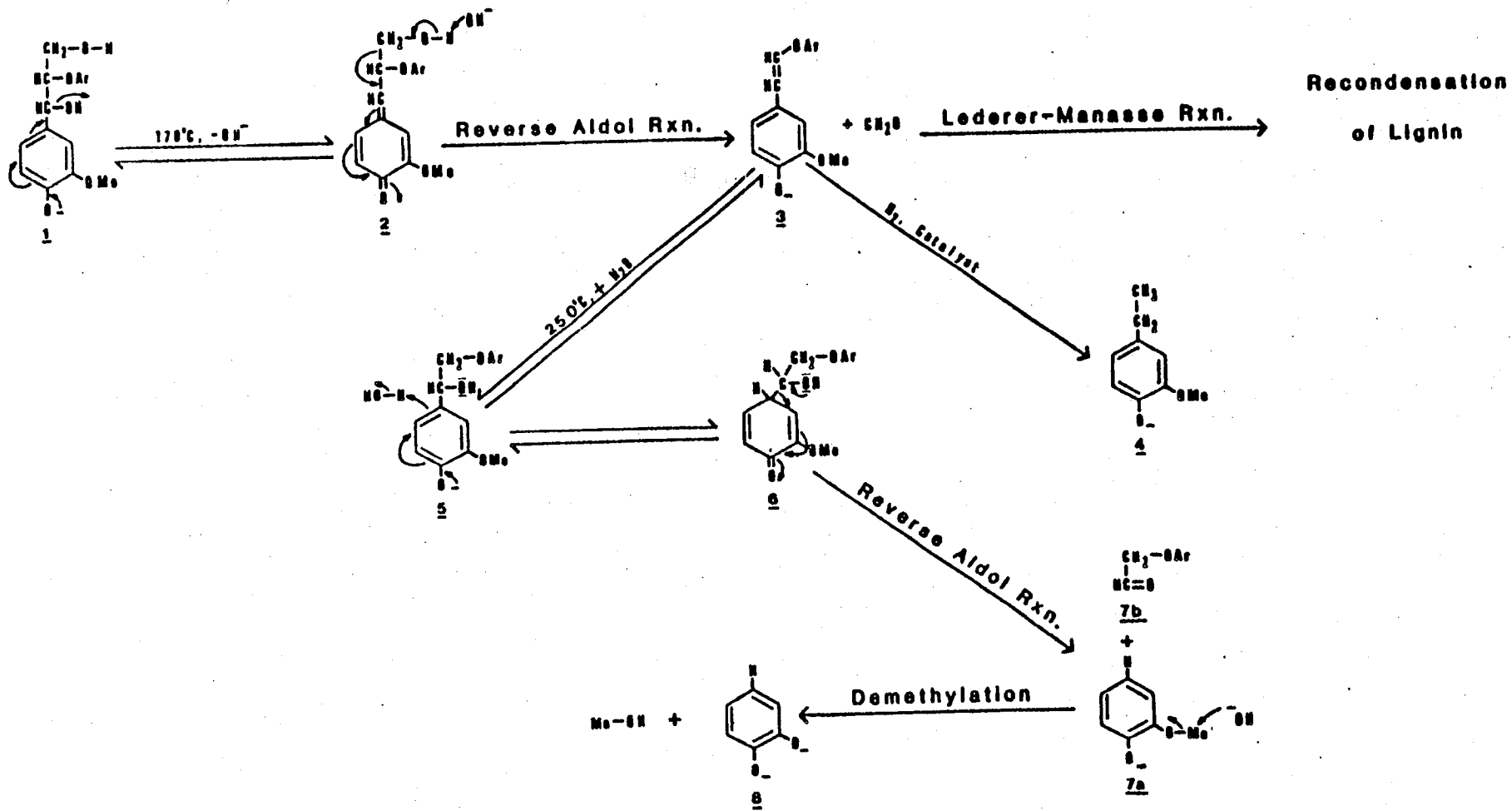
| Solvent   | Temperature<br>°C | Time<br>h | Distillable<br>Weight % |
|---|-------------------|-----------|-------------------------|
| Alkaline Hydrolysis                                   |                   |           |                         |
| Dioxane:3% NaOH                                       | 250               | 1.5       | 16                      |
| 1.5% NaOH   | 250               | 1.5       | 9                       |
| 70 atm Hydrogen and No Catalyst                       |                   |           |                         |
| Dioxane:3% NaOH                                       | 250               | 1.5       | 16                      |
| 70 atm Hydrogen and Ferric Oxide Catalyst             |                   |           |                         |
| Dioxane:3% NaOH                                       | 250               | 1.5       | 18                      |
| same  | 250               | 5.0       | 3                       |
| same  | 250               | 0.5       | 17                      |
| 3% NaOH   | 250               | 1.5       | 1                       |
| Same  | 300               | 1.5       | 6                       |
| Same  | 350               | 1.5       | 11                      |
| 70 atm Hydrogen and Cobalt-molybdenum Oxides Catalyst |                   |           |                         |
| Dioxane:3% NaOH                                       | 250               | 1.5       | 16                      |
| 3% NaOH   | 250               | 1.5       | 8                       |

Note: No distillable weight was obtained with dioxane and water without base, in the presence of hydrogen and catalysts.

directly without further separation by extraction or other procedures. Nevertheless, for most of the distillates analyzed this way the yield of identified phenols was in the range of 36 to 69%. The compounds with hydroxylated side chains were also detected in this procedure at the longer retention times. Identification was performed by comparison of retention times with those of authentic samples. No mass spectroscopic identification was performed on phenols from lignins.

From Table 3-14 it can be seen that the yield of distillates was 16-18% when HCl lignin was reacted in dioxane:aqueous alkali solutions in the presence of hydrogen. Alkaline hydrolysis alone under these conditions gave 16% distillable materials. When comparing the composition of the phenolic compounds (1 hour at 250°C), the ratios of ethylguaiacol:guaiacol, ethylsyringol:syringol, and ethylcatechol:catechol for the alkaline hydrolysis were 0.17, 0.20, and 0.67, respectively. In the presence of cobalt-molybdenum oxides, these ratios increased to 0.22, 0.41, and 1.0, respectively. If the reaction was carried out under alkaline aqueous conditions, lower yields of distillable materials were obtained. Longer reaction times did not favor depolymerization but appeared to have favored recondensation as shown by the 3% yield of distillable material after 5 hours of reaction (see Table 3-14). The need for base to catalyze the hydrolysis reactions was confirmed by the results in dioxane:water mixtures (i.e., no distillable phenols). The higher ratios of ethylated versus dealkylated phenols, the need for base hydrolyses, and the additional experiments carried out with Klason lignin support the mechanism shown in Scheme 3-2. Similarly to the scheme proposed by Hrutfiord (see Scheme 3-1) the quinone methide is the active postulated intermediate. A reverse aldol reaction leads to the aryloxyvinyl intermediate (in both mechanisms) which can be partially hydrogenated to the p-hydroxyethylguaiacol or fully hydrogenated to p-ethylguaiacol. Hydrolytic reaction at temperatures higher than 250°C lead to the benzyl alcohol intermediate which can undergo a reverse aldol reaction to form the dealkylated guaiacol; demethylation leads to the observed catechols.

The low yields of monomeric phenols in these batch experiments could be related to the agitation provided by the autoclave employed. As will be reported in Section III.3.2, the type of agitation can have profound effect on



Scheme 3-2. Mechanism proposed by Schultz, Chen and Goldstein (1982) of lignin dealkylation and hydrogenation in aqueous alkali.



the effectiveness of the catalysts. In addition, no details were given concerning the physical characteristics of the catalysts. Though the experimental results do provide very good comparison between alkaline hydrolysis and alkaline hydrogenolysis, it is still very difficult to compare these results with others under similar conditions. Analysis of the neutral fraction would also have been extremely useful. The catalysts employed could indeed lead to a fair amount of perhydrogenation with formation of cyclohexane and derivatives (alcohols).

#### III.2.2.4 Hydrogen - Donor Solvents

The thermal degradation of kraft lignin in tetralin, a hydrogen-donor solvent, was thoroughly investigated by Connors, Johansson, Sarkanen and Winslow (1980) in the 375°-400°C temperature range with a hydrogen pressure of 54-102 atm. In parallel, experiments were performed with simpler lignin model compounds. The literature is reviewed in that 1980 publication relative to lignin investigations in tetralin (see also Section III.3.2). Under these conditions, it was found that aliphatic oxygen functions reacted most rapidly. Methoxyl groups underwent aliphatic carbon-oxygen and aromatic carbon-oxygen cleavages leading to catechol and phenol groups, respectively. Carbon-carbon cleavages, primarily between  $\alpha$ - and  $\beta$ -carbon atoms though cleavages between the aliphatic  $\alpha$ -carbon and the aromatic rings, also occurred. Upon prolonged treatment, guaiacols and catechols were shown to be transformed into a mixture of phenol, cresols, and ethylphenols, which was relatively resistant towards further conversion. An example of the evolution of yields of phenolics (as ether-soluble phenols) can be seen in Table 3-15. From these results, a maximum yield of ether-soluble phenolics of 37.4% was observed at 15 minute reaction time as a result of a large decrease in the acetone-insoluble lignin fraction. Longer reaction times favored further degradation into gases and hydrocarbons which were not determined (only the residual pressure was measured). The yield of non-volatile neutrals increased as reaction times increased.

The sequence of reaction times of oxygenated fraction cleavage was described as: aliphatic OH > aromatic OCH<sub>3</sub> > aromatic OH. The yields of monomeric phenols from the ether-soluble phenols were also determined in the acetylated form by gas chromatography on a K-20M column (1.8 m length) using a flame

Table 3-15. Influence of reaction time on product distribution of lignin thermal degradation in the presence of hydrogen and of the hydrogen-donor solvent tetralin. Reaction temperature = 400°C, Tetralin:Indulin AT = 4.0:1.0. (Connors et al. 1980)

Yields, wt% of original lignin

|                                     | 0     | 15   | 75   | 255  | 615  |
|-------------------------------------|-------|------|------|------|------|
| Reaction Time, min.                 | 0     | 15   | 75   | 255  | 615  |
| Maximum Pressure, atm               | 0     | 55   | 71   | 103  | 108  |
| Residual Pressure, atm <sup>a</sup> | 0     | 0    | 1.7  | 9.8  | 13.2 |
| Acetone-insoluble Lignin            | 60.2  | 2.6  | 2.8  | 2.2  | 2.4  |
| Acetone-soluble Lignin              | 38.2  | 37.8 | 13.4 | 12.6 | 5.8  |
| Ether-soluble Phenols               | 2.5   | 37.4 | 31.0 | 26.7 | 22.7 |
| Total Phenolic Products             | 100.9 | 77.8 | 47.2 | 41.5 | 30.9 |
| Acids                               | 0.6   | 2.3  | 1.9  | 1.5  | 1.2  |
| Non-volatile Neutrals               | 0.7   | 3.3  | 5.3  | 8.0  | 7.0  |
| Chars                               | 0.1   | 9.7  | 6.2  | 4.2  | 3.4  |
| Total Isolated Products             | 102.3 | 93.1 | 60.6 | 55.2 | 42.5 |

a) Indication of lignin depolymerization and fragmentation into permanent gases and volatile hydrocarbons.

ionization detector. Identification was made by comparison of retention times of authentic samples and mass spectral patterns (for all peaks except catechols). At 15 minute reaction time, identified phenols, guaiacols and catechols made up 6.7% of the starting lignin. The yields of guaiacols and substituted catechols decreased as the reaction times increased. The main products were then phenols and catechol. The product distribution follows the following distribution:

guaiacols:  $C_2 > C_1 > \text{no side chain} > C_3$   
 catechols: early stages  
                    $C_1 > \text{no side chain} > C_2 > C_3$   
                   later stages  
                   no side chain  $> C_1 > C_2 > C_3$   
 phenols:  $C_1 > C_2 > \text{no side chain} > C_3$

Model compound studies were also carried out with p-ethylguaiacol and dihydrodehydrodisoeugenol. In tetralin, cleavage of p-ethylguaiacol to p- and o-ethylphenol as well as to p-ethylcatechol and catechol occurred. At short reaction times at 375°C with tetralin and hydrogen, the yields of catechols were higher than those of phenols. Longer reaction times reversed these findings. At higher temperatures, the yields of catechols were always higher than those of phenols (compare with Bredenberg results discussed in Section III.4). The dimeric model compound gave products in which cleavages of bonds 1- $\alpha$ (ether),  $\alpha$ (ether)- $\beta$  and  $\beta$ -5 had occurred. The rate of  $\alpha$ (ether)- $\beta$  cleavage was faster than  $\beta$ -5 and 1- $\alpha$  cleavages in the dimeric model compound investigated.

Schultz, Preto, Pittman and Goldstein (1982) extended previous investigations of depolymerization/hydrogenolysis of hydrochloric and sweetgum lignin as reported in Section III.2.2.3, by investigating the hydrotreating of this lignin in tetralin as a hydrogen-donor solvent. The temperature range of 375°-425°C was investigated. Comparisons were made with anthracene as a non-hydrogen donor solvent. A maximum yield of monomeric phenols of 11% was found. Cleavages of ether and C- $\alpha$  and C- $\beta$  bonds were the main thermal depolymerization reactions. The reaction kinetics were found to be first order with an activation energy of 24 kcal. The addition of a heterogeneous catalyst did not increase the yield of monomeric phenols.

The maximum yield of soluble phenolics was found to be approximately 35% (Schultz et al., 1982), which compares well with 37% found by Connors et al. (1980) from kraft lignin. While the total yields of phenolics from these two studies were similar, the detailed composition of the phenolic compounds showed some differences. High yields of p-methylphenol were reported by Connors et al. (1980). Schultz, Preto, Pittman, and Goldstein (1982) found catechol and p-methylcatechol in amounts greater than those found for p-methylphenol. Schultz et al. suggest that these larger values for p-methylphenol may be analytical errors. It is more likely that the differences in product distribution reflect the structural differences of the starting materials--an acid hydrolysis hardwood in one case and a commercial softwood kraft lignin in the other. Differences in the work-up procedures employed could also affect the yields of the various fractions.

Davoudzadeh, Smith, Avni and Coughlin (1985) have investigated the depolymerization of alkaline-extracted steam exploded aspen lignin as well as a few experiments using Westvaco's kraft Indulin, at low pressure using primarily tetralin as hydrogen donor solvent, in the absence and presence of various heterogeneous catalysts (such as Pd/Alumina,  $\text{Cr}_2\text{O}_3$ , Ni-Mo/alumina, NiO/SiO<sub>2</sub>Al<sub>2</sub>O<sub>3</sub>, NiO-MoO<sub>3</sub>/alumina) and a homogeneous catalyst AlCl<sub>3</sub>. The reaction hydrogen pressure was 120 atm and the reaction time 3 hours at 300°C. An Autoclave Engineering, Inc. autoclave (1000 ml) was employed with a stainless steel magnetic stirrer. Lignin samples were about 20-50 g in about 200-500 ml solvent. The liquefaction of lignin was measured as a conversion yield  $Y_F$  defined as  $(M_L^0 - M_L^f) / M_L^0 \times 100$ , where  $M_L^0$  = mass of lignin at the beginning of the experiment;  $M_L^f$  = mass of filtered and dried residue after reaction. The conversion yield in the absence of catalysts was about 30%. The yields of liquefied materials increased to 37-38% ( $\text{Cr}_2\text{O}_3$ , SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Ni-Mo), 40-41% (MnO<sub>2</sub>, NiO), 47% (AlCl<sub>3</sub>) and 52% (NiO-MoO<sub>3</sub>) when catalysts were used.

At one atmosphere hydrogen, in the 110°-200°C range, only about 25% of the lignin was converted to liquid regardless of the presence of phenol, tetralin or catalysts. At 300°C, in the presence of tetralin, about 39% conversion was observed. The yields of recovered materials increased if phenol or guaiacol were added to the solvent. In the presence of phenol, a new conversion yield

was defined as  $(M_0 - M_p) / M_L^0 \times 100$  where  $M_0$  is the mass of distillables (includes phenols) and  $M_p$  is the mass of added phenol. This yield was 63% in the presence of phenol. By raising the temperature from 300°-400°C, in experiments with tetralin, yields ( $Y_F$ ) as high as 90% were obtained. The steam exploded lignin gave higher conversion yields than kraft lignin. Some reaction products were identified by mass spectral patterns (computer searches, no comparison with authentic products), such as methoxyphenols, cresols, alkylcresols, guaiacol, anisole, etc. Unfortunately, no phenolic products quantitation was given.

### III.3 REVIEW OF PETROCHEMICAL/COAL TECHNIQUES APPLIED TO LIGNIN HYDROTREATING

#### III.3.1 Inventa A.-G. für Forschung und Patentverwertung

During the 1950's a number of patents were issued to Johann Giesen and Inventa A.-G. für Forschung und Patentverwertung in which they produced a distillable product that contained phenols, by hydrogenolysis of lignin at high temperatures (300°-380°C) and pressures (350-680 atm). Most of the processes used "Schöller lignin" which is obtained by the saccharification of wood with dilute sulfuric acid. Concentrated sulfite liquor was also used (Inventa 1955a). In the earliest work, (Inventa 1955a), catalysts were of a copper or cobalt chromium oxide type, e.g. copper chromate, Adkins catalyst (see III.2.2.2) (Giesen 1956b), etc. Generally a mixture of lignin, catalyst and water (approximately 3:1:5 weight ratio) was processed with hydrogen in a stirred autoclave at pressures of 350-680 atm and 300°-340°C for about 6 hours. Hydrogen uptake of about 1.5 moles of hydrogen per 100 g of lignin charged were observed. A phenolic distillate (boiling point  $\leq 275^\circ\text{C}/-15$  mmHg) could be obtained in yields up to 50%. About 75% of this distillate was soluble in aqueous alkali which, plus some catechols, allowed them to claim phenolic yields of 30-40% based on the lignin charged.

In later work, (Inventa 1956b; Giesen 1959), the scale of the process was increased from about the 200 g level up to approximately 10 kg of lignin per run. The reactor was also changed from the stirred autoclave to a tubular flow through reactor in which high conversions of lignin were obtained in a single pass. The reactor was connected into a system (Fig. 3-4) that allowed separation of products and recycle of hydrogen. The catalyst was also changed to ferrous sulfate. As Scholler lignin contains dilute sulfuric acid, calcium

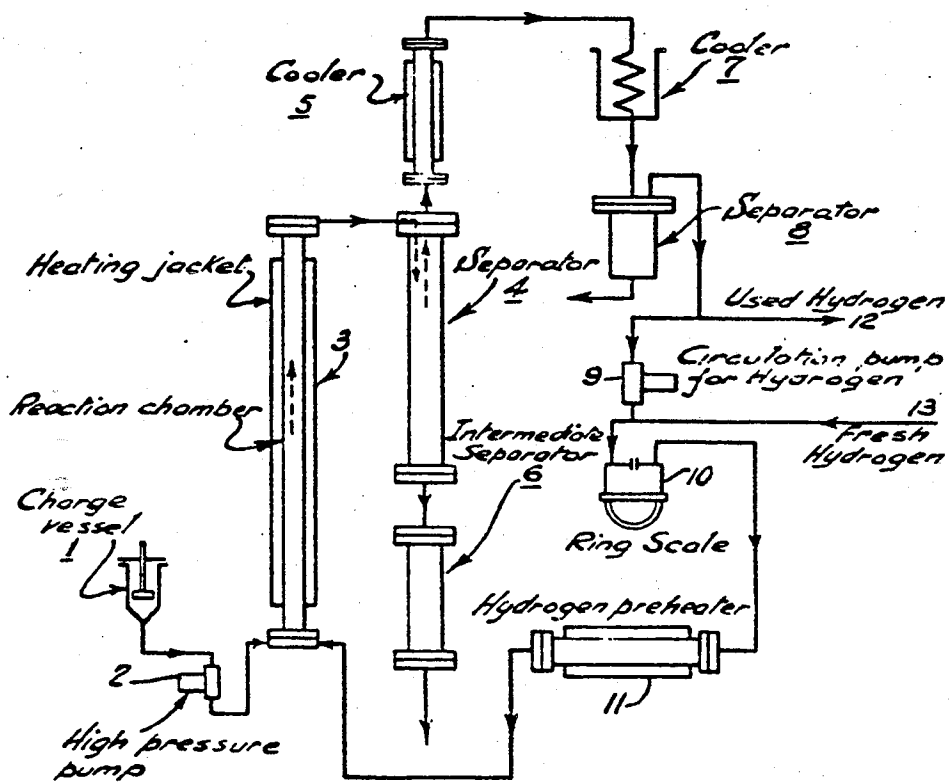


Fig. 3-4. Process Diagram for Cleavage of Lignin to Produce Phenols.  
 Inventor J. Giesen (1959).

hydroxide was added to neutralize it. Xylenol was added as a dispersion vehicle. Thus to about 10 kg of Scholler lignin, 0.24-1 kg of catalyst, 0.5 kg of calcium hydroxide, and about 40 kg of xylenol were added to make a thin paste which could be fed continuously by means of a high pressure pump to the inlet of the tubular reaction chamber where it was mixed with hydrogen. The reactor was maintained at temperatures above 250°C and pressures greater than 300 atm. When operated at 300°-350°C and 680 atm with residence times in the reactor of 0.6-1.2 hours a phenolic distillate (boiling point  $\leq 350^\circ\text{C}/6\text{mm Hg}$ ) could be obtained in yields of up to 60%. In the absence of the catalyst lower yields (about 47%) of phenolic distillate were obtained under similar conditions (Giesen 1957a; Giesen 1961). Distillates produced without use of a catalyst were claimed to contain more than 40% of phenolics giving a yield of about 20% of phenols based on the lignin charged. In none of these patents is the high capital cost of the equipment necessary to handle such high pressures (680 atm) addressed. These pressures are higher by a factor of 5-10 than those employed in the bulk of the work reviewed in this report.

Another patent (Ploetz et al. 1963), describes the hydrogenation of a precipitated, purified ( $\leq 1\%$  ash) lignin from black liquor suspended in five times as much of a liquid obtained from previous hydrogenations. The lignin was processed in a two-stage treatment, initially at 430°C for 12 minutes and then at 480°C for 1 hour, both with a hydrogen partial pressure of 410 atm. The products were 21% of low boiling phenols (consisting of 15% phenol, 45% cresols, and 40% higher molecular weight phenols), 28% of neutrals, 8% high boiling point oils, 26% gaseous products and 18% water.

In other work (Giesen 1955b), thiomolybdate and thiotungstate catalysts were used to convert sulfite spent liquor lignin to an oily distillable product (20% yield) containing 35% phenols. This was accomplished by treating one liter of sodium hydroxide neutralized spent sulfite liquor containing 234 g of dry lignin, with ammonium thiomolybdate at 300 atmospheres of hydrogen and 250°C for 5 hours.

### III.3.2 Noguchi Institute of Japan and Crown Zellerbach Corporation Process

The initial discovery by the Noguchi Institute of Japan of a method for converting lignin into monophenols and its development with the Crown

Zellerbach Corp. have already been well reviewed (Goheen 1966a).

During the '50's, the Noguchi Institute of Japan applied their experience in coal hydrogenation to the liquefaction of lignin. All of the early work was carried out using lignosulfonates mixed with a variety of solvents such as petroleum (Oiwa 1959), phenol, cyclohexanol, tetralin (Kashima 1961a) and most often a lignin tar recycled from previous experiments. A wide range of hydrogenating conditions were covered by the patent (Oshima 1961) including 250-450°C and 150-450 atmospheres but more typically 380°-430°C and 160-200 atmospheres were used. Most of this early work was carried out batchwise in an autoclave with continuous agitation. The catalyst was developed over several years starting simply with  $\text{Fe}(\text{OH})_3$  (Oiwa 1959), later mixing it with sulfur (Kashima 1962) and also modifying this catalyst with other metals e.g.,  $\text{FeS}$  activated with  $\text{Cu}$  (Oshima 1961);  $\text{Fe}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$  and  $\text{S}$  [ $\text{Fe}:\text{Zn}:\text{S} = 10:1:11$  mole ratio (Noguchi 1963)], until what became their standard catalyst was developed (Oshima 1966) a mixture of iron, copper, tin and sulfur (10:1:1:12 atomic ratio) powder that was ball milled in water for one day. The desired products were monophenols (e.g. phenol, cresols, ethylphenols, xylenols and propylphenols) in typical yields of about 28%. Also formed were acetone, methanol and various aromatic hydrocarbons (e.g. xylenes, ethylbenzene and propylbenzene). There was always a certain amount of higher boiling pitch formed (Oshima 1966b).

A pilot plant process for producing monophenols was developed using lignin from spent sulfite liquor that was desulfonated by a two-stage treatment with calcium hydroxide and sulfur dioxide. The lignin mixed with a pasting oil (usually phenol) and the standard catalyst (1-10% of the lignin) was hydrogenated in a stirred autoclave at 370°-430°C with hydrogen at 100 atm or more for 0.5 to 4 hours. A yield of about 44% of monophenols (phenol, cresols, p-ethylphenol and p-propylphenol) was claimed with an additional 20-24% heavy oil suitable for recycling as pasting oil.

In 1961 Crown Zellerbach Corp. obtained an option on the Noguchi process and a great deal of work was carried out trying to make it economically viable, resulting in one patent being issued to Crown Zellerbach (Goheen 1966b). One of the major problems with the process was that monophenol yields were not as high as claimed because the phenol used as solvent was incorporated into the



products by alkylation. Other substances such as diphenyl ether, anthracene oil and toluene were tried unsuccessfully, even recycled, liquefied "green" lignin tar (boiling point  $\geq 240^{\circ}\text{C}$ ) had similar problems to those of phenol. The best pasting oil that was found was obtained by exhaustively hydrogenating the "green" lignin tar to stabilize it. Pasting oil recoveries of  $\geq 100\%$  and monophenol yields of 21-23% were then obtained. The monophenol products consisted of phenol (~ 3% yield), cresols (~ 10%), ethylphenols (~ 4%), propylphenols (~ 2%) with small amounts of 2,4- and 2,6-xylenols (~ 2%). It was originally thought that the cresols could be obtained as almost pure p-cresol, but, in fact, a mixture of cresols was always formed that was very difficult to separate. The ratio of the isomers was strongly affected by the pasting oil. When phenol was used, a 97:3 ratio of the p- to m- ratio was obtained mostly because p-methylation of phenol was strongly favored over m-. When the stabilized lignin tar was used, the isomeric ratio was roughly 1:1, which was another adverse economic factor. A small amount (~ 13%) of phenol was reintroduced into the pasting oil to improve the meta:para ratio (to 12:88).

To try to further improve the process economics, different lignin preparations were experimented with to decrease the cost of the lignin feed. The Noguchi lignin produced by a two-stage process cost about 3 cents per pound. Poor results were obtained using just dried sulfite waste liquor solids. Considerable work was performed using a 55% concentrate of desugared calcium base-spent liquor. Eventually this lignin feed was abandoned because the presence of so much water kept the operating pressure too high. A modification of the original Noguchi lignin preparation was then developed that could be carried out in a single stage. The desugared liquor was heated with lime in an autoclave at  $200^{\circ}\text{C}$  and then deashed with sulfur dioxide. This method required only one filtration and gave a higher lignin yield from the spent liquor so that desulfonated deashed lignin could be prepared at less than 1.5 cents per pound. Precipitated kraft lignin and wood flour were run also but gave lower yields of monophenols.

The standard Noguchi catalyst was compared with a number of other materials to find a better catalyst (Oshima 1966). Selenium was found to give high yields of neutral materials and low boilers with twice as much gasification as the

Zellerbach Corp. have already been well reviewed (Goheen 1966a).

During the '50's, the Noguchi Institute of Japan applied their experience in coal hydrogenation to the liquefaction of lignin. All of the early work was carried out using lignosulfonates mixed with a variety of solvents such as petroleum (Oiwa 1959), phenol, cyclohexanol, tetralin (Kashima 1961a) and most often a lignin tar recycled from previous experiments. A wide range of hydrogenating conditions were covered by the patent (Oshima 1961) including 250-450°C and 150-450 atmospheres but more typically 380°-430°C and 160-200 atmospheres were used. Most of this early work was carried out batchwise in an autoclave with continuous agitation. The catalyst was developed over several years starting simply with  $\text{Fe}(\text{OH})_3$  (Oiwa 1959), later mixing it with sulfur (Kashima 1962) and also modifying this catalyst with other metals e.g., FeS activated with Cu (Oshima 1961);  $\text{Fe}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$  and S [Fe:Zn:S = 10:1:11 mole ratio (Noguchi 1963)], until what became their standard catalyst was developed (Oshima 1966) a mixture of iron, copper, tin and sulfur (10:1:1:12 atomic ratio) powder that was ball milled in water for one day. The desired products were monophenols (e.g. phenol, cresols, ethylphenols, xylenols and propylphenols) in typical yields of about 28%. Also formed were acetone, methanol and various aromatic hydrocarbons (e.g. xylenes, ethylbenzene and propylbenzene). There was always a certain amount of higher boiling pitch formed (Oshima 1966b).

A pilot plant process for producing monophenols was developed using lignin from spent sulfite liquor that was desulfonated by a two-stage treatment with calcium hydroxide and sulfur dioxide. The lignin mixed with a pasting oil (usually phenol) and the standard catalyst (1-10% of the lignin) was hydrogenated in a stirred autoclave at 370°-430°C with hydrogen at 100 atm or more for 0.5 to 4 hours. A yield of about 44% of monophenols (phenol, cresols, p-ethylphenol and p-propylphenol) was claimed with an additional 20-24% heavy oil suitable for recycling as pasting oil.

In 1961 Crown Zellerbach Corp. obtained an option on the Noguchi process and a great deal of work was carried out trying to make it economically viable, resulting in one patent being issued to Crown Zellerbach (Goheen 1966b). One of the major problems with the process was that monophenol yields were not as high as claimed because the phenol used as solvent was incorporated into the

products by alkylation. Other substances such as diphenyl ether, anthracene oil and toluene were tried unsuccessfully, even recycled, liquefied "green" lignin tar (boiling point  $\geq 240^{\circ}\text{C}$ ) had similar problems to those of phenol. The best pasting oil that was found was obtained by exhaustively hydrogenating the "green" lignin tar to stabilize it. Paste oil recoveries of  $\geq 100\%$  and monophenol yields of 21-23% were then obtained. The monophenol products consisted of phenol (~ 3% yield), cresols (~ 10%), ethylphenols (~ 4%), propylphenols (~ 2%) with small amounts of 2,4- and 2,6-xylenols (~ 2%). It was originally thought that the cresols could be obtained as almost pure p-cresol, but, in fact, a mixture of cresols was always formed that was very difficult to separate. The ratio of the isomers was strongly affected by the pasting oil. When phenol was used, a 97:3 ratio of the p- to m- ratio was obtained mostly because p-methylation of phenol was strongly favored over m-. When the stabilized lignin tar was used, the isomeric ratio was roughly 1:1, which was another adverse economic factor. A small amount (~ 13%) of phenol was reintroduced into the pasting oil to improve the meta:para ratio (to 12:88).

To try to further improve the process economics, different lignin preparations were experimented with to decrease the cost of the lignin feed. The Noguchi lignin produced by a two-stage process cost about 3 cents per pound. Poor results were obtained using just dried sulfite waste liquor solids. Considerable work was performed using a 55% concentrate of desugared calcium base-spent liquor. Eventually this lignin feed was abandoned because the presence of so much water kept the operating pressure too high. A modification of the original Noguchi lignin preparation was then developed that could be carried out in a single stage. The desugared liquor was heated with lime in an autoclave at  $200^{\circ}\text{C}$  and then deashed with sulfur dioxide. This method required only one filtration and gave a higher lignin yield from the spent liquor so that desulfonated deashed lignin could be prepared at less than 1.5 cents per pound. Precipitated kraft lignin and wood flour were run also but gave lower yields of monophenols.

The standard Noguchi catalyst was compared with a number of other materials to find a better catalyst (Oshima 1966). Selenium was found to give high yields of neutral materials and low boilers with twice as much gasification as the

standard catalyst. Tellurium and zinc iodide both gave much higher yields of pitch residue. Comparable performance to the standard catalyst was observed using nickel sulfide, nickel oxalate and Raney iron comparing liquefaction and pitch yields. Mixtures of ferrous sulfides with sulfides of Mo, Mn, Cd, V, Ce, Ag, Pb, Bi, Sb, and Hg were also less effective than the Noguchi catalyst (Goheen 1966a). A cobalt activated molybdenum sulfide catalyst gave good liquefaction yields but produced large amounts of neutrals. Iron phenoxide and a chelated iron catalyst were also poor catalysts. Zinc oxide was slightly inferior to the standard catalyst while zinc sulfide, boron and sulfur alone showed no activity at all. Preliminary examination indicated higher activities for cobalt sulfide, cobalt octacarbonyl, iron pentacarbonyl and ammonium molybdate. The cobalt compounds were too expensive to warrant further investigation. From a commercial point of view considering the phenol yield and the recovery of pasting oil (100%) the catalysts iron pentacarbonyl and ammonium molybdate were almost identical to the standard catalyst. Thus, no change was made in the choice of catalyst because of the lower cost of preparing the standard catalyst. All of these catalysts were used in their pure form without use of a support.

Apart from one reference (Kashima et al. 1963) to a continuous process, all the work was conducted batchwise in stirred or rotated autoclaves. It was found that agitation was very important. Only when the impeller shaft was lengthened so that there was only a 1/4 inch clearance of the reactor bottom and when the blade was designed to have a scooping action was good performance achieved. This was probably because of the necessity to have the catalyst powder well mixed into the liquid phase in the reactor.

The parameters time, temperature, and pressure of reaction were varied to devise a more economic process. Initially the process was carried out in two-stages of 2 hours each, with addition of fresh catalyst and hydrogen before the second stage. It was then found that only a single stage of two hours was necessary. The reactor was initially charged with hydrogen to 110-125 atm while it was cold. The pressure then was allowed to rise as it was heated so that an operating pressure of 250-290 atm was attained at the normal operating temperature (-430°C). Later work showed that a final pressure of 170 atm was sufficient. A programmed rise in temperature and pressure was also found to

be unnecessary. Later work showed that reaction times of 1 hour and half an hour were as good as 2 hours. Combinations of short times (down to 5 minutes) and high temperatures (up to 475°C) were experimented with until an optimum temperature (450°C) and optimum time (15 minutes) were chosen. The reaction time could be further shortened to 5 minutes if the lignin to pasting oil ratio was decreased from 1:1.3 to 1:2. One negative aspect of using shorter reaction times and higher temperatures was the effect on the m- to p- ratio of cresols formed. Using the new conditions the m:p- ratio was increased from 15:85 (using 13% phenol in the pasting oil) to 35:65. Doubling the phenol content of the pasting oil did not substantially change this ratio.

The original Noguchi product separation procedure involved atmospheric pressure distillation to remove water and light oil followed by a difficult reduced pressure distillation of the monophenols and lignin tar pasting oil from the non-volatile residue. This work-up was also improved upon by initially filtering or centrifuging insoluble materials from the crude mixture found in the autoclave at the end of a reaction. After the atmospheric pressure distillation and reduced pressure distillation of the monophenols, the residue could then be used directly as the pasting oil. A further improvement was to decrease the amount of catalyst used (from 7% to 3%) and then only filter every two cycles. The residue from the distillations plus a make-up of 1% of catalyst were then used in the pasting oil. Thus, the recycled oil could be used for many cycles before high boilers or pitch needed to be removed and catalyst usage was kept down to 2% per cycle.

Thus the original Noguchi process was refined and operating costs reduced by using cheaper lignin, lower pressure, shorter reaction time and improving the product separation. After removal of the phenol used in the pasting oil by fractional distillation of the monophenol cut, the remaining monophenols were extracted from the neutrals with 10% sodium hydroxide. Tables 3-16 and 3-17 show the yields of all products and specific monophenols formed respectively. Economic evaluation of the process still showed that it could not be used to produce pure phenol and cresols profitably despite the substantially reduced costs mostly because of a lower charge of lignin solids to the reactor and the lower yield of p-cresol. In addition, the steady and drastic decline in monophenol prices over the several years of process

Table 3-16. Product yields (%) based on net organic content in the lignin charge (Goheen 1966 ).

| Product  | Yield, wt. % |
|--|--------------|
| Gas  | 17.5         |
| Water  | 27.5         |
| Light Oils   | 5.0          |
| Monophenols  | 21.0         |
| Neutrals   | 9.0          |
| Excess paste oil (boiling point $\geq 240^{\circ}\text{C}$ ) | 20.0         |

Table 3-17. Monophenol yields (%) based on net organic content in the lignin charge (Goheen 1966 ).

| Phenolic Compound    | Yield, wt % |
|----------------------|-------------|
| Phenol               | 3           |
| o-Cresol             | 4           |
| m,p-Cresol           | 6           |
| o-Ethylphenol        | 1           |
| p-Ethylphenol        | 3.25        |
| p-Propylphenol       | 2           |
| 2,4-Xylenol          | 1.25        |
| Unidentified phenols | <u>0.5</u>  |
| Total                | 21.0        |

development contributed to make the process less attractive at that time. Combining this process with those for forming dimethyl sulfide and vanillin was also evaluated but no advantages were found.

### III.3.3 Hydrocarbon Research, Inc. (HRI)

#### III.3.3.1 Description of Patents

HRI first studied the production of monoaromatics via lignin hydrocracking in the '60's. Between then and 1983 they published a number of papers and were issued several patents on a process they designed, based on coal technology, in which lignin was cracked to a mixture of products including phenols and benzenes in a continuous ebullated bed reactor. HRI also registered the Lignol<sup>TM</sup> process in which the hydrocracking process was to be coupled to hydrodealkylation so that the major products would be phenol and benzene themselves.

Although the scope of the patents covers a large range of conditions for the cracking of lignins into phenols and benzenes, two distinctly different processes are described in detail. In the earliest patents a process for the catalytic hydrocracking of lignosulfonates, slurried in a heavy oil recycled from the reactor, is described. The bulk of the reported work details the hydrocracking of kraft lignin in a similar manner using an ebullated catalyst bed reactor. Contrastingly, the cracking of kraft lignin to phenols was also reported at much higher temperatures using a series of two fluidized bed reactors without slurrying oil, hydrogen or a hydrogenating catalyst but instead with a diluent gas such as steam and a particulate carrier material such as char. The goal of all these processes was to produce phenol in as high a yield as possible. Phenol has a higher value than benzene; in addition, at the time, no uses for mixtures of alkylated phenols and benzenes were proposed.

The process using lignosulfonates is the largest scale operation that has been described in any detail, processing lignosulfonate at a rate of 100 pounds per hour (Alpert and Schuman 1970, 1972). The use of lignosulfonates with a variety of cations including ammonium, alkali and alkaline earth metals was covered in the patent. The lignosulfonate was slurried with a recycled heavy oil and then mixed with hydrogen and possibly fresh catalyst before being fed

to the reactor, as shown in Fig. 3-5. The gas and slurry were maintained at such a flow rate as to keep the catalyst in constant turbulent motion whilst retaining the expanded catalyst bed in the reactor. These early lignosulfonate patents covered operation of the reactor from 150°C to 450°C and 20 atm to 140 atm.

A wide variety of hydrocracking catalysts are mentioned in the patents, usually oxides or sulfides of metals from groups V, VI and VIII supported on neutral or acidic supports such as alumina, silica-alumina or alumina activated with fluoride. Those catalysts particularly covered by the patents are those consisting of iron, cobalt, molybdenum or chromium and mixtures thereof supported on alumina. It is mentioned that whereas the use of an iron (20-50 wt %) on alumina catalyst will favor formation of monophenols, use of cobalt (1-5 wt % of the oxide)/molybdenum (10-15 wt % of the oxide) on alumina will favor cyclohexane and benzene formation. It should be remembered that because of the sulfur content of the lignin all these catalysts will be fully sulfided in the reactor. The only detailed comparison of catalysts comes from work using a lignin model, diphenyl ether as feed. The reactor employed for these studies contained the catalysts in a fixed bed. Despite the limitations of diphenyl ether as a model compound, this study did show that a cobalt/molybdenum on alumina catalyst was much better at reducing aromatic rings to cyclohexanes than iron (20%) on alumina which at 70 atm and 427°C gave the highest net yield of phenol (35%) with a reasonable diphenyl ether conversion (40%). HRI claimed that catalysts could be used in pelletized or extruded form with 1/16 inch diameter or less. The catalyst was also effective as particles in the size range of 15 to 270 mesh although preferably as 30 to 200 mesh. Catalyst replacement rates were always less than 0.1 lb of catalyst per 100 pounds of feed and normally less than 0.001 lb of catalyst per 100 pounds of feed. The extended catalyst bed contained a fairly high catalyst concentration of at least 5 lb of catalyst per cubic foot to a maximum of 70 lb per cubic foot. It can be estimated from the patent examples that between 20 and 30 lb per cubic foot were used. The high catalyst concentration was claimed to allow the use of less active, less easily poisoned catalysts which were more rugged and less expensive. The catalyst in the reactor was described as influencing the hydrocracking of the lignin



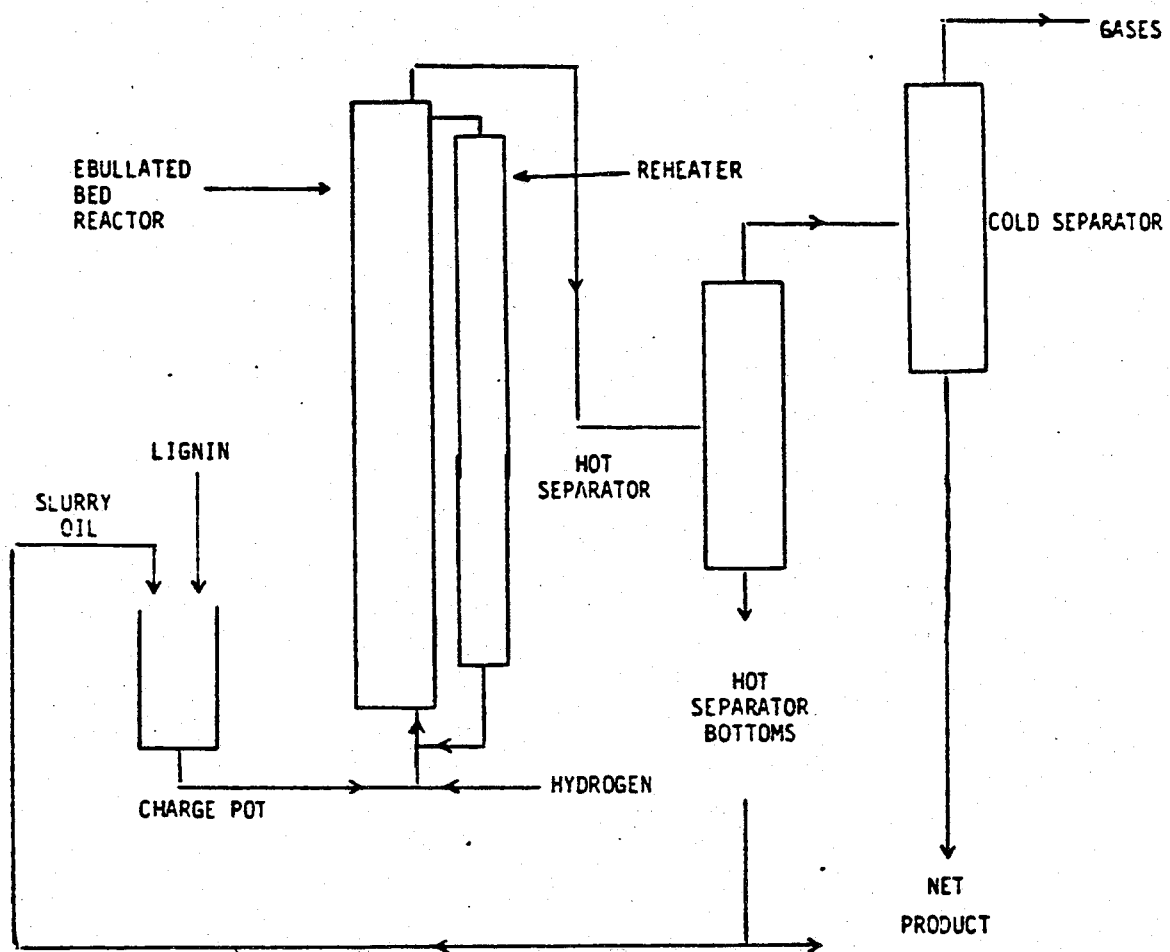


Fig. 3-5. Schematic of HRI's Lignin Hydrocracking Unit (Gendler et al. 1983).

polymer only after lignin had been thermally hydrocracked to lower polymers such as trimers to pentamers. These fragments were then catalytically hydrocracked to monomers. The rate of thermal hydrocracking was described as much faster than the catalytic hydrocracking.

In the patent (Alpert and Schumann 1972), it is stated that, after passage through the reactor, very little solid material remained, with the lignin almost completely converted to liquid and gaseous products which were disengaged at the top of the reactor. The liquid stream, containing a small amount of solids, could then be recycled back into the reactor with part of it being used as the slurring oil for the fresh lignin feed. Part of this liquid stream could also be passed through a separator system to remove the solids and heavy liquids from the higher boiling oxygenated liquids. The high boiling oxygenates could also be recycled back to the reactor or split off as product for possible use as fuel oil.

The primary product of the process was contained in the vapor effluent leaving the top of the reactor. After passage through a separator, this stream was split into a substantially hydrogen gaseous recycle, a gaseous product stream containing light hydrocarbons, and the primary product stream of low boiling oxygenated liquids and benzenes. The gaseous product stream could be used for fuel or, more preferably, to produce hydrogen required in the process. The primary product stream could be passed to another separator to separate the various phenolic and hydrocarbon components or, as was registered under the Lignol<sup>TM</sup> process, be passed to a hydrodealkylation reactor to give phenol and benzene as the major products.

The details of the example given in the patents for conversion of lignosulfonates are given in Table 3-18. The most surprising feature of this example is the low temperature (300°-330°C) that was used to hydrocrack the lignosulfonate. This temperature range is much lower than that used in the examples of kraft lignin hydrocracking and even outside the range of the later kraft lignin patents. Only a very limited description of the products is given but a yield of 38% of monophenols is mentioned. At such a low temperature the amount of hydrocracking would be quite limited and any monophenols formed should be of relatively high molecular weight.

Table 3-18. Summary of Hydrocarbon Research, Inc. Results On Lignin Cracking to Low-Molecular Weight Compounds

|   | Calcium<br>Lignosulfonate<br>~1965 | Patent<br>Coverage<br>~1971   | Kraft<br>~1965                          | Kraft<br>1981                  | Patent<br>Coverage<br>1983  | Preferred<br>Embodiment<br>1983 | Kraft<br>Pyrolysis/<br>Steam Cracking<br>~1980 |
|---|------------------------------------|---|---|--------------------------------|---|---------------------------------|--|
| T, °C                                     | 300 - 330                          | 150 - 450   | 440                                     | 440                            | 340 - 450   | 370 - 440                       | 815 <sup>a</sup><br>870 <sup>b</sup>           |
| P (psig)                                  | 1250                               | 250 - 2000  | 1000                                    | 1014                           | 500 - 2500  | 600 - 2000                      | 15 - 150                                       |
| Lignin Feed Rate<br>lb/hr                 | 100                                |   | 0.33                                    | 1.0                            |   |                                 |  |
| H <sub>2</sub> Feed Rate<br>SCF/lb Lignin | 143                                |   | 44                                      |                                |   |                                 | Steam<br>5 ft/s                                |
| Reactor<br>Volume (ℓ)                     | -120                               |   | 0.4                                     | 1.0                            |   |                                 |  |
| A   |                                    |   | -2 <sup>c</sup>                         | 1.6                            | 1.0 - 10  | 0.3 - 6.0                       |  |
| B   | -24 <sup>c</sup>                   |   | 23.4                                    | 28.3                           |   |                                 |  |
| Catalyst<br>Metal (wt%)                   | Co(1)/Mo(3-10)                     | Fe, Co, Mo<br>Cr  | Fe <sub>2</sub> O <sub>3</sub><br>(20%) |                                | oxides of<br>Fe, Co, Mo, Ni   | MoO <sub>3</sub><br>(12-18%)    | Coke/<br>Char                                  |
| Catalyst<br>Support                       | Al <sub>2</sub> O <sub>3</sub>     | Al <sub>2</sub> O <sub>3</sub><br>Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub><br>Al <sub>2</sub> O <sub>3</sub> -F | Al <sub>2</sub> O <sub>3</sub>          |                                | Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub><br>or<br>Al <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub>  |  |
| Catalyst<br>Particle Size<br>(U.S. Mesh)  | 40                                 | 16-270  | 12-16                                   |                                | 6-35  |                                 | 100-350  |
| Lignin dilution<br>in heavy oil           | 1:3.3                              |   | 1:3                                     |                                |   |                                 | None   |
| Reactor                                   | Continuous<br>ebullated<br>bed     | Continuous<br>ebullated<br>bed  | Continuous<br>ebullated<br>bed          | Continuous<br>ebullated<br>bed | Continuous<br>ebullated<br>bed  | Continuous<br>ebullated<br>bed  | 2-stage<br>particle<br>fluidized bed           |
| References                                | 1,2                                | 1,2   | 2-6                                     | 6                              | 5   | 5                               | 7  |

a) fast fluidized bed reactor    b) slow fluidized bed reactor    c) estimated  
 A Weight hourly space velocity (WHSV) = Lignin Feed Rate + weight of catalyst (lb/hr/lb)  
 B Lignin feed rate per unit reactor volume (lb/hr/cu.ft)  
 See Table 3-20 for References.

In the late '60's, HRI completed a 60 hour run in an ebullated bed reactor establishing the feasibility of hydrocracking kraft lignins to hydroxyaromatics (Alpert and Schumann 1972). The data on a particular example disclosed in this early kraft lignin patent was reproduced many times in papers (Huibers and Jones 1980; Parkhurst, Huibers, and Jones 1980) and also cited in the later patents in 1983 (Huibers and Parkhurst) where it was used to compare HRI's process with the Noguchi catalytic batch hydrocracking process (see Section II.3.2). However, the project was discontinued because of the lower cost of petroleum derived phenols. The sharp increase in oil prices in the '70's renewed interest in lignin-produced phenols and by 1981 HRI had completed a seven-day pilot-plant-scale run, hydrocracking 163 lb of kraft lignin in a one liter, continuous ebullated-bed reactor (Gendler, Huibers, and Parkhurst 1983).

There is little difference in the conditions covered in the patents on the hydrocracking of lignosulfonates and kraft lignins except for an increase in the lower limit of the temperature (from 150°C to 340°C) at which the process should be operated. The same sort of difference can be seen in the examples used in the patents. All examples of hydrocracking kraft lignins have the reactor at 440°C compared to the lignosulfonate example which employed only 300°C. This low temperature process used a cobalt/molybdenum on alumina catalyst to produce at least 35 weight percent of benzene and cyclohexane. It is cited that lignosulfonate was hydrocracked at higher temperature (-400°C) with iron (20%) on alumina to yield 35 weight percent of monophenols. Thus there seems to be some discrepancy between the example and the text of the patent, but it would appear the processes for hydrocracking lignosulfonates and kraft lignins were ostensibly the same. From the published information on the work carried out in the '80's and the patents of that period, there was one major change in the process for hydrocracking kraft lignins to phenols, from the process developed in the '60's, and that was in the preferred catalyst. To hydrocrack kraft lignin to monophenols the catalyst of choice from the early work was iron (20%) on alumina, the later patents describe molybdenum oxide (12-18%) on alumina as the preferred catalyst because it leads to less hydrogenation thus giving lower yields of cyclohexanes and other saturated hydrocarbons. The product slate detailed for the kraft lignin

process in the '60's is fairly similar to that of the '80's process if the projected phenol composition for complete lignin conversion is used as can be seen in Tables 3-19 and 3-20. The main differences are the decreases in gas and neutral fraction yield at the expense of increased yield of the heavy liquids (boiling range 240°-425°C). The yield of the phenolic fraction remained about the same at about 37%. The major difference in the types of phenols produced was an increased proportion of phenol and decrease in propylphenols in going from the process of the '60's to that of the '80's. This was probably due to the change in catalyst. Ethylphenols were the major phenolic products.

In all this work the ebullated bed reactor was expounded as an excellent reactor for the catalytic hydrocracking of lignins. Upward pumping of the slurry/gas mixture through the tubular reactor expanded the catalyst bed to occupy a volume at least 10% greater than in its settled state, maintaining the catalyst in constant turbulent motion. HRI suggests that these features lead to good temperature control of the reactor, good contact between lignin, hydrogen and catalyst, and ease of replacement of spent catalyst in a continuous or semi-continuous manner. This reactor design is also described as being optimal for separation of the products, which are vapors that are swept from the reactor with the excess hydrogen, leaving the catalyst which remains in the reactor.

### III.3.3.2 Economic Evaluations of the Lignol™ Process

An economic analysis of the Lignol™ process was published in 1980 (Huibers and Jones) and then later updated (Parkhurst, Huibers, and Jones 1980). This analysis was based on the estimate that kraft lignin could be processed to yield 20.2 wt% phenol, 14.4wt% benzene, 13.1 wt% fuel oil and 29.1% fuel gas. For a Lignol™ facility processing 160,000 ton/yr of kraft lignin a total 1979 capital investment of \$37.6 million was calculated based on the process scheme shown in Fig. 3-6. Hydrogen would be produced in the plant (see Fig. 3-6) at 15.8 MMSCFD. It was assumed that all hydrogen and process fuel requirements would be supplied from the lignin derived oil. Revenues came from production of 65 million lb/yr of phenol at 30¢/lb, 6.4 million gal/yr of benzene at \$1.50/gal and 500 billion BTU/yr of fuel oil at \$3/MMBTU. With a total production cost of \$14.9 million a 20% return on total investment could be

Table 3-19. Product Yields as Weight % of Lignin Charged.

|                                 | Calcium<br>Lignosulfonate<br>~1965 | Kraft<br>~1965 | Kraft<br>1981 | Kraft<br>Predicted <sup>a</sup><br>1981 | Kraft Pyrolysis/<br>Steam Cracking<br>1980 |
|---------------------------------|------------------------------------|----------------|---------------|---|--|
| Gases                           |                                    | 25.2           | 15.4          | 17.8                                    | 37.0                                       |
| Water                           |                                    | 17.9           | 18.8          | 16.8                                    | --   |
| Neutrals ≤240°C                 |                                    | 14.0           | )<br>) 23.3   | 10.8                                    | 1.7  |
| Phenols ≤240°C                  | 38                                 | 37.5           | )             | 37.4                                    | 49.6                                       |
| Heavy Liquid 240°-425°C         | 42                                 | )<br>) 11.1    | 23.3          | 22.0                                    | 11.7                                       |
| Residue ≤425°C                  | 20                                 | )              | 23.3          |   |  |
| Calculated Hydrogen Consumption |                                    | 5.7            | 4.1           | 4.8                                     | --   |
| References                      | 1,2                                | 2-6            | 6             | 6                                       | 7  |

a) Yields if all the tar was converted.

See Table 3-20 for References.

Table 3-20. Phenol Yields as Weight % of Total Phenols.

|                                    | Kraft<br>-1965 | Kraft<br>1981 | Kraft<br>Predicted <sup>a</sup><br>1981 | Kraft Pyrolysis/<br>Steam Cracking<br>1980 |
|------------------------------------|----------------|---------------|---|--|
| Phenol                             | 6.5            | 16.2          | 14.4                                    | 22.8                                       |
| o-Cresol                           | 3.6            | 3.8           | 5.7                                     | --   |
| m-Cresol                           | 11.9           | )             | )                                       | 18.1                                       |
| p-Cresol                           | 9.7            | ) 25.8        | ) 20.7                                  | 39.9                                       |
| Ethylphenols                       | 33.2           | 29.6          | 31.8                                    | --   |
| Xylenols                           | 7.0            | 6.2           | 9.5                                     | --   |
| Propylphenols                      | 28.0           | 18.4          | 17.9                                    | --   |
| Catechols                          |                |               |   | 19.2                                       |
| Calculated Hydrogen<br>Consumption | 5.7            | 4.1           | 4.8                                     | --   |
| References                         | 2-6            | 6             | 6                                       | 7  |

a) Yields if all the tar was converted.

### References

1. Alpert and Schuman 1970, Schuman and Field 1970.
2. Alpert and Schuman 1972.
3. Huibers and Jones 1980.
4. Parkhurst, Huibers and Jones 1980.
5. Huibers and Parkhurst 1983.
6. Gendler, Huibers and Parkhurst 1983.
7. Snell and Huibers 1983.

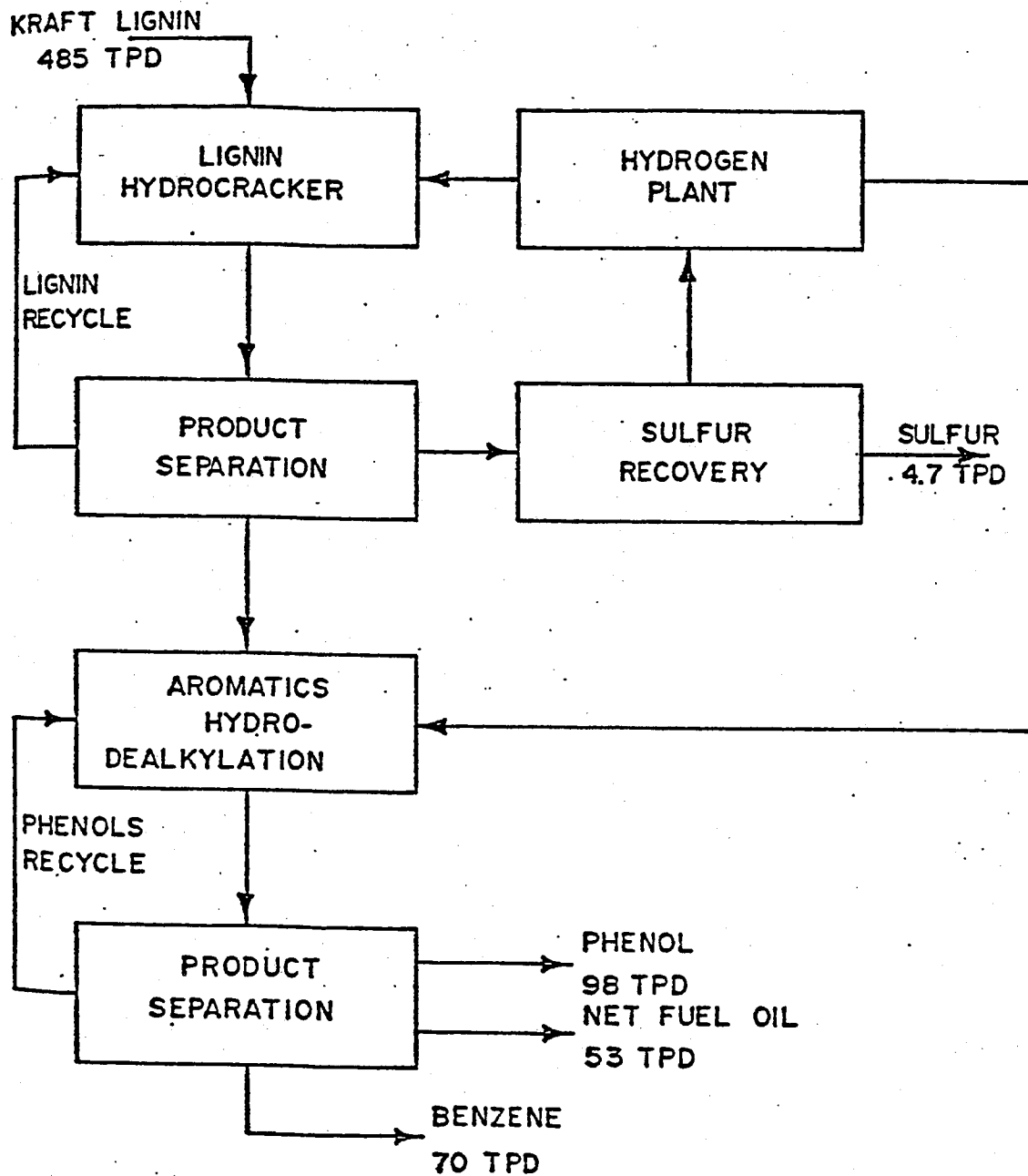


Fig. 3-6. Lignol™ process scheme. Conversion of kraft lignin into phenol, benzene, fuel oil, fuel gas with sulfur recovery and hydrogen plant (Huibers and Jones 1980).



realized provided lignin cost was roughly 5¢/lb. It was estimated that if the phenol yield of the Lignol<sup>TM</sup> process could be improved from 20 to 38% then a price for kraft lignin of 7¢/lb could be acceptable. It was noted that the economics of lignin hydrocracking could be much more attractive if markets for alkylphenols could be found.

A more recent evaluation of the conversion process-wood-to-butanol, acetone, ethanol (ABE) through fermentation of intermediate sugars produced in the wood-carbohydrate hydrolysis was performed by Chem Systems, Inc. (1984). These analysts calculated the costs of the ABE fermentation. In addition, various options were included in the analyses such as continuous fermentation and the use of the lignin fraction to generate phenol and benzene by the Lignol<sup>TM</sup> process. These authors adapted the kraftlignin process and deleted the sulfur recovery and the hydrogen plant from the scheme in Fig. 3-6. Simplifying assumptions were made because of lack of data on the real lignin system. They assumed that the lignin produced in this process would give the same yields of phenol, benzene, fuel gas and fuel oil mentioned above for kraft lignin. They provided make-up hydrogen to the plant at a cost and used the fuel oil and fuel gas to meet all steam requirements for both the Lignol<sup>TM</sup> process and other ABE fermentation plant sections. Figures 3-7 and 3-8 show the process flow sheets employed by the Chem Systems, Inc. analysts. They credited 10.9 wt% based on original lignin net fuel for process steam and used 18.2% to meet all Lignol<sup>TM</sup> process steam requirements. All fuel gas produced (13.1%) was used to generate process steam for other parts of the plant (not for hydrogen production by steam reforming).

The comparison of the base fermentation case with the addition of the Lignol<sup>TM</sup> process is made in Table 3-21. The selling price at 10% discounted cash flow is reduced by about 10¢/gal with the Lignol<sup>TM</sup> process. The energy requirements with the Lignol<sup>TM</sup> process is only 60% of the energy required in the base case alone. The inside battery limits investment for the fermentation and Lignol<sup>TM</sup> process can be broken down as follows:

- 1) Raw materials + pretreatment = 21.2%
- 2) Enzyme sections (production and hydrolysis) + fermentation = 17%
- 3) Purification of products and CO<sub>2</sub> recovery = 11.7%

PHENOL, BENZENE PRODUCTION VIA LIGNOL PROCESS

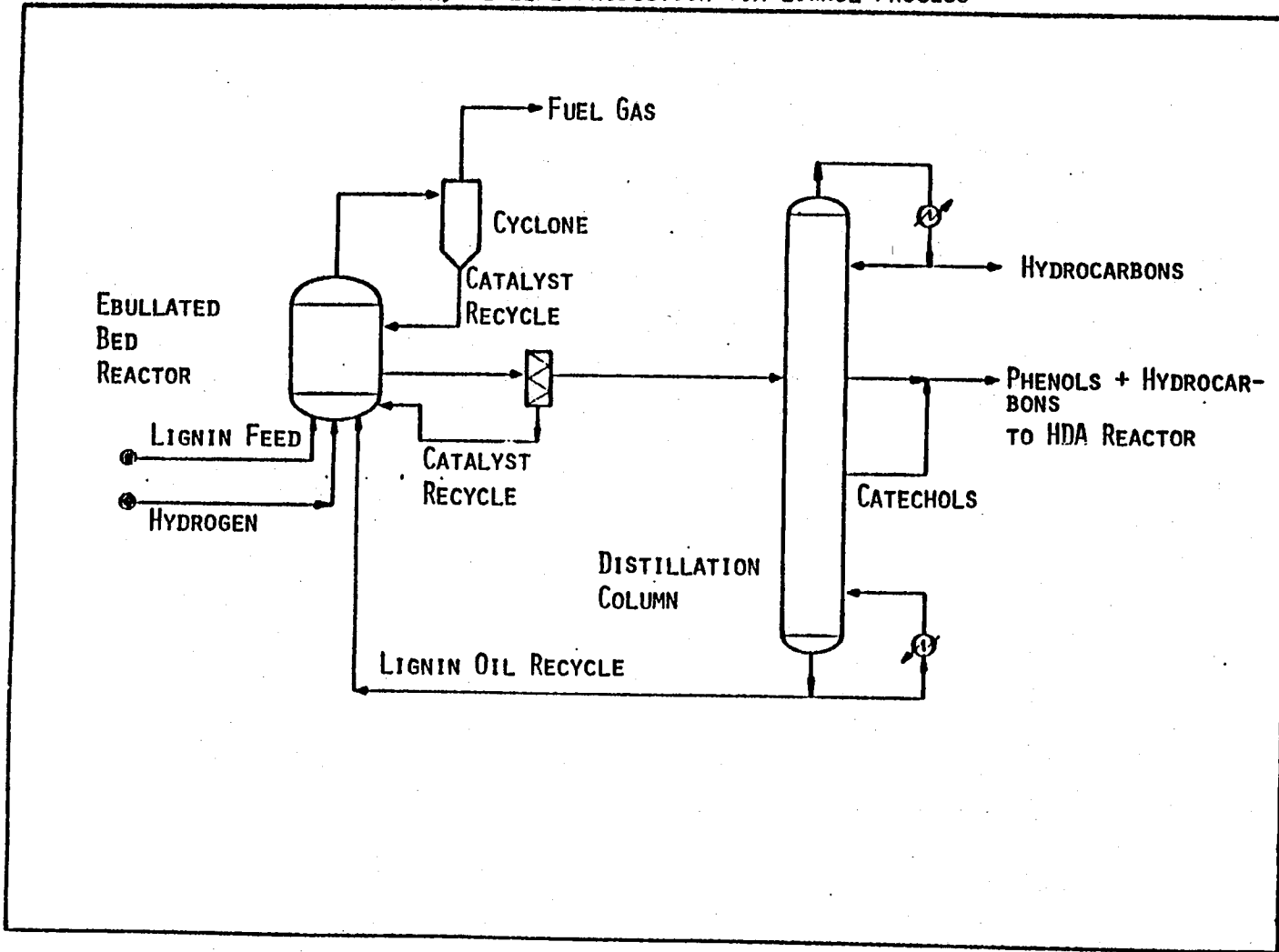


Fig. 3-7. Lignin hydrocracking step of HRI's Lignol™ process (Chem Systems, Inc. 1984).

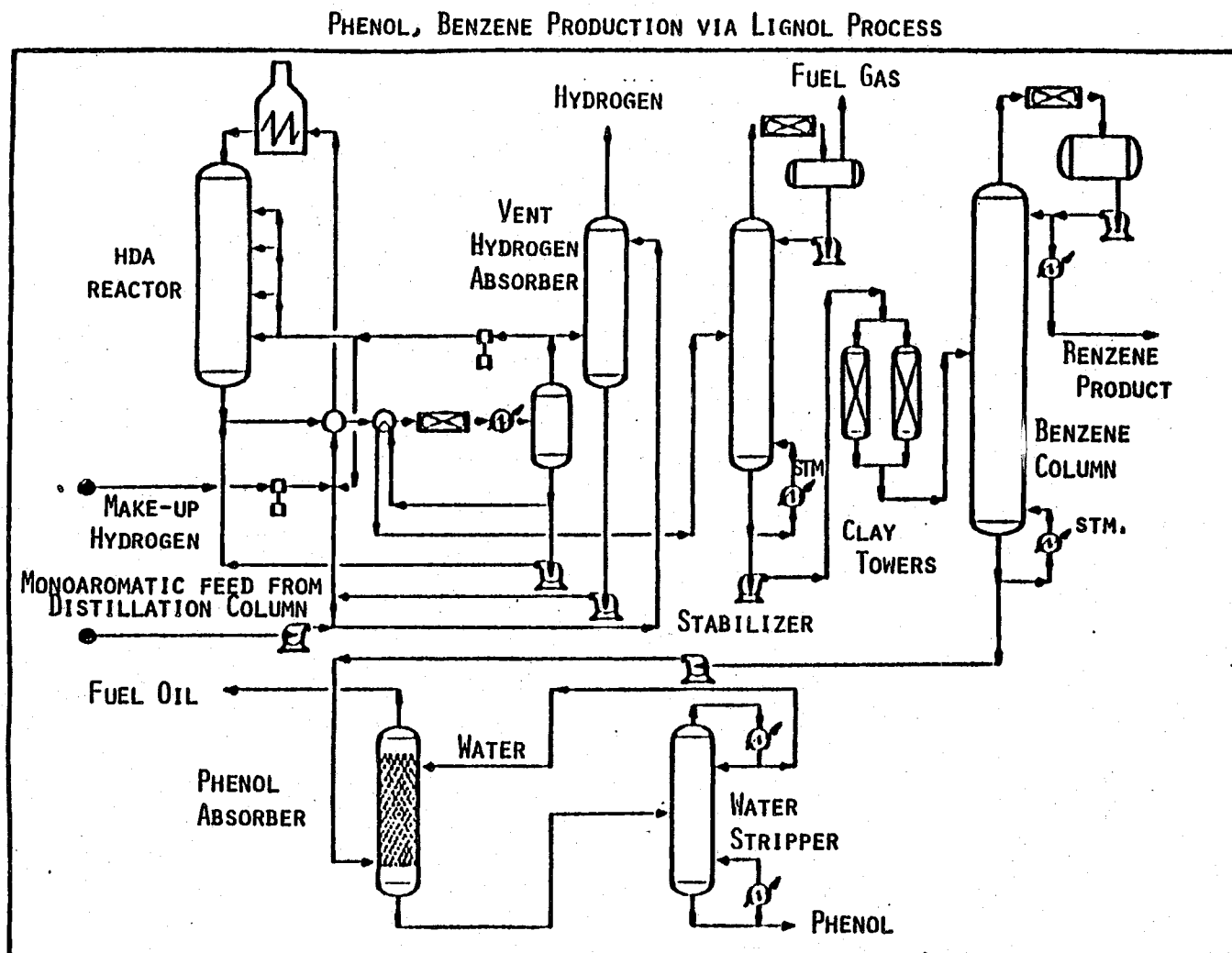


Fig. 3-8. Hydrodealkylation and purification steps of the Lignol™ process (Chem Systems, Inc. 1984).

Table 3-21. Process Economics Data For a 50 Million Gallon/year Plant Wood-to-acetone, butanol, ethanol. (Chem Systems, Inc. 1984)

U.S. Gulf Coast/Louisiana Mid 1982.

|  | Base Case    | Lignol       |
|--|--------------|--------------|
| Investment \$MM                        |              |              |
| Battery Limits                         | 92.8         | 135.6        |
| Off Sites                              | <u>97.3</u>  | <u>89.8</u>  |
| Total Fixed Investment                 | 190.1        | 225.4        |
| Cost of Production, ¢/gal              |              |              |
| Raw Materials                          | 86.59        | 104.01       |
| Utilities                              | 43.37        | 36.88        |
| Operating Costs                        | 15.16        | 20.29        |
| Overhead Expenses                      | 17.37        | 21.76        |
| By-Product Credit                      | (23.20)      | (71.58)      |
| Cash Cost of Production                | 139.28       | 111.37       |
| Depreciation                           | <u>56.58</u> | <u>72.20</u> |
| Net Cost of Production                 | 195.85       | 183.57       |
| Selling Price @10% DCF                 | 259.8        | 249.4        |
| Energy Consumption<br>MBTU/Gal Product | 107.4        | 65.4         |

---

- 4) Lignol<sup>TM</sup> = 25.2%
- 5) Overhead and Contingencies = 24.9%

The evaluation is obviously simplified and the error limits are certainly higher than  $\pm 35\%$ . Evaluations of the wood-to-ethanol processes taking into consideration the Lignol<sup>TM</sup> process, including a hydrogen generation plant (rather than purchase of hydrogen), should be made. The recovery costs and fermentation system in the ABE system are also quite different from ethanol manufacture.

### III.3.3.3 Comparison of Lignin Hydrocracking/Hydrodealkylation with Fluidized-Bed Pyrolysis

A much different process was described in a 1983 HRI patent (Snell and Huibers 1983) in which kraft lignin was cracked at high temperature in a two-stage fluidized bed reactor system as shown in Figure 3-9. In this process a lignin containing material (70-95 wt% lignin) such as obtained by precipitating kraft lignin from black liquor, was pressurized and mixed with a diluent gas such as steam or process gas. The material was then preheated (200°-315°C) and fed into the first reactor containing refractory chars or carbonaceous carrier materials (melting point  $\geq 1100^\circ\text{C}$ ) maintained in a fast fluidized bed condition. Cracking conditions in the bed were maintained at 650° to 925°C and 2 to 11 atm. High superficial gas velocities (5-20 ft/s) were used to keep residence times in the 0.3 - 3 second range. Superheated steam was supplied to the reactor to provide fluidizing gas and control the hydrogen partial pressure. The solids density of the fluidized bed should be at least 3 lb/cu ft and usually in the range 5-25 lb/cu ft. The effluent product vapors with entrained coke-laden carrier material, exited the reactor and were separated in two stages. The separated vapor was quenched with a compatible quench liquid and then fed to other recovery unit processes. The separated solids were fed into a second slow fluidized bed (upward superficial gas velocity 0.3 - 3 ft/second) where the coke was burnt off the carrier material (at 750° to 1100°C) with air and superheated steam producing a flue gas. The decoked carrier material was then recycled to the fast fluidized bed reactor.

The example given in the patent is summarized in Tables 3-18, 3-19 and 3-20. It can be seen that a large amount of gas is produced which mostly consists of

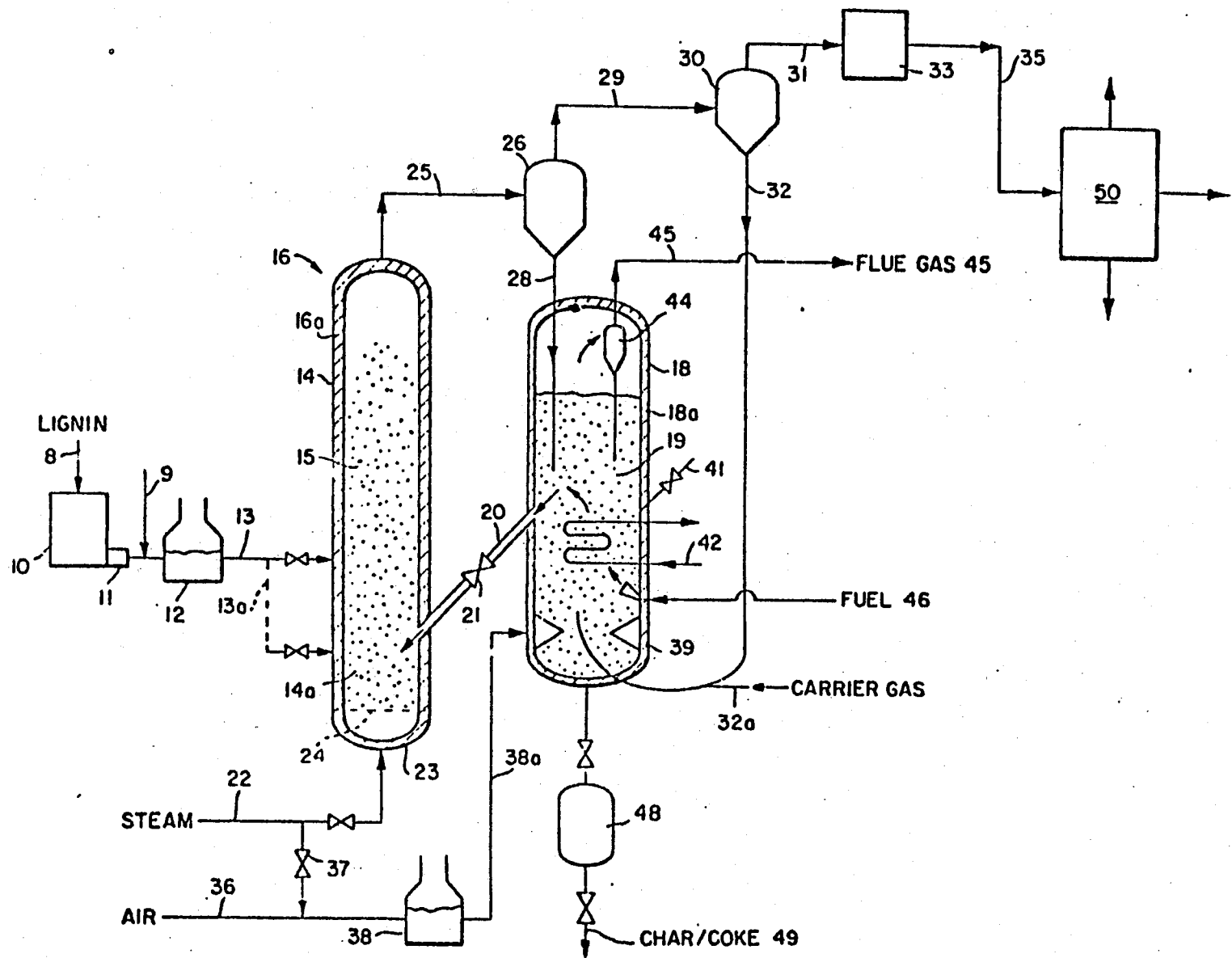


Fig. 3-9. Fast Fluidized-Bed Pyrolysis Process Diagram Inventors G. J. Snell and D. T. A. Huibers (1983).

carbon monoxide, carbon dioxide and ethylene as in other fast pyrolysis processes. There is also a high yield of phenolic products mostly phenol, cresols and catechols. No higher molecular weight phenols were reported in the patent. If secondary reactions are minimized the principal product was methyl catechol. With increased process severity methyl catechol was further cracked to phenol, catechol, cresols, toluene and benzene.

This process is much different from the Lignol<sup>TM</sup> process but appears to offer the promise of higher phenolic yields already cracked to at least the cresol level. Comparative economic assessment of this process with hydrocracking should be made.

#### III.3.4 Other Processes - Lignin as Catalyst for Coal or Oil Residue Hydroprocessing

Morita and Sato (1980) patented a process for co-liquefaction and gasification of lignin and coal by hydrogenation (115-675 atm of hydrogen) at 400°-500°C. The paste of coal and lignin in a heavy hydrocarbon oil was passed through two or more vertical reactor tubes into which streams of hydrogen were introduced in a turbulent flow (Reynolds number higher than  $10^4$ ).

Coughlin and Davoudzadeh (1983, 1985) have investigated coliquefaction of lignin and coal in hydrogen-donor solvents. These authors found that lower temperatures can be used for the depolymerization of coal in the presence of lignin. For instance, by adding 35 g of lignin to 15 g of coal (Illinois No. 6) and 200 ml of tetralin, with 5 g of  $\text{SiO}_2\text{-Al}_2\text{O}_3$  at 36 atm of hydrogen at 300°C for two hours, 36% total organics were converted to liquids or 43% of the coal were converted into solubilized liquid products. Under these conditions, 50 g of the coal without lignin gave a much lower conversion (5%) to liquid products. Thermal depolymerization of the lignin is believed to form resonance-stabilized phenoxy radicals which can attack the coal causing cleavage of the aliphatic carbon-carbon bonds in the coal. Lignin model compound experiments were also performed. Using guaiacol as a solvent increased the coal conversion to up to about 80% under similar conditions.

A patent assigned to Mobil Oil Corp. covers the area of coal liquefaction and petroleum residue processing in the presence of lignins (1-10 wt%) (Rudnick 1983). The conditions indicated in the patent are temperature 600°-800°C, 4-205 atm of hydrogen, and residence times of 0.5-180 min. For coal processing,

in the presence of 1-4% lignin, higher quality coal extracts were obtained. In the case of petroleum residue processing, addition of lignin (0.1-10 wt%) led to higher yields of premium fuel products.

Another process patented by Nippon (1981a) used coal fly ash (70 g), lignin (150 g) and bamboo sawdust (150 g) that was pelletized (5 mm diameter) and calcined (up to 1200°C) and used at temperatures of greater than 300°C to crack heavy petroleum to an oil (88%) and gas (12%) at similar yields of a commercial allophane catalyst.

The catalytic cracking of heavy petroleum oils (boiling point >300°C) has been patented by Nippon Kaihatsu Kogyo (1981b). The cracking occurs at 350°C or higher temperatures in the presence of 5-30 wt% of powdered lignin and/or sawdust as catalysts to manufacture light oils and fuel oils containing light olefins (3-4 carbon atoms).

### III.4 REVIEW OF SELECTED LIGNIN MODEL COMPOUND HYDROTREATING

The study of lignin model compound hydrodeoxygenation is beneficial to the understanding of the hydroprocessing chemistry of real lignins. Elucidation of reaction mechanisms, determination of rate constants and mapping out the effects of temperature, pressure, catalysts, solvents and reactor design are examples of important information gained by such studies. Care must be taken however in extrapolating the results to macromolecules due to possible competing reactions in these materials such as condensation and char formation.

Several compounds have been used as lignin models including phenol, cresols, anisole, guaiacol, and 4-propylguaiacol. In this summary the research of Bredenberg and coworkers will be reviewed separately due to the large amount and comprehensive nature of their work. Thermal reaction studies are important because depolymerization of lignin to low molecular weight units, capable of reaction with heterogeneous catalysts, must occur first in hydroprocessing schemes.

#### III.4.1 Thermolysis

All of the thermal reactions studied by Bredenberg and coworkers were carried out batchwise either in a stainless steel autoclave or in sealed glass ampoules in the temperature range of 300°-400°C. It was discovered that



### C) CATALYSTS

With some exceptions, the bulk of the work described in this Section neglects to characterize the heterogeneous catalysts employed. Simple characteristics such as supplier of the catalysts or particle size employed are often missing. This was obviously not the case with the development of the Noguchi catalyst. On going from this type of work to that of HRI, the catalysts are again not fully described. The catalyst selection for kraft and lignosulfonates, which contain some form of sulfur species, followed coal and petroleum processing. Thus, the catalysts Fe, Ni, Co, Ni/Mo, Co/Mo, Mo on  $\gamma$ -alumina or, at times, on the more acidic alumina-silica supports were employed, and most often, the catalysts were fully sulfided.

With the emerging lignins, an opportunity exists of utilizing catalysts that are developed for lignins (not for coal or petroleum), and with the process requirements in mind. Thus, issues such as the degree of sulfidation needed, how acidic the support should be, and what is the best metal ion, can be dealt with systematically. From the past literature, the mild hydrodeoxygenation catalyst, sulfided Mo on  $\gamma$ -alumina, appears the best for avoiding excess buildup of neutrals. From HRI data, this catalyst yielded a larger proportion of ethylphenols than propylphenols, the main products on sulfided Fe on  $\gamma$ -alumina. Systematic comparison of sulfided vs. non-sulfided forms and systematic variations of the support acidity are lacking.

Moving from the supported catalyst area to the work carried out on unsupported materials such as CoS, FeS, CuS, preferred by the Russian workers, again, there is little data on the catalysts.

Can special catalysts be developed that are more selective and operate at lower pressure and temperature in hydrogen-donor solvents or in lignin pasting oil? What is the role of the catalyst in tetralin? In order to expedite catalyst screening and to allow better understanding of the various parameters affecting these complex reactions, pertinent lignin model compounds should be investigated. The model compound should contain the most important lignin functionalities.

### D) TYPE OF LIGNIN/PRODUCT YIELDS

In much of the work described in this section, the aim was the determination of the lignin structure, aided by reductive degradation techniques. The more

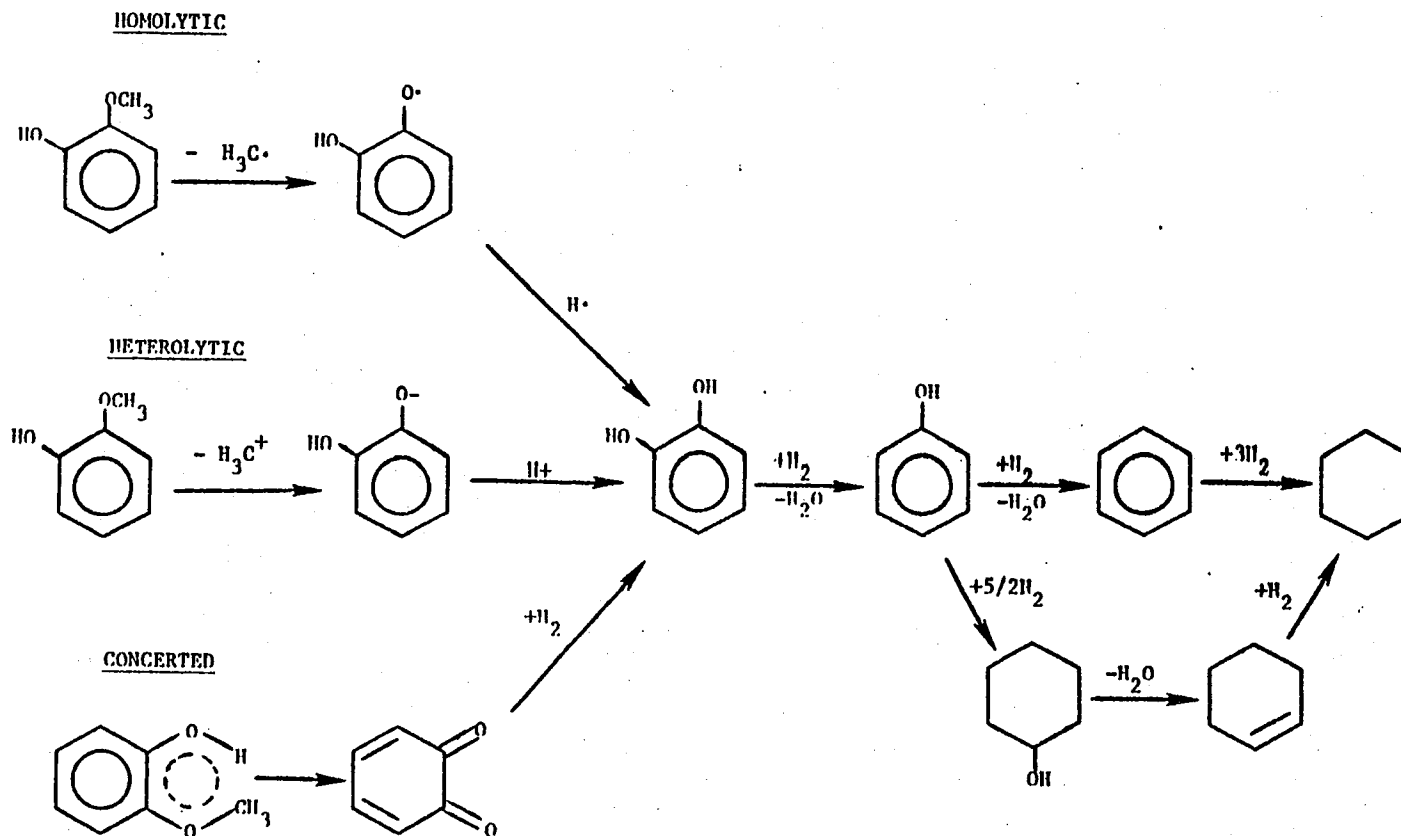


Fig. 3-10. Dissociation, hydrodeoxygenation and hydrogenation mechanisms of guaiacol (Vuori and Bredenerg, 1985).

Table 3-22. Comparison of Thermal and Catalytic Hydrocracking of 4-Propyl-guaiacol. (Vuori and Bredenberg 1984)

| Solvent                                  | Thermal |      | Al <sub>2</sub> O <sub>3</sub> | Sulfur Free Co/Mo |      | Presulfided <sup>a</sup> Co/Mo |
|--|---------|------|--------------------------------|-------------------|------|--------------------------------|
|  | T       | N    | T                              | T                 | N    | T                              |
| Conversion, %                            | 57.8    | 63.5 | 87.0                           | 98.6              | 98.0 | 99.3                           |
| Selectivity for 4-propyl-pyrocatechol, % | 32.2    | 28.8 | 32.0                           | 2.9               | 2.7  | --                             |
| Selectivity for 4-propyl-phenol, %       | 1.6     | 2.8  | 0.7                            | 10.0              | 6.5  | 12.8                           |
| Selectivity for 3-propyl-phenol, %       | 1.4     | 2.8  | 0.9                            | 24.2              | 16.5 | 28.3                           |
| Propyl-cresols, %                        | --      | --   | --                             | 10.0              | 5.5  | 10.1                           |

Common Conditions: 345°C, initial hydrogen pressure = 290-320 psi.  
 Batch 750 ml Stainless Steel Rocking Autoclave  
 Solvents: T=tetralin, N = Napthalene  
 Reaction Time = 124 ± 4 min

a) S = 4.3 wt% of catalyst.

Bredenberg 1984). It illustrates the effects of Co/Mo catalysts and the  $\text{Al}_2\text{O}_3$  support on the reactions. The presence of a catalyst greatly increased the conversions and promoted oxygen removal as evidenced by the low yields of 4-propylpyrocatechol. Demethylation to 4-propylpyrocatechol was the initial reaction in all cases, however, only in the presence of a catalyst was any significant amount of that intermediate deoxygenated. In this study the effect of presulfiding the catalyst was not found to be significant, probably because the amount of sulfur was low ( $\text{S/S}_{\text{max}} = 0.36$ ). In other studies it had been found that increasing the sulfur content increases hydrogenation ability (Weisser and Landa 1973; Bredenberg et al. 1984). Apparently no attempt was made to identify or quantify any hydrocarbons in this research by Bredenberg and coworkers.

### III.4.3 Catalytic Hydrocracking

The following conditions were general for the research results summarized in this section:

- o Reactor: Continuous flow, fixed tubular stainless steel. Two sizes were used, 15 ml and 140 ml (Vuori and Bredenberg 1984).
- o Temperature: 250° - 400°C (523-673 K)
- o Pressure: 25 - 100 atm (363-1451 psi or 2.5 - 10 MPa)
- o Catalysts: Presulfided Ni/Mo on  $\text{SiO}_2\text{-Al}_2\text{O}_3$  and presulfided Co/Mo on  $\gamma\text{-Al}_2\text{O}_3$ ,
- o Space Velocity: LHSV (Liquid Hourly Space Velocity) in ml feed/ml catalyst hour, ranged from 0.25 - 2.5  $\text{h}^{-1}$ .

Within the limits of these experiments it was found that hydrogen pressure had a small effect on conversion and product distribution. At higher pressures, the promotion of hydrogenation occurred. Space velocity effects were seen in the reaction of neat 4-propylguaiacol on Co/Mo -  $\gamma\text{-Al}_2\text{O}_3$  where increasing the LHSV decreased conversion and increased the phenolic product selectivity (Vuori and Bredenberg 1984). An LHSV of  $2\text{h}^{-1}$  was equal to a residence time of 1/2 h. Most experiments were not carried out under kinetic control.

Temperature has dramatic effects on conversion and selectivity as illustrated in Tables 3-23 and 3-24. In general, the reactions proceeded first by breaking the oxygen to methyl carbon bond either homolytically on metal sites

Table 3-23. Temperature Effect on Reaction of 44.9% Anisole in Benzene and Neat Guaiacol on Ni/Mo-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. (Bredenberg et al. 1982)

| Temp °C  | Anisole <sup>a</sup> |      |      |      | Guaiacol <sup>b</sup> |      |      |      |
|--|----------------------|------|------|------|-----------------------|------|------|------|
|  | 275                  | 300  | 325  | 350  | 250                   | 275  | 300  | 325  |
| Conversion, %  | 45.1                 | 85.0 | 88.3 | 99.6 | 5.1                   | 14.5 | 48.4 | 86.1 |
| Selectivities <sup>c</sup><br>for Phenolics, %:            |                      |      |      |      |                       |      |      |      |
| Phenol   | 65.5                 | 64.9 | 53.1 | 40.9 | 10.5                  | 30.9 | 45.7 | 53.5 |
| Cresols  | 22.6                 | 25.0 | 21.0 | 17.3 | ≤1.0                  | 6.4  | 24.3 | 18.3 |
| 2,6-Dimethylphenol   | 5.6                  | 4.5  | 4.5  | 0.2  |                       |      |      |      |
| Pyrocatechol   |                      |      |      |      | 68.5                  | 61.4 | 26.7 | 8.7  |
| Selectivity <sup>c</sup><br>for Total Neutral<br>Compounds | 6.6                  | 5.3  | 20.2 | 38.8 |                       |      |      |      |

a) Anisole LHSV = 1.5 (44.9% in Benzene)

b) Guaiacol LHSV = 2.0 (neat guaiacol)

c) Selectivity defined as:  $\frac{\text{total moles of desired product}}{\text{total moles converted}} \times 100$

Table 3-24 Temperature effect on the reaction of neat 4-propyl guaiacol on Co/Mo - Al<sub>2</sub>O<sub>3</sub>

| Temp °C                     | 200  | 225  | 250  | 275 <sup>a</sup> | 300 <sup>b</sup> | 325 <sup>b</sup> |
|-----------------------------|------|------|------|------------------|------------------|------------------|
| Conversion, %               | 20.6 | 39.3 | 85.0 | 90.9             | 99.3             | 99.3             |
| Selectivity of Phenolics, % | 88.8 | 82.8 | 72.5 | 77.0             | 60.3             | 30.3             |
| Selectivity of Neutrals, %  | 12.3 | 16.9 | 27.5 | 22.9             | 39.6             | 69.8             |

LHSV 0.24 except for:

- a) 0.26
- b) 0.23

Pressure 50 atm

or heterolytically on support sites. The resulting intermediates can react with hydrogen to form, for instance, phenol from anisole, and pyrocatechol (1,2-dihydroxybenzene) from guaiacol. The methyl radicals may react with hydrogen to form methane or may attack the aromatic ring (along with methyl cations from heterolytic cleavage) to form methyl substituted phenols, predominantly in the ortho position. At temperatures above 300°C the dihydroxyaromatics underwent dehydroxylation to give significant amounts of phenol and/or alkylated phenols. The last oxygen may be removed subsequently either by direct dehydroxylation or by hydrogenation to cyclohexanols followed by dehydration to cyclohexenes (Vuori and Bredenberg 1984). Higher temperatures favored this last deoxygenation step while phenolics were the predominant products at temperatures below 300°C. Direct demethoxylation was not considered a major reaction path at temperatures below 400°C. The lower reactivity of guaiacol compared to anisole is believed to be due to the strong bonding of guaiacol's free phenolic hydroxy group to  $\text{Al}_2\text{O}_3$ . Higher temperatures decreased this chemisorption and allowed reactions similar to those of anisole to occur (Bredenberg 1982).

The effect of using benzene as a diluent was insignificant. Using tetralin as a solvent lowered the conversion of 4-propylguaiacol slightly and decreased the amount of methylated products. Reactions run with tetralin and nitrogen deactivated the catalyst but improved the selectivity for phenolic products (Vuori and Bredenberg 1984). The level of sulfidation can effect the reaction routes with increasing hydrodeoxygenation and ring hydrogenation at higher sulfur contents (Bredenberg et al. 1984). Unsulfided catalysts may be more active for HDO than presulfided catalyst. The work of Vogelzang et al. (1983) has shown that oxidic  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  is 7 times more active than sulfidic  $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$  for the conversion of 1-naphthol. This could be advantageous to hydroprocessing of the emerging lignins that contain no sulfur.

There are some problems in interpreting research results reported by Bredenberg and coworkers. Frequently gas phase analyses were not performed and neutral hydrocarbons were not always reported. Meaningful comparisons from article to article were made difficult because of varying reactor designs. Comparative experiments on the different reactors would have allowed more meaningful comparisons.

#### III.4.4 Catalytic Hydrocracking Studies by Other Researchers

Other researchers have investigated lignin model compound hydrotreating reactions; examples are listed in Tables 3-25 and 3-26. The Russian workers Bronovitskii et al. used aqueous alkaline solutions incorporating phenol and ethanolamines as inhibitors to recondensation. Three fractions were usually isolated: aromatic acids, phenolics and neutrals. The aromatic acids could be decarboxylated by distillation at reduced pressures to give phenolic compounds (as described in Section III.2.1.1).

The research of Hurff and Klein 1983, using anisole and guaiacol as model compounds, shows large differences in reaction rates and product selectivities when compared to Bredenberg's work. The differences appear to be due primarily to the type of reactor employed batch (Klein et al.) vs. continuous (Bredenberg et al.). Table 3-27 compares the reaction parameters for the HDO of anisole and guaiacol employed by these workers.

Hurff and Klein propose two reaction routes to cyclohexane. Under their conditions there was always more cyclohexane than benzene. In the continuous flow reactor, benzene formation was always equal to or greater than that of cyclohexane. Another difference lies in the relative reactivities of anisole and guaiacol. The batch reactor studies showed that, in the temperature range studied, guaiacol reacted approximately 30 times faster than anisole. Conversely in the continuous reactor anisole was more rapidly converted than guaiacol. Klein's studies also revealed the possibility that ortho oxygen substituted aromatics were involved in the formation of coke.

The mechanistic studies of substituted phenols hydrotreated over a Co-Mo/Y-Al<sub>2</sub>O<sub>3</sub> catalyst illustrate the effects of steric hindrance on hydrogenolysis reactivity, and the effects of coordinating poisons (e.g. H<sub>2</sub>S, NH<sub>3</sub>, and H<sub>2</sub>O) on the competing hydrogenolysis and hydrogenation reactions. Table 3-28 summarizes the stereochemical effects of the substrate on hydrogenolysis. Most noteworthy are the high yields from the 3,4- and 3,5-dimethylphenols and the strong inhibiting effect of longer alkyl side chains e.g. o-ethylphenol. These results again point to the importance of lignin depolymerization prior to HDO.

The overall effects of a poison on the course of the reactions are that



**Table 3-25. Summary of Russian Hydrogenolysis of Lignin Model Compounds**  
(Hydrogen Pressure 100 atm and 360°-380°C)

| <u>Authors &amp; Date</u>                       | <u>Models</u> | <u>Catalyst</u>         | <u>Solvent</u>   | <u>Major Products</u>                      |
|---|---------------|-------------------------|--|--|
| Ikramova,<br>Bronovitskii,<br>Kalinskya 1970    | 1,2,3         | CoS                     | Aqueous 5%<br>NaOH/<br>Ethanol<br>Amine or<br>Phenol as<br>Inhibitor | Hydroquinone<br>pyrocatechol, phenols      |
| Bronovitskii,<br>Ikramova,<br>Kalinskaya 1968   | 1,2,4,5       | CoS<br>FeS              | Aqueous<br>Alkali  | Phenols, phenolic acids<br>saturated acids |
| Bronovitskii,<br>Kalinskaya 1967                | 1,2,4,5       | MoS <sub>3</sub><br>CoS | Aqueous<br>Alkali<br>Phenol as<br>Inhibitor                          | Phenols, cresols<br>C-C bond cleavage      |
| Bronovitskii,<br>Kalinskaya,<br>Kuznetsova 1966 | 1,2,6         | MoS <sub>3</sub>        | Aqueous<br>Alkali  | Phenols (high yields)                      |

Compound Codes:

- 1 =  $\alpha$ -Keto-4-Propylphenol
- 2 =  $\alpha$ -Keto-4-Propylguaiacol
- 3 = Dehydrodiguaiacol
- 4 = 4-Hydroxy-2-Methylacetophenone
- 5 = Dehydrodivanillin
- 6 =  $\alpha$ -Hydroxy-4-Propylguaiacol

le 3-26. Summary of Lignin Model Compound Hydrogenolysis

| <u>Authors &amp; Date</u>   | <u>Models</u>               | <u>Catalyst</u>                              | <u>Solvent</u>     | <u>Pressure<br/>amt</u> | <u>Temperature<br/>(°C)</u> | <u>Major Products</u>                         |
|-----------------------------|-----------------------------|--|--------------------|-------------------------|-----------------------------|---|
| Lin, Hurff 1983             | A<br>G                      | Sulfided<br>Co/Mo on<br>$\gamma$ - $Al_2O_3$ | $C_{16}H_{34}$     | 34                      | 250-325                     | Phenol, cyclohexane,<br>benzene               |
| Zny, Mihalov,<br>Bacik 1983 | $\beta$ -0-4<br>Models      | Mild<br>Thermolysis                          | Neat               |                         | 275-315                     | Ether cleavages,<br>condensations             |
| Bus, Dence<br>5             | Mono &<br>Dimeric<br>Models | Homo-<br>geneous<br>Ni<br>Hydride<br>Complex | NS                 | $\geq 102$              | $\geq 220$                  | Cyclohexanes<br>Aromatics                     |
| Man, Schweers<br>5          | PrG<br>PrV                  |  |                    |                         |                             |   |
| Veers, 1969                 | 4AP, 4AG                    | Pt   | Gl. Acetic<br>Acid |                         |                             |   |
| ay 1963                     | AV, E,<br>DCA               | Cu<br>Chromite                               | Dioxane            | 136                     | 230                         | Ethylcyclohexane,<br>4-propylcyclohexane      |
| er, Hibbert<br>3            | DDE<br>VPE<br>DVB           | Raney Ni<br>Cu<br>Chromite                   | Ethanol/<br>$H_2O$ | 206                     | 150-280                     | Hydrogenation Products                        |
| er, Cooke,<br>Bert 1943     | 4AG                         | Cu<br>Chromite                               | Dioxane            | 206                     | 280                         | 3-Cyclohexylpropanol,<br>4-propylcyclohexanol |
| ce, McCarthy,<br>Bert 1941  | EPrV                        | Cu<br>Chromite                               |                    | 250                     | 250                         | 4-Propylcyclohexanol                          |
| amoto 1939                  | C                           | Ni   |                    |                         |                             | Methylcyclohexanols                           |

el Compound  
es:

|      |                                  |     |  |
|------|----------------------------------|-----|--|
| A    | = Anisole                        | PrG | = Propylguaiacol   |
| C    | = Cresols                        | PrV | = Propylveratrole  |
| E    | = Eugenol                        | 4AP | = 4-Alkylphenols   |
| G    | = Guaiacol                       | 4AG | = 4-Alkylguaiacols                                       |
| AV   | = Acetovanillone                 | VPE | = 1-Veratroyl-1-(2 methoxy-<br>4-propionylphenoxy)ethane |
| DCA  | = Dihydroconiferyl alcohol       |     |  |
| DDE  | = 2,2'-Divanilloyl diethyl ether |     |  |
| DVB  | = 2,3-Diveratroylbutane          |     |  |
| EPrV | = methoxypropiovanillone         |     |  |

Table 3-27. Comparison of Reaction Conditions

|           | Hurff & Klein (1983)   | Bredenberg et al. (1982)  |
|-----------|--|---|
| Reactor:  | Autoclave Engineers<br>1 liter stainless steel<br>stirred batch reactor    | Fixed bed tubular stainless<br>steel continuous flow<br>11 x 160 mm |
| Feed:     | Anisole and guaiacol<br>as 5 wt % soln. in C <sub>16</sub> H <sub>34</sub> | Anisole and guaiacol neat<br>or as 44.5 mole % soln. in<br>benzene  |
| Catalyst: | Sulfided Co/Mo on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>                 | Sulfided Ni/Mo on $\gamma$ -Al <sub>2</sub> O <sub>3</sub>          |
| Temp:     | 250-325°C  | 250-325°C   |
| Pressure: | 34 atm H <sub>2</sub>  | 48 atm H <sub>2</sub>   |

Table 3-28. Effect of Substrate Stereochemistry on Hydrogenolysis of Phenols in the Presence of a Co-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst at 300°C. (Weigold 1982)

| Phenol                | Aromatic Product       | Yield wt % |
|-----------------------|------------------------|------------|
| Phenol                | Benzene                | 8          |
| o-Cresol              | Toluene                | 19         |
| m-Cresol              | Toluene                | 48         |
| p-Cresol              | Toluene                | 23         |
| 3,4 Dimethylphenol    | o-Xylene               | 45         |
| 3,5 Dimethylphenol    | m-Xylene               | 31         |
| 2,3 Dimethylphenol    | o-Xylene               | 13         |
| 2,4 Dimethylphenol    | m-Xylene               | 7          |
| 2,5 Dimethylphenol    | p-Xylene               | 10         |
| 2,3,5 Trimethylphenol | 1,2,4 Trimethylbenzene | 17         |
| o-Ethylphenol         | Ethylbenzene           | <1         |

increasing concentrations of poison inhibit HDO while having little effect on hydrogenation. The explanation Weigold (1982) gave is that the hydrogenation and hydrogenolysis reactions occur competitively at identical sites. If a coordinatively unsaturated metal site is available, hydrogenolysis is facilitated (see Fig. 3-11). If, on the other hand, this metal site is blocked by a poison, then hydrogenation predominates because hydrogen ion transfer does not require the presence of the unsaturated metal site.

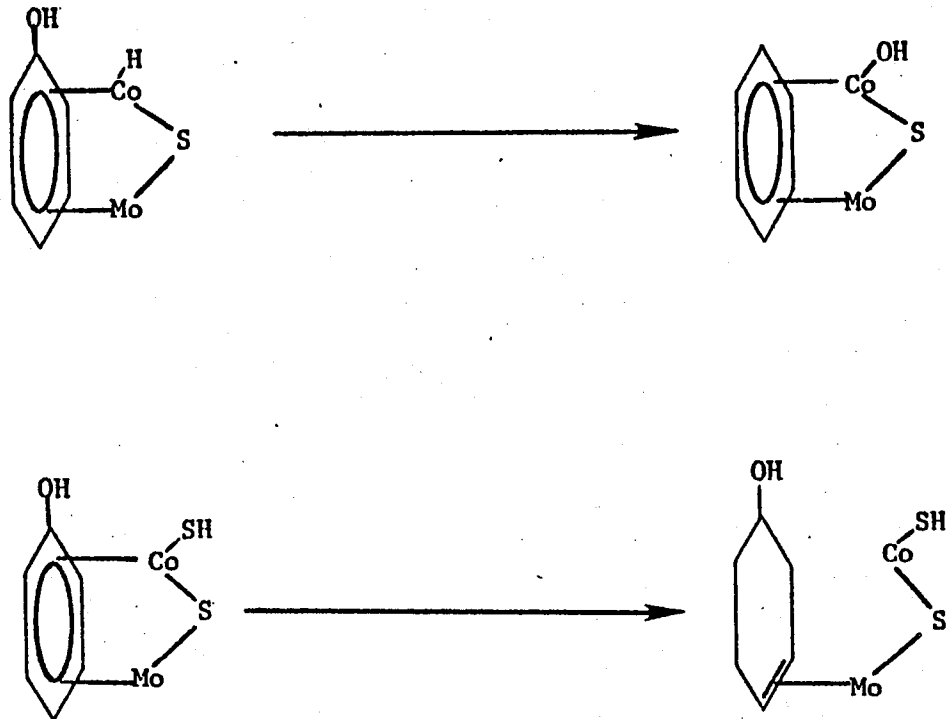


Fig. 3-11. Hydrodeoxygenation and hydrogenation reactions on sulfided Co-Mo/ $\gamma$ - $\text{Al}_2\text{O}_3$ . Adapted from Weigold (1982).

### III.5 Summary and Recommendations for Future R&D.

Lignin hydrotreating has been reviewed in Sections III.2 and III.3 and the hydroprocessing of relevant lignin model compounds was summarized in Section III.4. The more recent work has been described in more detail such as the work performed in the laboratories of Bredenberg, Coughlin, Goldstein, Klein, Sarkanen, and Schweers (discussed in Sections III.4, III.2.2.4, III.2.2.3 and 4, III.4, III.2.2.4, and III.2.2.2, respectively) and the more recent process-oriented research (section III.3). While the process-oriented research envisioned the production of phenolics or phenol and benzene, the other work reported here had either a structural goal--lignin structure determination, or was oriented towards syntheses of phenolics or neutrals (cyclohexanol and derivatives). Tables 3-29 to 3-33 summarize most of the work reported here, with emphasis on phenolic compounds. The important parameters affecting these reactions are discussed as follows:

#### A) REACTOR DESIGN

From the work at the Noguchi Institute it was very clear that in order for the results of batch experiments to be translated into a process, it was necessary to have extremely good agitation of the lignin/catalyst/hydrogen slurry, which was accomplished by lengthening the impeller shaft to a small (1/4 in) clearance of the reactor bottom. The strategy taken by Hydrocarbon Research, Inc. was to utilize the ebullated bed, previously employed in coal research, and adapt it to kraft lignin or lignosulfonates. This concept allowed the upward pumping of the slurry/gas mixture through the tubular reactor to expand the catalyst bed to occupy a volume at least 10% greater than in its settled state, while maintaining the catalyst in constant turbulent motion. This design allowed good temperature control in the reactor, good contact between lignin, hydrogen, and catalyst, and ease of replacement of spent catalyst in a continuous or semi-continuous manner. Another feature of the reactor was the continuous separation of the volatile products from the reaction; the products were swept with the excess hydrogen, leaving the catalyst in the reactor. Many continuous concepts were operated with lignins from moderate (Parkhurst et al. 1980) to high pressures (Giesen 1959). Section III.3 details these processes and Table 3-33 presents a summary.

In contrast with the more developmental work, the bulk of experimental research was performed in the static mode using batch reactors. While in some cases, types of autoclave were given as well as an idea of agitation effects (e.g. Davoudzadeh et al. 1985), in most cases, such effects were not discussed at all. Rarely did researchers who operated continuous and static processes report results on the same lignin materials (or compounds) and under similar solvents in both types of reactors.

From both the lignin model compound and lignin hydroprocessing investigations, the type of reactor appears to determine the reaction product mix. Further work on static batch and continuous experiments are necessary, but primarily those in which the experimental set-up allows the removal of volatile products as they are formed. If static reactors could be used, much faster screening of catalysts could be obtained. However, the results may not be meaningful because of the increased likelihood of condensation to prevailing (see Section IV.3). The reactor vessel material has been known to alter the reaction product mixture. For instance, Pepper and coworkers (1978) find a different product mixture from a chrome steel versus a stainless steel reactor. Catalytic effects are known to be important at high temperatures in char forming processes (Albright and Tsai 1983).

It is recommended that experimental sections fully describe the reactors utilized as well as the agitation used. Varying agitation until no product changes are observed is a reasonable approach.

#### B) SOLVENT/VEHICLE

It has long been known that the presence of phenols or cresols decreases condensation reactions and leads to higher yields of monomeric phenols (see, for instance, Section III.2.1 for aqueous alkali medium data and more recently, Davoudzadeh et al. 1985). Extensive work at the Noguchi Institute and at Crown-Zellerback Corp. (see Section II.3.2) demonstrated that the phenol solvent was methylated to p- and m- cresol. The ratio of p-:m- isomers was high when phenol itself was used and decreased to 1:1, when the exhaustively hydrogenated lignin residue (often referred to as pasting oil) was employed as a solvent. Therefore, to synthesize preferentially p-cresol may be difficult unless phenol is continuously added to the system. To synthesize a mixture of phenolics, a pasting oil is probably the most



practical solvent. However, in most laboratory experiments, such solvents were replaced by relatively inert solvents such as anthracene oil and 1-methyl naphthalene (commonly employed in coal liquefaction experiments). These types of experiments are quite distinct from those of a) no solvent at all (good agreement between various laboratories that these experiments lead to char formation), b) aqueous alkali medium in the presence of phenols (conditions employed primarily by the Russian workers). These experiments have only been reported successfully by Eastern Europe researchers. c) Organic/aqueous alkali media such as dioxane/1.5-3 wt % aqueous NaOH have been employed by a number of investigators, and the most recent results (Schultz et al. 1982) produced disappointingly low yields of phenolics (the effectiveness of the agitation employed may be questionable). d) Tetralin as a hydrogen-donor solvent was investigated by Connors et al. (1980), Schultz et al. (1982), and Davoudzadeh et al. (1985). In the presence of this solvent, much more moderate pressures are employed (55 atm vs. 100-200 atm in the absence of tetralin). While the first two groups report no effects of added heterogeneous catalysts on Indulin A.T. and superconcentrated HCl sweetgum lignin, respectively; the latter workers (Davoudzadeh et al.) find a pronounced effect (increase by a factor of two) of soluble products for steam exploded aspen lignin. Unfortunately, Davoudzadeh et al. (1985) did not quantitate phenolic compounds. Therefore, it is difficult to interpret the observed effects of the catalysts.

From these facts (and the material in the remainder of this section) the following questions still remain:

- 1) Can the hydrogenolyses of acid hydrolyses lignins under the conditions employed by the Eastern European researchers be repeated? Can the high yields of monomeric phenols be reproduced?
- 2) Dioxane/aqueous alkali does not appear to be a suitable solvent system from the most recent literature, though the older literature did achieve reasonable yields of phenolic compounds.
- 3) What is the role of heterogeneous or homogeneous catalysts in tetralin for the lower molecular weight lignins? Are the yields of phenolic compounds high as suggested by the high liquefaction yields? Is tetralin consumed by a number of irreversible side reactions?

### C) CATALYSTS

With some exceptions, the bulk of the work described in this Section neglects to characterize the heterogeneous catalysts employed. Simple characteristics such as supplier of the catalysts or particle size employed are often missing. This was obviously not the case with the development of the Noguchi catalyst. On going from this type of work to that of HRI, the catalysts are again not fully described. The catalyst selection for kraft and lignosulfonates, which contain some form of sulfur species, followed coal and petroleum processing. Thus, the catalysts Fe, Ni, Co, Ni/Mo, Co/Mo, Mo on  $\gamma$ -alumina or, at times, on the more acidic alumina-silica supports were employed, and most often, the catalysts were fully sulfided.

With the emerging lignins, an opportunity exists of utilizing catalysts that are developed for lignins (not for coal or petroleum), and with the process requirements in mind. Thus, issues such as the degree of sulfidation needed, how acidic the support should be, and what is the best metal ion, can be dealt with systematically. From the past literature, the mild hydrodeoxygenation catalyst, sulfided Mo on  $\gamma$ -alumina, appears the best for avoiding excess buildup of neutrals. From HRI data, this catalyst yielded a larger proportion of ethylphenols than propylphenols, the main products on sulfided Fe on  $\gamma$ -alumina. Systematic comparison of sulfided vs. non-sulfided forms and systematic variations of the support acidity are lacking.

Moving from the supported catalyst area to the work carried out on unsupported materials such as CoS, FeS, CuS, preferred by the Russian workers, again, there is little data on the catalysts.

Can special catalysts be developed that are more selective and operate at lower pressure and temperature in hydrogen-donor solvents or in lignin pasting oil? What is the role of the catalyst in tetralin? In order to expedite catalyst screening and to allow better understanding of the various parameters affecting these complex reactions, pertinent lignin model compounds should be investigated. The model compound should contain the most important lignin functionalities.

### D) TYPE OF LIGNIN/PRODUCT YIELDS

In much of the work described in this section, the aim was the determination of the lignin structure, aided by reductive degradation techniques. The more

developmental work employed pulping lignins and achieved continuous operation with monomeric phenolic yields up to 37.5 wt % of the starting lignin. This fraction could be converted by dealkylation into 24.4% phenol, 13.1% benzene, 22.5% light hydrocarbons, and 22.0% heavy liquid (based on original lignin) (Gendler et al. 1983). Economic evaluations performed to date are summarized in Section III.3.3.2. Evaluations of the first step alone, in the context of wood-to-ethanol plants, have not been made. In fact, yields of these processes with other lignins are not known. Literature indicates that the low molecular weight steam exploded aspen lignin can be liquefied much more easily than softwood kraft lignins (Davoudzadeh et al. 1985). Though the total yields of liquefaction are higher, the yields of monomeric phenols are unknown to date.

Lower yields of monomeric phenols were achieved by Schultz and coworkers (1985) on sweetgum lignin from superconcentrated HCl treatment both in tetralin (with or without catalysts) or in dioxane aqueous alkaline solutions. Similarly low yields of phenols were obtained from Indulin AT in tetralin (absence of heterogeneous catalyst). These yields, primarily those from sweetgum acid hydrolysis lignins, are lower than those expected based on other work in the area or on the results from Eastern European workers (see Tables 3-29 to 3-32).

Product yields are intimately related to the quantitative determination of reaction products. At this point, the literature contains good methods, but also a fair amount of misidentification, and in many cases quantitation is only performed on a fraction of about 50% of the materials. With the present progress with chromatographic techniques, these separations and quantitations should become progressively easier.

In order to perform meaningful economic evaluations of these processes, it is important to have mass balances of these processes. Yields of water, gases, neutrals, phenolics, solid residues, and oils should be obtained.

We would like to recommend that investigators involved in this area of research adopt a lignin (e.g., a milled wood lignin) and possibly one model compound such that, by reporting results on those substrates, a kind of independent calibration of the reactor, conditions, and analytical procedures

employed by each laboratory could be achieved, and cross-comparison between experiments of different investigators using different reactors and catalysts could be performed.

Table 3-29. Summary of Lignin Hydrotreating from Eastern Europe

| Reference                        | Lignin                                      | T<br>°C | p <sup>d</sup><br>atm | Time<br>h | Catalyst                       | Solvent               | Soluble<br>Tars, % | Phenols<br>%        | Neutrals<br>%     |
|----------------------------------|---|---------|-----------------------|-----------|--------------------------------|-----------------------|--------------------|---------------------|-------------------|
| Bronovitskii, Kalinskaya<br>1967 | Cotton hull, H <sub>2</sub> SO <sub>4</sub> | 360-380 | 100                   | 2         | CoS                            | Phenol, 5% NaOH (aq)  | 58.6               | 27 <sup>a</sup>     | 40.3 <sup>a</sup> |
|                                  | Spruce H <sub>2</sub> SO <sub>4</sub>       | 360-380 | 100                   | 2         | CoS                            | Phenol, 5% NaOH (aq)  | 73.5               | 34.5 <sup>a</sup>   | 26.0 <sup>a</sup> |
| Bronovitskii, et al. 1967        | Cotton hull, H <sub>2</sub> SO <sub>4</sub> | 360-380 | 100                   | 2         | CoS                            | Phenol, 5% NaOH (aq)  | 75                 | 50 <sup>b</sup>     | 35 <sup>b</sup>   |
| Bronovitskii, et al. 1968        | Cotton hull, H <sub>2</sub> SO <sub>4</sub> | 360-380 | 100                   | 2         | CoS                            | Phenol, 5% NaOH (aq)  | 60-85              | ≤70 <sup>c</sup>    |                   |
|                                  | Spruce, HCl                                 |         |                       |           |                                |                       | 60-85              | ≤70 <sup>c</sup>    |                   |
| Bronovitskii, et al. 1971a       | Spruce, HCl                                 | 360-380 | 100                   | 2         | CoS                            | Phenol; 15% NaOH (aq) | 85.7               | 47 <sup>b</sup>     | 26 <sup>b</sup>   |
| Bronovitskii, Kalinskaya 1972    | Spruce, HCl                                 | 360-380 | 100                   | 2         | CoS                            | Phenol; 5% NaOH (aq)  | ≤80                | 45 <sup>b</sup>     | 45 <sup>b</sup>   |
| John, Dobrev 1973                | Corncob, hydrolysis                         | 330     | 240                   | 2         | Fe <sub>2</sub> O <sub>3</sub> | Anthracene Oil        |                    | 46.2 <sup>a</sup>   |                   |
| Rieche, et al. 1964, 1966        | Acid hydrolysis,<br>Alkali Lignin           | 350     | 240                   | 2         | FeS, CuS                       | Phenol                | 52-75              | -40 <sup>b</sup>    | -8 <sup>b</sup>   |
| Moldavskii, Vainshtein 1935      | Acid Hydrolysis                             | 400-450 | 50-70                 | --        | MoS <sub>2</sub>               | Phenol                | 44                 | -30-50 <sup>b</sup> |                   |
| Borchers, et al. 1975            | Kraft or sulfite                            | 350-550 | 200-400               | 0.25-1.5  | Cu-Doped Fe                    |                       |                    |                     |                   |
| Bronovitskii, et al. 1973a       | Spruce, HCl                                 | 360-380 | 100                   | 2         | CoS                            | Ethanolamine          |                    | 70                  | 59                |
|                                  | Cotton hull, H <sub>2</sub> SO <sub>4</sub> | 360-380 | 100                   | 2         | CoS                            | Ethanolamine          |                    | 70                  | 59                |
| Karpunin 1981                    | Spruce (wood)                               | 170     |                       | 4.5       | Ni(CO) <sub>4</sub>            | 25% aq NaOH           | e                  |                     |                   |
| Vasyunina, et al. 1960           | Pine  | 300-320 | 200                   | 2.5-3     | 0.5% Ru-on-C                   | 2% aq NaOH            |                    | 30-40 <sup>a</sup>  |                   |

a) based on starting lignin; b) % of soluble tar; c) includes phenolics from neutral and acid fraction; d) initial pressure; and e) aromatics.

Table 3-30. Summary of Lignin Hydrotreating from North America

| Reference                   | Lignin   | T<br>°C | P <sup>c</sup><br>atm | Time<br>h | Catalyst  | Solvent                                | Soluble<br>Tars, %        | Phenols<br>%       | Neutrals<br>%      |
|-----------------------------|--|---------|-----------------------|-----------|---|--|---------------------------|--------------------|--------------------|
| Coscia, et al. 1961         | MWL Birch  | 240-260 | 100                   | 48        | Cu Chromite                                     | Dioxane                                |                           | 21.2 <sup>a</sup>  |                    |
|                             | MWL Oak  | 240-260 | 100                   | 48        | Cu Chromite                                     | Dioxane                                |                           | 16.7 <sup>a</sup>  |                    |
| Olcay 1962                  | MWL Spruce   | 240     | 134                   | 48        | Cu Chromite                                     | Dioxane                                | 60-70<br>Distill-<br>able | 19.6 <sup>a</sup>  |                    |
| Pepper, et al. 1969         | Spruce (wood)  | 195     | 35                    | 5         | Rh/C  | Dioxane:water                          | 95(CHCl <sub>3</sub> )    | 33.8 <sup>b</sup>  |                    |
|                             | Spruce (wood)  | 195     | 35                    | 5         | Raney Ni  | Dioxane:water                          | 68(CHCl <sub>3</sub> )    | 16.4 <sup>b</sup>  |                    |
| Pepper, et al. 1966         | Spruce (wood)  | 195     | 35                    | 10        | Pd/C  | Dioxane:water                          | 78(CHCl <sub>3</sub> )    | 17.2 <sup>b</sup>  |                    |
|                             | Spruce (wood)  | 195     | 35                    | 5         | Pd/C  | Dioxane:H <sub>2</sub> O, HCl          | 128(CHCl <sub>3</sub> )   | 10.5 <sup>b</sup>  |                    |
|                             | Aspen (wood), HCl  |         |                       |           |   |  |                           | 26 <sup>d</sup>    |                    |
| Adkins, et al. 1941         | Soda (hardwood)  | 250-300 | 200-350               | 4.5-12    | Cu Cr oxide                                     | Dioxane                                |                           |                    | 75 <sup>a</sup>    |
| Sherrard, et al. 1941, 1942 | Methanol/HCl, soda<br>pulpig liquors   | <300    | 140                   | 2-6       | Ni, Pd, Pt, Mo, W<br>and deriva-<br>tives       | Water (suspension)<br>5% NaOH (aq)     | e                         | e                  | e                  |
| Harris, et al. 1940         | Methanol, HCl, Soda<br>liquor, H <sub>2</sub> SO <sub>4</sub><br>process, Cellosolve | 225-250 | 100-175               | 6-10      | Raney<br>Ni                                     | Aq. NaOH (1%)                          | e                         |                    |                    |
| Adkins 1944                 | Lignin   | 200-350 | 50-500                | --        | Cu oxide, Cu<br>Chromite                        | --                                     | e                         |                    |                    |
| Harris, et al. 1949         | Hardwood Soda  | 300-27  |                       |           | Cu Chromite<br>w/Ni, Sn<br>sulfide/<br>iodoform |  | 75                        | 8-10 <sup>b</sup>  | 50-60 <sup>b</sup> |
|                             |  | 400     |                       |           |   |  | 75                        | 10-12 <sup>b</sup> | 60-65 <sup>b</sup> |
| Benigni, Goldstein 1971     | Kraft (softwood)   |         |                       |           |   | Water, organic<br>solvents, aq. alkali | 36-58                     | 4-13               | 3-22               |

## Summary of Lignin Hydrotreating from North America - continuation

| Reference                                   | Lignin  | T<br>°C        | p <sup>c</sup><br>atm | Time<br>h | Catalyst   | Solvent                            | Soluble<br>Tars, % | Phenols<br>%   | Neutrals<br>%                            |
|---|---|----------------|-----------------------|-----------|--|------------------------------------|--------------------|--|--|
| Schultz, 1981, Schultz et al.<br>1981, 1982 | Sweetgum<br>HCl   | 375-425<br>250 |                       | 1.5       | Fe <sub>2</sub> O <sub>3</sub><br>CoMoO <sub>4</sub> | Tetralin<br>Aqueous Alkali/dioxane |                    | 35 <sup>f</sup> (11) <sup>a,g</sup><br>16 <sup>f</sup> |  |
| Snajberk, Zavarin 1970                      | White Fir (sapwood)   |                |                       |           | Metallic Ni  | Methanol                           |                    | -30 <sup>d</sup>                                       |  |
| Parker 1967                                 | Maple (wood)  |                |                       |           | Raney Ni   | 5% aq NaOH                         |                    | 70 <sup>d</sup>  |  |
| Nahum 1965                                  | Red Spruce (wood)   | 170            |                       |           | Co <sub>2</sub> (CO) <sub>8</sub>                    | Benzene                            | h                  |  |  |
| Godard, et al. 1940                         | Maple (wood)<br>Spruce (wood)   | 250-60         | 350-400               | 12-16     | Cu Chromite  |                                    |                    |  | 60-70 <sup>d</sup><br>35-40 <sup>d</sup> |
| Bhaskaran, Schuera 1969                     | Sugar Maple (wood)  |                |                       |           |  |                                    | 35-40 <sup>d</sup> |  |  |
| Pepper, Steck 1963                          | Aspen (sapwood)   | 150-220        | 35                    | 24        | Raney Ni   | Dioxane:water                      |                    | 52 <sup>d</sup>  |  |
| Sudo, et al. 1981                           | Aspen (wood)  | 195            | 35                    | 5         | Rh-on-charcoal                                       | Dioxane:water                      |                    | 68.3 <sup>d</sup>                                      |  |
| Brewer, et al. 1948                         | Maple (wood)<br>Hydroly Lignin<br>(From previously<br>hydrogenated maple) | 165-70<br>250  | 200<br>200            | 4<br>5    | Raney Ni<br>Cu Chromite                              | EtOH/water<br>Dioxane              |                    | 70-80 <sup>d</sup>                                     | 44 <sup>d</sup>                          |
| Bowen, Nash 1926                            | Lignin  | 350-500        |                       | 1-4       | NiO on Al <sub>2</sub> O <sub>3</sub>                |                                    | -60                | >9 <sup>a</sup>  |  |
| Harris, et al. 1938                         | Methanol Aspen, HCl   | 250-60         | 200-350               | 18        | Cu Chromite  | Dioxane                            | 101                |  | 44 <sup>a</sup>                          |
| Sherrard, Harris 1939                       | Lignin  | >250           | 140                   |           | Cu Chromite  | --                                 | e                  |  |  |
| Cook, et al. 1941 a,b                       | Maple ethanol, HCl  | 250            | 400                   | 18        | Cu Chromite  | Dioxane                            | 71 <sup>a</sup>    |  | 16.7 <sup>a</sup>                        |

Summary of Lignin Hydrotreating from North America - continuation

| Reference             | Lignin   | T<br>°C | P <sup>c</sup><br>atm | Time<br>h | Catalyst           | Solvent                         | Soluble<br>Tars, % | Phenols<br>%                          | Neutrals<br>%     |
|-----------------------|--|---------|-----------------------|-----------|--------------------|---------------------------------|--------------------|---------------------------------------|-------------------|
| Connors, et al. 1980  | Indulin AT   | 400     | 55                    | 0.25      | None               | Tetralin                        |                    | 37.4 <sup>f</sup> (7) <sup>a, g</sup> |                   |
| Harris, Adkins 1938   | MeOH, HCl<br>Alkali H <sub>2</sub> SO <sub>4</sub> | 250-60  | 170-400               |           | Cu Chromite        | Dioxane                         | 64 <sup>a, e</sup> |                                       |                   |
| Sherrard, Harris 1940 | Lignin   | 100-350 | 35-350                |           | Cu Chromite        | Dioxane, glycol<br>ethers, MeOH | e                  |                                       |                   |
| Harris 1940           | Lignin   | 250     | 200-350               |           | Cu Chromite,<br>Ni | Dioxane                         | e                  |                                       |                   |
| Pepper, et al. 1951   | Aspen (wood)                                       | 165-175 | 200                   | 2-3       | Raney Ni           | Dioxane:water                   |                    | 16.9 <sup>d</sup>                     | 51.8 <sup>d</sup> |

a) based on starting lignin; b) % of soluble tar; c) initial pressure; d) percent of klason lignin present in wood; e) Percentage of products are not given. Product mentioned include propylcyclohexane and its derivatives including substituted cyclic alcohols and resinous compounds; f) Products obtained as distilled fractions. Phenols obtained from an oily distillate fraction; g) Number in parentheses refers to % of monomeric phenols; h) Phenols and substituted guaiacols were isolated.



Table 3.31. Summary of Lignin Hydrotreating from Western Europe

| Reference                  | Lignin   | T °C | P <sup>d</sup> atm | Time h | Catalyst  | Solvent                          | Soluble Tars, % | Phenols %                   | Neutrals %                   |
|----------------------------|--|------|--------------------|--------|---|----------------------------------|-----------------|-----------------------------|------------------------------|
| Freudenberg, et al. (1941) | Spruce   | 340  | 80-140             |        | Raney Ni,<br>Rupe Catalyst                              | ≤5% NaOH(aq)                     | 55              | 15 <sup>a</sup>             | 40 <sup>a</sup>              |
|                            | Spruce waste<br>Liquor (S-contg.)                                | 340  |                    |        | Raney Ni,   | ≤5% NaOH(aq)                     | -50             | -15 <sup>a</sup>            | -40 <sup>a</sup>             |
| Lautsch (1941)             | Lignosulfonates  | 250  | --                 | --     |   | Dilute alkali                    |                 | -60 <sup>a</sup>            |                              |
| Freudenberg, et al. 1943   | HCl Lignin<br>Sulfite waste<br>Liquor                            | 350  | 290 (max)          |        | Raney Ni  | NaOH/aq alcohol                  |                 | --                          | 77 <sup>a</sup>              |
|                            |  | 350  | 290 (max)          |        | Raney Ni  | Pulping liquor<br>Contg. 1% E+OH |                 | 7 <sup>a</sup>              | 48 <sup>a</sup>              |
| Freudenberg, Lautsch 1945  | Lignosufonic acid,<br>sulfite waste liquor,<br>alk. black liquor | ≤260 | 30-120             | --     | Ni or Pd  | --                               |                 | 50-60 <sup>a</sup>          |                              |
| Loubinoux, et al. 1980     | Maple, cherry,<br>eucalyptus, fir<br>beech                       | 180  | 128                | 3      | Ni(OAc) <sub>2</sub><br>reduced to<br>Ni <sub>2</sub> B | Aq. alkali                       |                 | 42(beech) <sup>a</sup>      |                              |
| Heitz, et al. 1982         | Wood wastes,<br>solvolysis lignins                               | 195  | 60                 |        | Ni  | EtOH/alkali                      |                 | 30 <sup>a</sup>             |                              |
| Kleinert 1952              | Sulfite spruce,<br>organosolv                                    | 300  |                    |        |   | Cyclohexanol                     |                 | Multi-<br>valent<br>Phenols | Aromatic<br>and<br>aldehydes |
| Halmeroski, Enkvist 1956   | Sulfate  |      |                    |        | Raney Ni  | Ethanol                          |                 | High<br>yield               |                              |

Summary of Lignin Hydrotreating from Western Europe

| Reference                | Lignin             | T °C | p <sup>d</sup> atm | Time h | Catalyst                             | Solvent           | Soluble Tars, % | Phenols %          | Neutrals %        |
|--------------------------|--------------------|------|--------------------|--------|--------------------------------------|-------------------|-----------------|--------------------|-------------------|
| Schweers 1966            | Corn               |      |                    |        | Cuchromite                           | Dioxane           |                 | 2.6                |                   |
|                          | Beech              |      |                    |        |                                      |                   |                 | 2.7                |                   |
|                          | Beech (wood)       |      |                    |        |                                      |                   |                 | 10                 |                   |
| Schweers 1969            | Spruce, HCl        | 350  | 100                | 24     | Fe,Co,Ni (metallocene complexes)     | Benzene           | 36 <sup>a</sup> | 32 <sup>a</sup>    | 32 <sup>a</sup>   |
|                          | Beech, HCl         | 350  | 100                | 24     |                                      |                   |                 | 40 <sup>a</sup>    |                   |
|                          | Bamboo, HCl        | 350  | 100                | 24     |                                      |                   |                 | 24 <sup>a</sup>    | 24 <sup>a</sup>   |
|                          | Corn, HCl          | 350  | 100                | 24     |                                      |                   |                 | 16 <sup>a</sup>    | 36 <sup>a</sup>   |
| Hoffman, Schweers 1975   | Spruce, HCl        | 350  | 180                | 22     | Nickelocene                          | Benzene           |                 | 15 <sup>a</sup>    |                   |
|                          | Beech, HCl         | 350  | 180                | 22     | Nickelocene                          | Benzene           |                 | 11 <sup>a</sup>    |                   |
|                          | Bamboo, HCl        | 350  | 180                | 22     | Nickelocene                          | Benzene           |                 | 12 <sup>a</sup>    |                   |
|                          | Spruce, HCl        | 350  | 200                | 22     | Nickelocene                          | Cyclohexane       |                 | 17 <sup>a</sup>    | 6.7 <sup>a</sup>  |
|                          | Beech, HCl         | 350  | 200                | 22     | Nickelocene                          | Cyclohexane       |                 | 22 <sup>a</sup>    | 11.0              |
| Hoffmann, Schweers 1975a | Spruce, HCl        | 350  | 165                |        | Nickelocene                          | Benzene           |                 | 6.1 <sup>a</sup>   | 7.7 <sup>a</sup>  |
|                          | Spruce, HCl        | 350  | 165                |        |                                      | Pt oxide/Rh oxide | Benzene         |                    | 3.6 <sup>a</sup>  |
|                          | Spruce, HCl        | 350  | 165                |        | 10% Pd-C                             | Benzene           |                 | 0.5 <sup>a</sup>   | 11.2 <sup>a</sup> |
|                          | Spruce, HCl        | 350  | 165                |        | Nickelocene                          | Methanol          |                 | 7.8 <sup>a</sup>   | 2.5 <sup>a</sup>  |
|                          | Spruce, HCl        | 350  | 165                |        | Pt oxide/Rh oxide                    | Methanol          |                 | 5.28 <sup>a</sup>  | 3.0 <sup>a</sup>  |
|                          | Spruce, HCl        | 350  | 165                |        | 10% Pd-C                             | Methanol          |                 | 8.34 <sup>a</sup>  | 7.25 <sup>a</sup> |
|                          | Spruce, HCl        | 350  | 165                |        | 5% Rh-Al <sub>2</sub> O <sub>3</sub> | Methanol          |                 | 11.53 <sup>a</sup> | 4.87 <sup>a</sup> |
|                          |                    |      |                    |        |                                      |                   |                 |                    |                   |
| Meier, Schweers 1981     | Beech, EtOH/water  | 300  | 100                | 5      | 10% Pd-C                             | Ethanol/water     | 60.6            | 29.0 <sup>a</sup>  | 31.5 <sup>a</sup> |
|                          | Oak, EtOH/water    | 300  | 100                | 5      | 10% Pd-C                             | Ethanol/water     | 63.5            | 33.6 <sup>a</sup>  | 29.9 <sup>a</sup> |
|                          | Birch, EtOH/water  | 300  | 100                | 5      | 10% Pd-C                             | Ethanol/water     | 66.4            | 37.1 <sup>a</sup>  | 29.3 <sup>a</sup> |
|                          | Spruce, EtOH/water | 300  | 100                | 5      | 10% Pd-C                             | Ethanol/water     | 73.9            | 38.2 <sup>a</sup>  | 35.7 <sup>a</sup> |
|                          | Pine, EtOH/water   | 300  | 100                | 5      | 10% Pd-C                             | Ethanol/water     | 67.3            | 32.4 <sup>a</sup>  | 34.9 <sup>a</sup> |

a) Based on starting lignin; b) % of soluble tar; and c) initial pressure.

Table 3-32. Summary of Lignin Hydrotreating from Asia

| Reference                   | Lignin   | T<br>°C        | P <sup>d</sup><br>atm | Time<br>hr | Catalyst                               | Solvent               | Soluble<br>Tars, %                         | Phenols<br>%      | Neutrals<br>%                                  |
|-----------------------------|--|----------------|-----------------------|------------|--|-----------------------|--|-------------------|--|
| Hachihama, Jodai 1941       | Picea jezoensis HCl                            | 260-270        | 100                   | 22-5       | Ni                                     | Dioxane               | 70(ether)                                  | 37 <sup>b</sup>   | 25 <sup>b</sup>                                |
|                             | Fagus sylvatica HCl                            | 250            | 150 (max)             | 4-6        | Ni                                     | Dioxane               | 47-50                                      | 27 <sup>b</sup>   | 6 <sup>b</sup>                                 |
| Hachihama, Jodai 1940       | Picea jezoensis HCl                            | 260-260        | 230 (max)             | 35-55      | NiO, CoS,<br>NH <sub>4</sub> molybdate | Dioxane               | 47(ether)                                  |                   |  |
| Sakakibara 1963             | Conc. H <sub>2</sub> SO <sub>4</sub>           | 400            | --                    | 1          | Ni(CO) <sub>4</sub>                    | Cyclohexane           |  | 45 <sup>a</sup>   |  |
| Sakakibara, Tadasu 1961     | Conc. H <sub>2</sub> SO <sub>4</sub><br>Alkali | 400            | 97                    | 1          | Cu Chromite                            | Cyclohexanol          |  | 47.3 <sup>a</sup> |  |
|                             |  | 400            | 97                    | 1          | Cu Chromite                            | Cyclohexanol          |  | 61.7 <sup>a</sup> |  |
| Sakakibara, et al. 1966     | Lignosulfonic acid                             | --             | --                    | --         | Fe(CO) <sub>5</sub>                    |                       |  | 15.9 <sup>a</sup> |  |
| Morohoshi, Sakakibara 1971a | P. jezoensis (MWL)<br>Hydrolysis Lignin        | 200            | 80                    | 1          | Cu Chromite                            | Dioxane:water         | 59   |                   |  |
|                             |  | 200            | 80                    | 1          |  |                       | 60   |                   |  |
| Morohoshi, Sakakibara 1971b | P. jezoensis (MWL)                             | 180            |                       | 0.5        | CuChromite                             | Dioxane:water         |  | 20 <sup>a</sup>   |  |
| Sakakibara, et al. 1969     | P. jezoensis (wood)                            | 160-200        | 78                    | 1          | CuChromite                             | Dioxane:water         |  | e                 |  |
| Wada, Sakakibara 1969       | P. jezoensis<br>(wood)                         | 160<br>180-220 | 78                    | 1-2        | CuCrO <sub>4</sub> ,<br>Raney Ni       | Dioxane:water<br>EtOH | 3.5-61 <sup>d</sup><br>60-140 <sup>d</sup> |                   |  |
| Hachihama, Jodai 1942       | Softwood                                       | >250           |                       |            | Raney Ni                               |                       | 80   | 50 <sup>b</sup>   |  |
| Sano, Sakakibara 1980       | Picea glehnii<br>milled wood (spruce)          | 240-320        |                       | 0.17-2     |  | EtOH/water            |  | 94.3 <sup>b</sup> | 3.6 <sup>b</sup>                               |
| Hachihama, Jodai 1950       | Ezomatsu<br>(softwood lignin)                  | 215            | 100                   | 4          |  | 15% alkali            | Hydrol Lignin                              |                   | C <sub>29</sub> H <sub>24</sub> O <sub>7</sub> |

a) based on starting Lignin; b) % of soluble tar; c) initial pressure; d) based on Klason lignin; e) Phenolic monomers, dimers and trimers isolated.

Table 3-33. Summary of Petrochemical/Coal Techniques Applied to Lignin Hydrotreating or Pyrolysis

| Reference                                 | Lignin                  | T<br>°C | p <sup>c</sup><br>atm | Lignin<br>Process-<br>ing Rate<br>(lb/h) | Catalyst   | Solvent                        | Reactor                                    | Soluble<br>Tars, %                        | Phenols<br>% | Neutrals<br>% |
|---|-------------------------|---------|-----------------------|--|--|--------------------------------|--|---|--------------|---------------|
| Giesen, (1959)                            | "Schöller"              | 380     | 700                   | 0.8                                      | FeSO <sub>4</sub>                                  | xyleneol,<br>CaSO <sub>4</sub> | Continuous<br>Tubular                      | 58% distillable product<br><325°C, 6mm Hg |              |               |
| Noguchi/Crown Zellerbach<br>(Goheen 1965) | desulfonated<br>sulfite | 450-425 | 170                   |  | Fe:Cu:Sn:S<br>(10:1:1:12)                          | Pasting<br>oil,<br>phenol      | Batch<br>Stirred<br>Autoclave              | 20  | 21           | 9             |
| HRI (Gendler et al. 1983)                 | Kraft                   | 440     | 70                    | 1.0                                      | MoO <sub>3</sub> /γ-Al <sub>2</sub> O <sub>3</sub> | Pasting<br>oil                 | Continuous<br>Ebullated<br>Catalyst<br>Bed | 22  | 37.2         | 10.8          |
| HRI Pyrolysis (Snell 1983)                | Lignin                  | 815     | 1-10                  |  | ---  | Steam                          | Continuous<br>Fluidized<br>Bed             | 11.7                                      | 49.6         | 1.7           |

SECTION IV.0  
EXPERIMENTAL HYDROTREATING OF LIGNIN AND MODEL COMPOUNDS

by

D. K. Johnson, M. Ratcliff, F. Posey, H. L. Chum  
Solar Energy Research Institute  
1617 Cole Boulevard  
Golden, Colorado 80401

and

R. Baldwin and S. Cowley  
Colorado School of Mines  
Golden, Colorado 80401

#### IV.1 INTRODUCTION

As has been previously stated, the goal of this project is to develop a process to convert lignins to a mixture of phenolics which on conversion to the corresponding methyl ethers could be blended with gasoline as octane enhancers which would not increase the fuel vapor pressure as much as ethanol or other oxygenates. Much work has already been carried out on kraft lignin, lignosulfonates, and some lignins from acid hydrolyses processes. We have concentrated on mild acid hydrolysis, steam exploded and organosolv lignins, which are relevant to biomass-to-ethanol processes.

Work on this task initiated March 15, 1985. The experimental work started late in April, 1985 at Colorado School of Mines and at SERI laboratories. The report presented in this Section is preliminary. It represents 6 months of actual experimental work, the bulk of which was used in setting up experiments and testing reactors and analytical procedures.

In the initial stages of our work it was decided that the difference between continuous and batch operation should be more carefully quantitated. The most successful process design to date is that of HRI, described earlier (Section III.3). The important features of their ebullated bed design were the very good mixing between catalyst, lignin and hydrogen, a narrow temperature distribution throughout the reactor; and that volatile reaction products were

easily separated from the reactants and rapidly removed from the reactor thus avoiding secondary reactions. A batch reactor is, however, simpler to operate and should allow a more rapid screening of catalysts/supports and operating conditions. The constraints on our reactor design were thus, a reactor that should have good mixing, be able to process small quantities of lignin, allow vapor products to be swept out and also be easily convertible to batch operation.

It was also felt necessary that a well characterized solvent be chosen rather than a less well defined material such as a recycled lignin oil. The solvent should also have a low vapor pressure to minimize the amount swept from the reactor with the products. 1-Methylnaphthalene, a solvent often used in coal hydrotreating studies was selected, because of its stability at high temperatures in hydrogen atmospheres. The main disadvantage of 1-methylnaphthalene is that it is a poor solvent for lignin. It only serves as a vehicle for the lignin so that there is a liquid phase in the reactor.

After it was established that more THF-insolubles were produced in the batch reactor than in the semi-continuous reactor, the next stage was to start screening catalyst/support materials. Before studying the effect of catalyst/support material on the hydrotreating of lignins themselves, it was decided to study the effect of catalyst/support on a small number of relevant model compounds. The use of model compounds has the advantage that the chemistry should be more easily understood. The first model compound studied was 4-propylguaiacol so that comparisons could be made with other model compound studies (see section III.4). Another consideration was that Bredenberg's work did not cover a sufficiently high temperature range. We felt based on HRI's work that it was important to go to at least 400°C.

In the evaluation of catalysts/supports one of the most important functions to examine is the ability of a catalyst to crack the propyl side chains found in lignins so that phenols and cresols are the major products. Selectivity for formation of monophenols instead of neutrals (benzenes, cyclohexanes, etc.) is another important function that a catalyst should fulfill. Using these criteria, a number of catalysts/supports will be screened using model compounds and then lignins, now that the experimental set-up and analytical procedures have been developed and checked.

## IV.2 EXPERIMENTAL

### IV.2.1 Lignin Hydrotreatment Set-Up

Figure 4.1 shows a schematic of the set-up used to study the hydrotreatment of lignin. Lignin hydrotreating was carried out in a small (10 ml) reactor constructed from high pressure stainless steel (0.5 inch O.D., wall thickness 0.035 inch) tubing and Swagelok<sup>TM</sup> fittings with the exception of a VCR fitting that was used because it allowed us to make and break the joint many times without needing to replace it. The reactor was loaded with two steel balls and connected to a mechanical shaker to improve mixing. The reactor was rapidly heated (~1 minute to 350°C) by raising a pre-heated fluidized sand bath up to cover the bottom half of the reactor. Hydrogen and krypton (5%) was supplied from a cylinder and the pressure was regulated by a back pressure regulator. For the flow experiments the regulator was set at about 1000 psi, readings during experiments varied from 69-74.5 atm (1000-1080 psig). In the flow experiments the flow of gas out of the reactor was controlled by a let-down valve. The gas flow rate out of the reactor was monitored using a rotameter and the gas composition was determined by analyzing the contents of a gas sample bottle. There was a problem in reading the rotameter because of fluctuations in the flow rate which was generally 35 ml min<sup>-1</sup>; readings of 20 to 50 ml min<sup>-1</sup> were not uncommon. The product vapors were condensed out in a cold finger trap (-10°C). The trap was made from a Fischer-Porter bottle and only stainless steel tubing with Swagelok<sup>TM</sup> fittings were used in connecting it to the let-down valve and to the rotameter to minimize leaks as much as possible. The stainless steel line and the let-down valve were heated (250°C) to maintain the products in the vapor phase. The trap was packed with glass wool to help knock-down any aerosols that might have been formed. A thermocouple was used to monitor the reactor temperature during the experiments.

In the batch experiments the equipment was modified such that the reactor was capped at the outlet before the let-down valve. The reactor was pressurized (to 69 atm or 1000 psig) at the start of the experiment prior to heating and

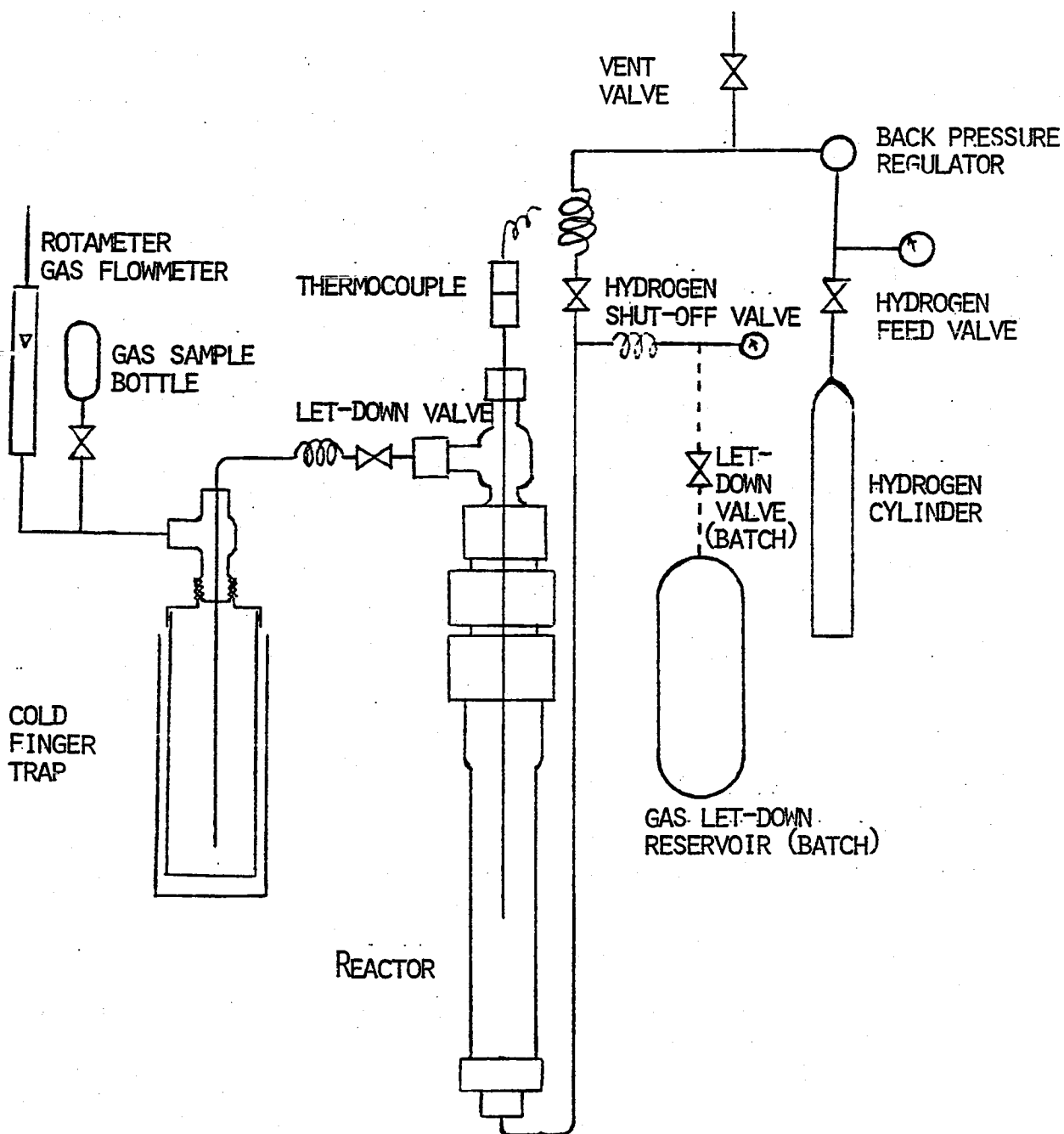


Fig. 4-1. Schematic of Lignin hydrotreatment system. The reactor was mounted on a support connected to a shaker so that with steel balls inside mixing was improved. For cold finger trap, a Fischer-Porter bottle packed with glass wool was used.



then the hydrogen shut-off valve was closed. On heating, the pressure was allowed to rise unchecked (to about 164 atm or 2400 psig). At the end of the batch experiments, the reactor was let-down into a large gas reservoir (2 l) from which gas samples were taken for analysis.

In all experiments, the reactor was loaded with a 1:2 ratio of lignin (-1.9 g) to solvent (-3.8 g). The lignin used was obtained from an organosolv (methanol:water = 70:30 v/v) pulping of aspen wood (4:1 liquid:wood) with phosphoric acid (0.05M) as catalyst at 165°C for 2.5 hours. The characterization of this sample is given by Chum et al. 1985c, d. 1-Methylnaphthalene (used as supplied by Aldrich Chemical Co.) was used as the solvent although its role was more likely that of a vehicle for the lignin. Most of the work was carried out using a Co/Mo catalyst supported on alumina (Harshaw Catalyst Co. Co/Mo-0601; 3% CoO, 15% MoO<sub>3</sub>, 230 m<sup>2</sup>g<sup>-1</sup>). Some early experiments were run using a Ni/Mo catalyst (Ketjen Catalyst Co. 153-1.5E) supported on alumina. Both catalysts were ground to a fine powder (>80 mesh) and then presulfided in batches (~50 g) with hydrogen sulfide gas (10% in hydrogen) at atmospheric pressure and 400°C for 4 hours. The treated catalysts were then stored in a dry box under an inert atmosphere of nitrogen or carbon dioxide. After the reactor was loaded with lignin and solvent, the catalyst (0.2-0.3 g) was added to the reactor in the dry box.

After the reactor had cooled at the end of an experiment, the weight loss from the reactor was measured and the reactor was washed of its entire contents using tetrahydrofuran (THF) as the solvent. The THF solution was filtered to recover the insoluble products and catalyst. Microanalyses for C, H and ash content were carried out on selected THF-insoluble residues at Huffman Laboratories, Wheat Ridge, Colorado. The filtrate was saved for quantitative analysis of the solvent and phenolic products by gas chromatography (GC) and high performance liquid chromatography (HPLC). The molecular weight distribution of the THF soluble residue was also determined by gel permeation chromatography (GPC). In the flow experiments the condensates were washed from the cold trap with THF after it had been weighed to determine the total weight of material collected. This sample was then quantitatively analyzed for the products, including water and solvent that had been flushed from the reactor. The washings from the reactor and cold trap were made up to known

volumes in volumetric flasks so that they could be analyzed quantitatively. The initial choice of solvent for washing out the cold trap was poor because THF obscured the region where all the neutral products would elute on the gas chromatogram. This is probably the reason that only about 50% of the weight of condensates could be accounted for.

#### IV.2.2 Model Compound Hydrotreatment Set-Up

A continuous differential plug-flow reactor was chosen for the lignin model compound studies. It was constructed of 1/2" 316 stainless steel tubing with a 0.035" wall thickness and Swagelok<sup>TM</sup> tube fittings. The catalyst bed was supported by a stainless steel fritted disk which itself was supported by the 1/16" K type thermocouple which entered the reactor through a fitting at the bottom. The reactor was suspended vertically in a Lindberg oven. The inlet and outlet lines were heat traced and controlled to temperatures in the 150°-200°C range. The pressure let-down valve was a Whitey SS-22RS-4 and was originally installed ahead of the condenser which was constructed from a 3 oz Fisher-Porter vessel. Problems with valve plugging lead to designing a high pressure condenser which was installed upstream of the let-down valve as shown in Fig. 4.2. The high pressure condenser was constructed from a stainless steel 150 ml Whitey gas sample cylinder, Swagelok<sup>TM</sup> fittings and copper tubing silver soldered to the outside of the cylinder.

4-Propylguaiaicol was used without further purification as supplied by Frinton Laboratories. Initially, the feed mixture was 75 volume % solution of 4-propylguaiaicol in reagent grade hexanes with 0.5 volume % dimethyl sulfide to maintain catalyst sulfidation. Research grade (99.99%) hydrogen was used as supplied.

The catalyst used was  $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$  (42-1500) supplied by Strem Chemicals. The  $\text{MoO}_3$  content was 10-12% and the surface area was  $64 \text{ m}^2/\text{g}$  in the form of 3/16" x 1/8" pellets. The pellets were ground with mortar and pestle, then sieved to 20-14 mesh before loading (1.5 g, 1.8 ml) into the reactor.

The catalyst was sulfided in the reactor by injecting 10 volume % of dimethyl sulfide in n-heptane at a liquid flow rate of 0.20 ml/min for the first two hours. The reactor temperature during this time was  $200 \pm 4^\circ\text{C}$  and the hydrogen flow rate was 14 ml/min at 100 psig. After two hours the reactor temperature

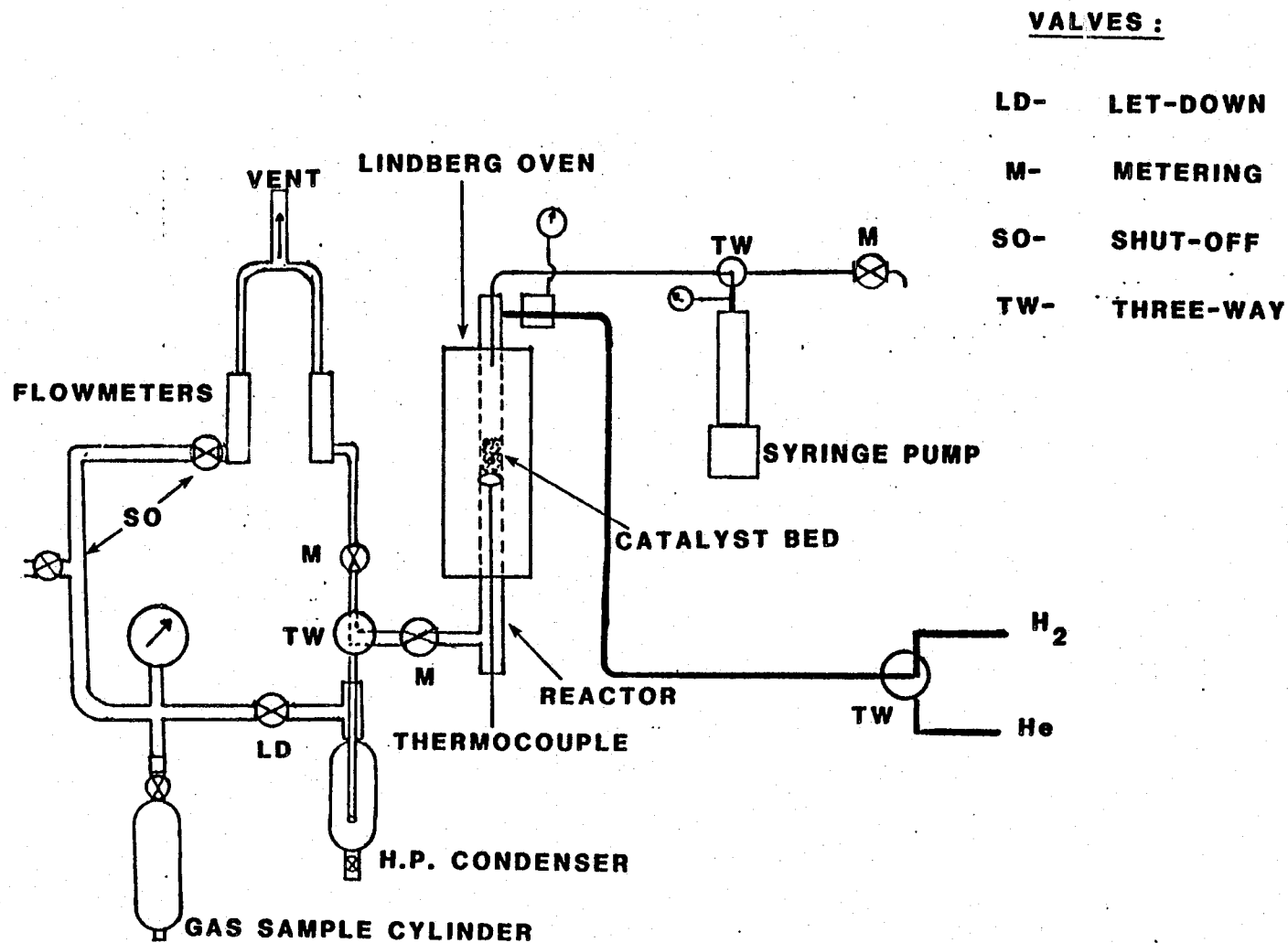


Fig. 4-2. SERI Tubular Fixed-Bed Reactor Employed For Model Compound Hydrodeoxygenation Studies.

was raised to  $405 \pm 3^\circ\text{C}$  and held there for an additional two hours. The dimethyl sulfide solution injection rate was decreased to 0.14 ml/min to maintain the desired 1:9  $\text{H}_2\text{S}:\text{H}_2$  ratio in the reactor throughout the sulfiding reaction.

The feed mixture was injected into the top of the tubular reactor by a LDC/Milton Roy SS 396-38 Minipump calibrated at 2.16 ml/h and 5.25 ml/h for the first set of experiments. The current system uses an Isco model LC-5000 high pressure syringe pump for pulse-free, precise metering.

Experiments were begun by preheating the reactor, inlet and outlet lines. When the reactor was at the desired temperature (measured at the bottom of the catalyst bed and adjusted to  $300^\circ$ ,  $350^\circ$ , or  $400^\circ\text{C}$ ) it was slowly pressurized to 70 atm (1000 psig) with hydrogen. The gas and liquid flow rates were calibrated (nominally 30 ml/min  $\text{H}_2$  although problems with plugging due to condenser/valve locations mentioned above gave erratic gas flow rates in some early experiments) and then the feed solution was injected into the reactor. One hour was allowed for the system to reach equilibrium before sampling began. Five liquid samples and one gas sample were collected over the next hour. If the temperature was readjusted after sampling, another hour was allowed for reequilibration before sampling again.

Air-free gas samples were obtained by evacuating the low pressure section between the let-down valve and the flowmeter (including the on stream gas sample cylinder) with a vacuum pump. The hydrogen and product gases were then metered into the cylinder with the let-down valve to about 10-15 psig (1.5-2 atm). Liquid samples were obtained from the high pressure condenser after isolation of the condenser using a three-way ball valve. This system allowed gas and liquid sampling without disturbing the reactor equilibrium.

#### IV.2.3 High Performance Liquid Chromatography (HPLC) and Gel Permeation Chromatography (GPC) Analyses Conditions

All HPLC and GPC analyses were carried out using a Hewlett-Packard HP1090 Liquid Chromatograph equipped with a UV-Visible diode-array detector (HP1040).

Analysis of the products in the condensate and THF-soluble residue was performed on an Alltech C18 reverse phase column (10  $\mu$  particle size, 25 cm x 4.6 mm) using a solvent program of acetonitrile/water (50/50 v/v held for 3

minutes) which was ramped to 100% acetonitrile after 10 minutes (held for 5 minutes), then ramped to 100% THF after 20 minutes. The flow rate was 1.0 ml min<sup>-1</sup> with an injection volume of 15 µl. These products were also analyzed on a Whatman Partisphere (C18 reverse phase column, 5 µ particle size, 12.5 cm x 4.6 mm) using a solvent program of acetonitrile/water (50/50 v/v) which was ramped to 60/40 after 5 minutes and then 100% acetonitrile after 10 minutes (held for 5 minutes) before finally ramping to 100% THF after 20 minutes. With this column a flow rate of 0.75 ml min<sup>-1</sup> was used and the injection volume was 5 µl.

The products from the hydrotreating of 4-propylguaiacol were analyzed in a similar manner but with a Polymer Laboratories PLRP-S reverse phase column (5 µ particle size, 100 Å pore size, 25 cm x 4.6 mm) using a solvent program of acetonitrile/water (50/50 v/v) ramped to 70/30 after 15 minutes and then 100% acetonitrile after 25 minutes. The flow rate used was 0.75 ml min<sup>-1</sup> with an injection volume of 5 µl.

All the gel permeation chromatography was carried out using a Polymer Laboratories PL-Gel 50A pore size (5µ particle size 30 cm x 7.5 mm). The column material is polystyrene-divinylbenzene copolymer. Analyses were carried out isocratically using THF as solvent at a flow rate of 1.0 ml min<sup>-1</sup> with injection volumes of 10 µl.

#### IV.2.4 Gas Chromatography (GC) and GC/Mass Spectrometry (GC/MS) Analysis Conditions

##### Water Determination

###### Samples:

Condensate samples were prepared by adding 0.50 ml of internal standard solution to 0.50 ml of neat sample (with Class A volumetric glassware). The internal standard solution contained absolute methanol as the internal standard in acetonitrile.

###### Calibration and Analysis:

The average response factor for the water was 0.96 (six determinations) with an average standard deviation of 3%. The calculated amounts of water in the sample were corrected for the amount of water in the internal standard.

###### Chromatographic Procedure:

The separation was performed on a glass column 6' x 0.2 mm ID packed with Porapak QS. The column, injector and thermal conductivity detector temperatures were 110°C, 240°C, and 260°C, respectively. At 3 minutes the column temperature was increased rapidly to elute solvent. High purity helium was used as a carrier at a flow of 20 ml/min.

#### Gas Analysis

Gas samples were analyzed on a Carle Model 111H gas chromatograph equipped with two thermal conductivity detectors, one for H<sub>2</sub> and the other for light hydrocarbons. After sample injection, hydrogen was separated by a Pd diffusion tube at 600°C and then a 5' x 1/8" Porapak Q(80/100) column using N<sub>2</sub> as the carrier gas. The remaining gases were separated on a series of three columns: 1) 6' x 1/8" Molecular Sieves, 2) 2.5' x 1/8" Squalane, and 3) 12' x 1/8" n-octane Poracil C using He as the carrier gas. The columns are accessed sequentially by automatic valves which are controlled by a Hewlett Packard 3388A Integrator. This system can handle more complex analyses than those reported here.

#### Hydrocarbon and Phenol Determination for 4-propylguaiacol and Lignin Hydrotreating Experiments

##### Identification:

The components of the products from the lignin hydrotreating and 4-propylguaiacol experiments were identified on the Hewlett Packard Model 5985 GC-MS. Each identification was checked by search and comparison of computer library spectra and by comparison of spectra generated from chromatograms of known standards. Some of the standard compounds identified have not yet been obtained. In preliminary runs, columns of different polarities were used to separate the complex mixture of hydrocarbons and phenols in the 4-propylguaiacol condensates and phenols and naphthalenes in the lignin hydrotreating solutions. The use of different columns was also necessary to optimize the method for identification of isomers and trace amounts of other components. The column used for quantitation of 4-propyl guaiacol condensates gave good separations in a minimum run time

but did not separate some phenol isomers and hydrocarbons (i.e. methylpropylphenols, methylpropylbenzenes, cresols, etc.) and hydrocarbons as well as separations obtained on a more polar column (e.g., SP1000, Carbowax 20 M).

Chromatographic Procedure (Lignin Hydrotreating Experiment):

A 30 m x 0.32 mm ID DB5 fused silica capillary column, 0.25 mm film, was held for 4 minutes at 40°C and then programmed at 5°/minute to 300°C. Helium carrier flow was 20 ml/min. The sample amount was 1.0 µl and the injection was splitless.

Chromatographic Procedure (4-Propylguaiaicol Experiments):

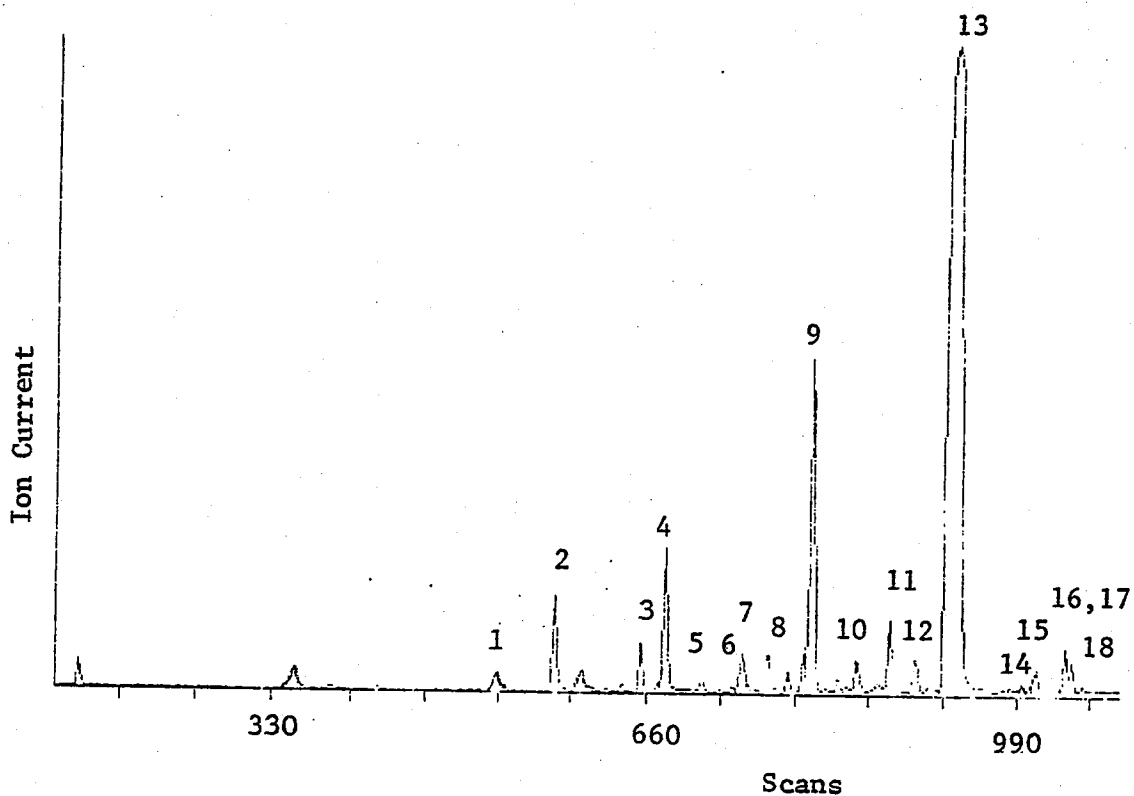
The chromatographic column used for this quantitation was a Supelco SPB5 wide bore capillary column, 30 m x 0.75 mm ID, 1 µm film. The column temperature was programmed starting from 40°C, held 2 minutes then increased by 3°/min to 280°C. The injector and flame ionization detector temperatures were 220°C and 280°C, respectively. The linear velocity was 26 cm/sec. Helium carrier was used at 12 ml/min.

Identification and Quantitation:

The components were verified again by retention time using standards made of single compounds. Then a standard composed of all possible compounds was used for calibration. The factors obtained for s-butylbenzene and s-butylphenol were used for the methylpropylbenzenes and the methylpropylphenols respectively since we have not yet prepared the methylpropyl compounds. The analysis was performed by the external standard method on the Varian 3700 gas chromatograph with automatic sampler. At least three runs (~45 min) of each sample were performed. The results given are ±15% for compounds with proper calibration standards and ± 25% for the methylpropyl derivatives.

Examples of the chromatographic procedures employed are given in Figs. 4-3 and 4-4.

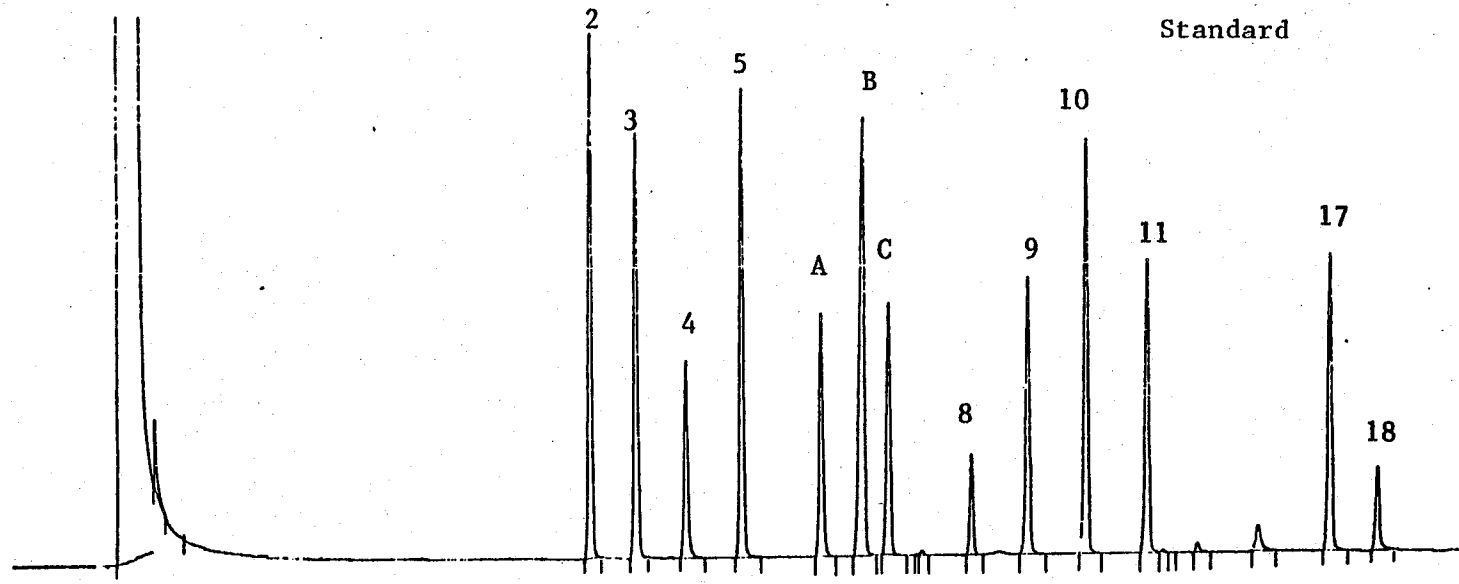
Figure 4-3. Condensate #16 from Lignin Hydrotreating Experiment



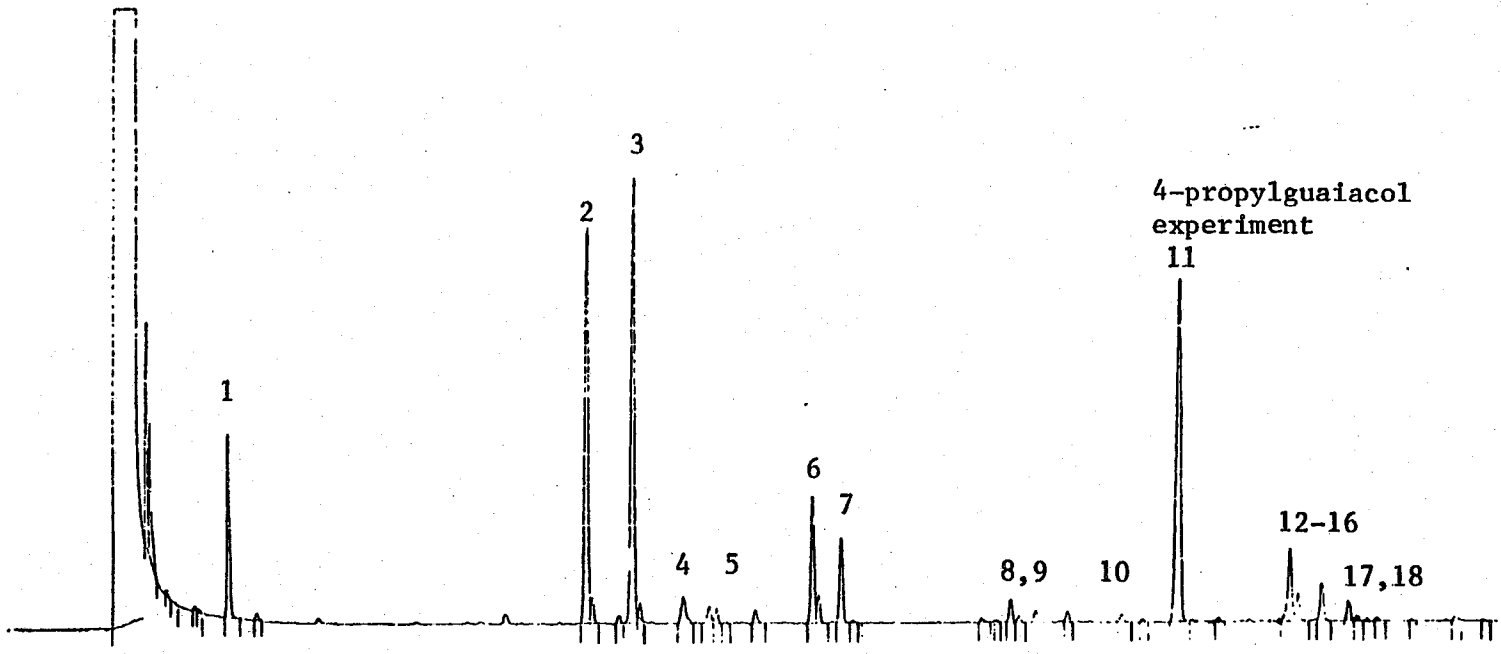
- |  |                              |
|--|------------------------------|
| 1. cyclopentane, propyl                | 11. naphthalene, 1,2,3,4     |
| 2. phenol                              | tetrahydro-6-methyl-         |
| 3. 2-methyl-phenol                     | 12. methyl-naphthalene       |
| 4. 4-methyl-phenol                     | 13. 1-methyl-naphthalene     |
| 5. 2-cyclopenten-1-one,3,4,5 trimethyl | 14. 1-ethyl-naphthalene      |
| 6. 2,4-dimethyl-phenol                 | 15. 1,2-dimethyl-naphthalene |
| 7. 2,3-dimethyl-phenol                 | 16. 1,4 dimethyl-naphthalene |
| 8. 3,4-dimethyl-phenol                 | 17. 1,8 dimethyl-naphthalene |
| 9. naphthalene                         | 18. 2-ethyl-naphthalene      |
| 10. 4-propyl-phenol                    |                              |



Standard



4-propylguaiacol  
experiment  
11



129

Figure 4-4. Chromatograms of Standard and of 4-propylguaiacol experiment.

1. Methyl hexane
2. Propyl cyclohexane
3. Propyl benzene
4. Phenol
5. Methylpropylbenzene (or s-butyl benzene in standard)
6. Methylpropylbenzene
7. Methylpropylbenzene
8. 2-Ethylphenol
9. 3-Ethylphenol
10. 2-Propylphenol
11. 4-Propylphenol
- 12-16. Methylpropylphenols (or s-butyl phenol in standard)
17. 4-Propylguaiacol
18. Propylcatechols (or i-propylcatechol in standard)
  - A. o-Cresol
  - B. m- and p-Cresol
  - C. Guaiacol

### IV.3 RESULTS AND DISCUSSION

#### IV.3.1 Lignin Hydrotreating Experiments

Although the reported results are preliminary, some inferences can be drawn from the results already obtained, particularly with regard to the amounts of THF-insoluble residue formed and whether the hydrotreatment should be carried out in a batch reactor or with continuous removal of products.

In all experiments a certain amount of THF-insoluble residue was obtained in the form of a black, free-flowing powder. In the batch experiments the yield of this residue increased with the severity of the hydrotreating conditions (Figure 4.5). In experiments at about 405°C more THF-insoluble residue was produced the longer the experiments were allowed to run. At 450°C about 40% of the lignin charged was converted to THF-insoluble residue in only 5 minutes. There was also less of this residue produced when the Co/Mo catalyst was used although the catalyst had much less effect at the higher temperature.

From Table 4-1 the effect of the reactor configuration on the yield of the THF-insoluble residue can be ascertained. When no catalyst was used, about 50% of the lignin charged was converted to THF-insoluble residue, using either configuration (60 minute experiments). However, when a catalyst was used, about half the amount of this residue was obtained when products were continuously swept from the reactor compared to the residue formed in batch experiments. With the reactor in the flow configuration, the Co/Mo catalyst produced less THF-insoluble residue than the Ni/Mo catalyst. With continuous removal of products from the reactor the possibility of recondensation of the phenols with the remaining lignin is minimized. With a catalyst present less THF-insoluble residue was produced because the reactive intermediate products from the hydrogenolysis of the lignin were quenched more quickly, also limiting their ability to recondense with the lignin.

The nature of these THF-insoluble residues has not yet been fully determined although from elemental analyses of selected examples (Table 4-1) they do appear char like. At 400°C, about 31% char is formed in biomass carbonization experiments; this char has 82.7% carbon, 3.8% hydrogen, and 13.5% oxygen (Soltes and Elder 1981). The elemental analyses of most of the THF-insoluble residues compare well with the char elemental analyses of Table 4-1. There is

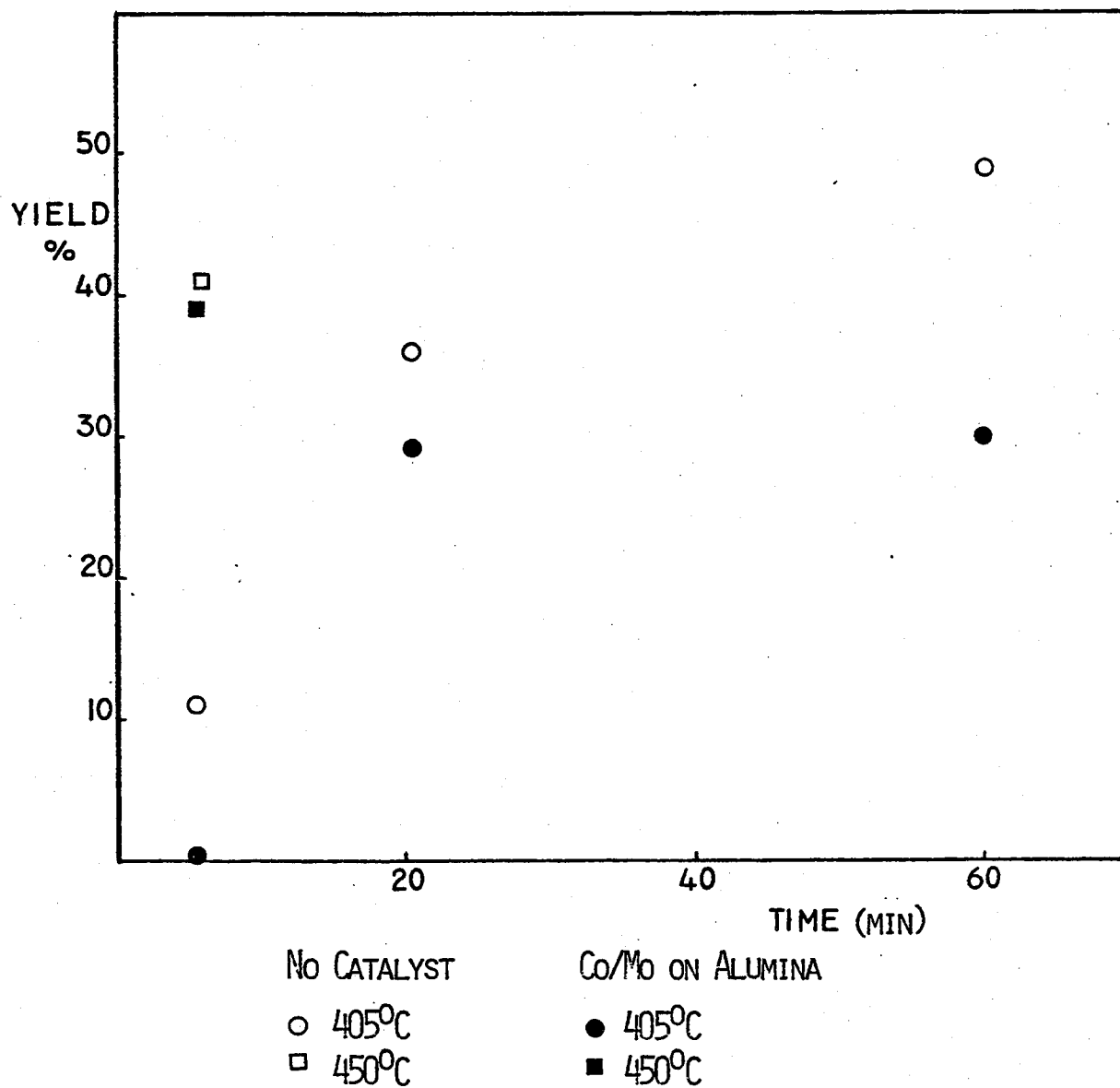


Fig. 4-5. Yield of THF-insoluble residue as a function of hydroprocessing time in batch reactor experiments with organosolv lignin.

Table 4-1. Comparison of THF-insoluble residue yields from lignin hydroprocessing experiments.

| T°C               | Duration (min) | Catalyst | THF insoluble residue<br>(wt% of lignin charged) | Combined<br>Phenols Yield<br>(wt% of lignin charged) | Elemental Analysis (%) |      |       |
|-------------------|----------------|----------|--|--|------------------------|------|-------|
|                   |                |          |  |  | C                      | H    | O     |
| Batch Experiments |                |          |  |  |                        |      |       |
| 404               | 5              | --       | 11   | <1   |                        |      |       |
| 399               | 5              | Co/Mo    | 0.5  | <1   |                        |      |       |
| 406               | 20             | --       | 36   | <1   | 79.92                  | 3.77 | 16.31 |
| 410               | 20             | Co/Mo    | 29   | <1   | 64.96                  | 3.64 | 31.40 |
| 407               | 60             | --       | 49   | 1.9  | 83.17                  | 4.01 | 12.82 |
| 404               | 60             | Co/Mo    | 30   | 2.2  | 83.76                  | 4.03 | 12.21 |
| 453               | 5              | --       | 41   | <1   |                        |      |       |
| 451               | 5              | Co/Mo    | 39   | <1   |                        |      |       |
| Flow Experiments  |                |          |  |  |                        |      |       |
| 418               | 60             | --       | 48   | 3.5  | 81.78                  | 3.85 | 14.37 |
| 406               | 60             | Co/Mo    | 10   | 8.2  |                        |      |       |
| 428               | 60             | Co/Mo    | 14   | 10.0   | 68.77                  | 3.83 | 27.40 |
| 415               | 60             | Co/Mo    | 19   | 7.6  |                        |      |       |

as yet no explanation of the two examples with much lower carbon contents.

Although the combined yield of phenols was low in all the experiments (Table 4-1), they demonstrate the differences in performing batch or flow experiments and with or without a catalyst. From the batch experiments, only those run for 60 minutes gave combined phenols yield greater than 1%. After 60 minutes, combined phenol yields of about 2% were obtained in the batch reactor. In the flow reactor up to 10% of the lignin charged was converted into monophenolic products with an added catalyst and only 3.5% without the catalyst. Considering the lowest THF-insoluble residue yield and highest combined phenols yield, the use of the Co/Mo catalyst in the reactor configured to allow the products to be flushed out gave the best results.

The reason for the low overall yields of phenols is not clear at this time. It is possible, despite the fact that the trap was packed with glass wool that some of the phenolic products escaped as aerosols which can be very difficult to knock down. Agitation may have been another factor. The main phenolic products were phenol (~30%) and cresols (~40%). The cresols could only be separated into two peaks, one for the o-isomer and the other for the p- and m-isomers combined. Xylenols, ethylphenols and propylphenols were also formed in small amounts.

Apart from some products formed from the solvent 1-methylnaphthalene, the only other product seen was toluene (~0.3% yield of lignin charged). There were undoubtedly other hydrocarbons (e.g. cyclohexanes) formed, unfortunately the solvent chosen to wash out the trap prevented their analysis by GC. There was a problem in accounting for the mass of the condensate collected (total 1-2 g) from the flow experiments which indicates the yield of these hydrocarbons may have been high. After quantifying for the phenols, naphthalenes and water only 45-70% of the weight of condensate was accounted for.

In both batch and flow experiments naphthalene (~6% yield of 1-methylnaphthalene charged) and dimethylnaphthalene (~8% yield of 1-methylnaphthalene charged) were formed by demethylation and methylation of the solvent, respectively. In the flow experiments, there was also a larger amount of 1-methylnaphthalene (~15%) than expected, flushed from the reactor. Although the solvent was not as inert or as high boiling as had been

expected, it did appear to give the reaction mixture the desired fluidity, and the recovery of combined naphthalenes was about 90%.

In the flow experiments, there was always a deficit between the weight lost by the reactor and the weight of condensate collected in the trap of 0.27 to 0.54 g. Most of this can be accounted for by the amount of gas produced. The exact amount of gas produced could not be determined accurately for each experiment due to the fluctuations in the gas flow rate out of the reactor. From the gas analyses and using the average gas flow rate ( $\sim 35 \text{ ml min}^{-1}$ ), about 0.35 g of the material charged to the reactor was converted to gases. The major components were carbon dioxide and methane with smaller amounts of butanes, propane, propene, ethane and carbon monoxide being formed. In the batch experiments a similar gas product slate was produced and, comparing experiments run under the same conditions (temperature, pressure, catalyst and run time), about twice as much gas was produced.

Very interesting results were obtained by comparing the gel permeation chromatograms of the THF-soluble fraction both from batch and continuous experiments. Figure 4-6 shows the GPC of three THF-soluble residues obtained in the batch reactor by hydrotreating the lignin at about  $405^\circ\text{C}$  in the presence of Co/Mo catalyst for varying lengths of time, and compares them with the untreated lignin. The sharp peak at about 5 minutes retention time is because part of the material is larger than the exclusion limit of the column ( $\sim 2000$  apparent molecular weight). The reason for choosing a column with such a small pore diameter ( $\sim 50 \text{ \AA}$ ) was to obtain maximum resolution in the low molecular weight region of the expected products. As can be seen, there is a large change in the molecular weight distribution of the lignin after only 5 minutes to a polymer of apparent average molecular weight of about 600 (about trimer size). A smaller decrease takes place over the next hour as can be seen from the GPC of the THF-soluble residues obtained after 20 and 60 minutes. This is in agreement with the work of Gendler et al. (1983) who notes that for the hydrogenolysis of kraft lignin there was a fast initial thermal reaction that depolymerized the lignin to trimers to pentamers before the catalytic reaction producing monophenols took place. Further agreement with this can be seen in Figure 4-7 which compares the GPC of the THF-soluble

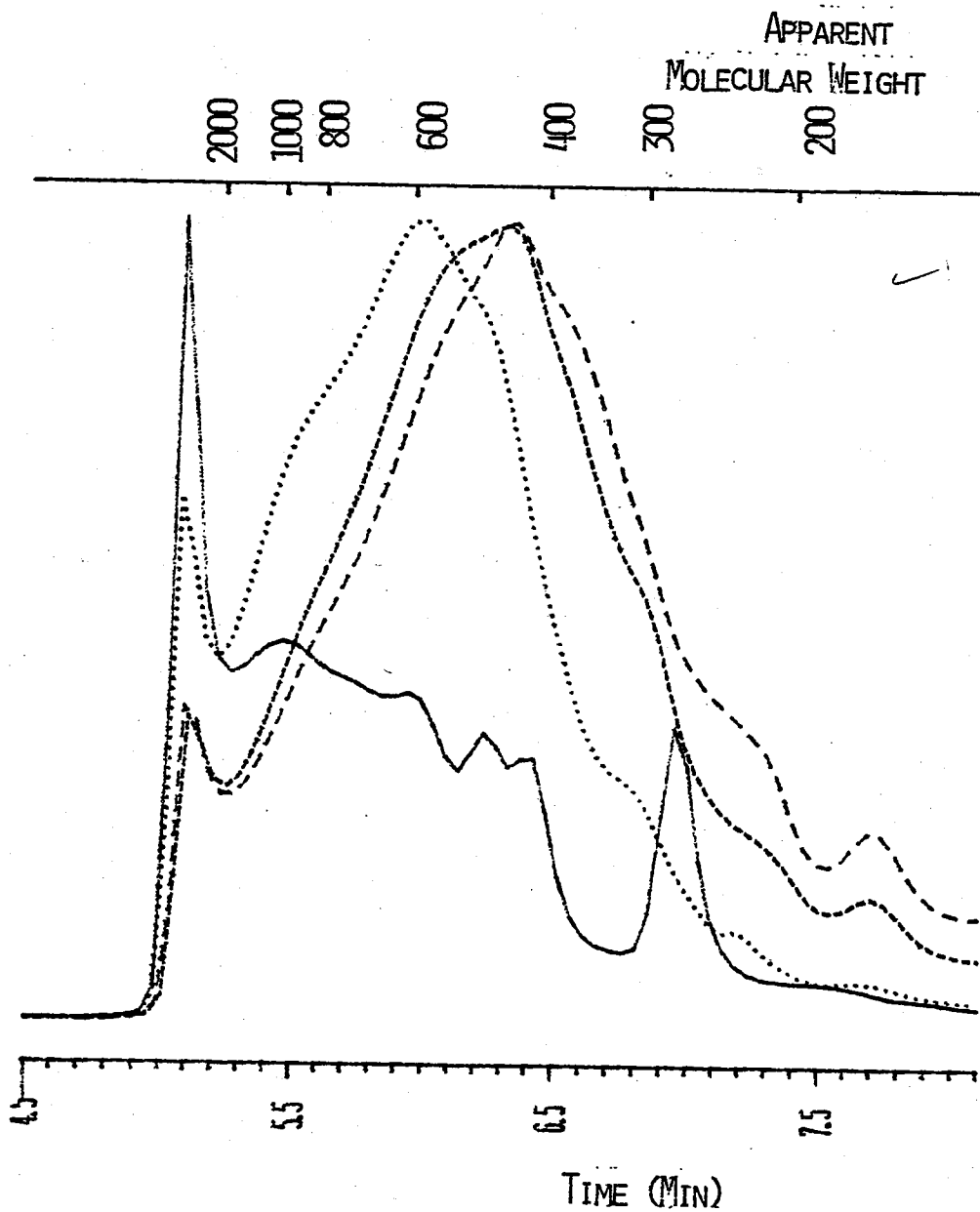


Figure 4-6. Effect of reaction time on THF-soluble residue. (Batch experiments at 405°C with Co/Mo catalyst added.)

- Untreated lignin
- ..... 5 minutes
- 20 minutes
- - - - - 60 minutes



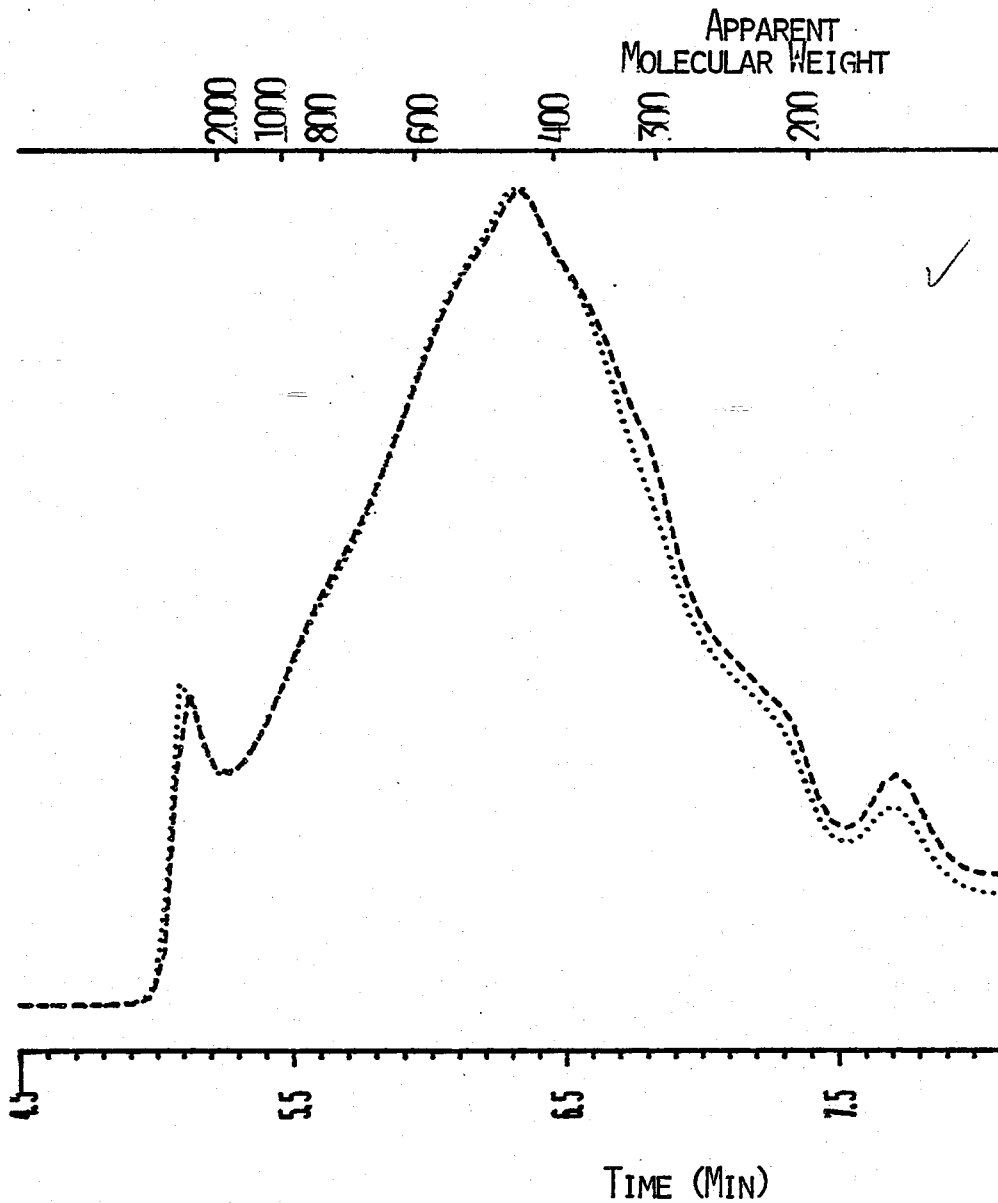


Figure 4-7. Comparison of THF-soluble residue obtained with (. . . . .) and without (-----) Co/Mo catalyst added. (Batch experiments at 405°C for 60 minutes)

residues obtained in the batch reactor after 60 minutes at 405°C with and without catalysts. The use of Co/Mo catalyst appears to have had very little or no effect on the lignin depolymerization. At higher temperatures lignin depolymerization took place to a much greater extent in 5 minutes producing a THF-soluble residue with apparent molecular weight of about 450 (about dimer size) (Figure 4-8). At the same time it should be remembered that a much greater yield of THF-insoluble residue was produced at the higher temperature. There was also about twice as much gas produced at the higher temperature, about 0.85 g at 450°C compared to about 0.4 g at 405°C. As would be expected at the higher temperature all the reactions, depolymerization, gasification and char formation, take place more rapidly. Similar molecular weight distributions were obtained for the THF-soluble residues and after 60 minutes at 405°C. The gas yields were also similar after 5 minutes at 450°C and 60 minutes at 405°C.

The molecular weight distributions of the THF-soluble residues obtained from the flow reactor are shown in Figure 4-9. Comparison between the residues obtained with and without catalyst are more difficult to make here because of the 10°C difference in reactor temperature. However, the residue produced with the catalyst contained the largest relative amount of low molecular weight (>300) components and the least amount of high molecular weight (<1000) components compared to all other experiments. The fraction of the THF-soluble residue that was insoluble in hexane was also examined for 2 samples. Lignins have virtually no solubility in hexane so the fraction insoluble in hexane might be considered as the more lignin-like fraction of the THF-soluble residue. The hexane-insoluble fraction was obtained by first evaporating the THF from the THF-soluble residue and then adding hexane to the resulting dark brown liquid. After filtration and drying a brown powder was obtained as the hexane-insoluble fraction. When this procedure was applied to the THF soluble residue obtained from a batch reactor experiment carried out at 405°C for 5 minutes without catalyst, a yield of hexane-insoluble a fraction equal to 58% of the weight of lignin charged, was obtained. A yield of only 20% of hexane-insoluble fraction was obtained from the THF-soluble residue of a flow reactor experiment carried out at 405°C for 60 minutes with Co/Mo catalyst. Obviously more lignin depolymerization took place in the flow reactor experiment.

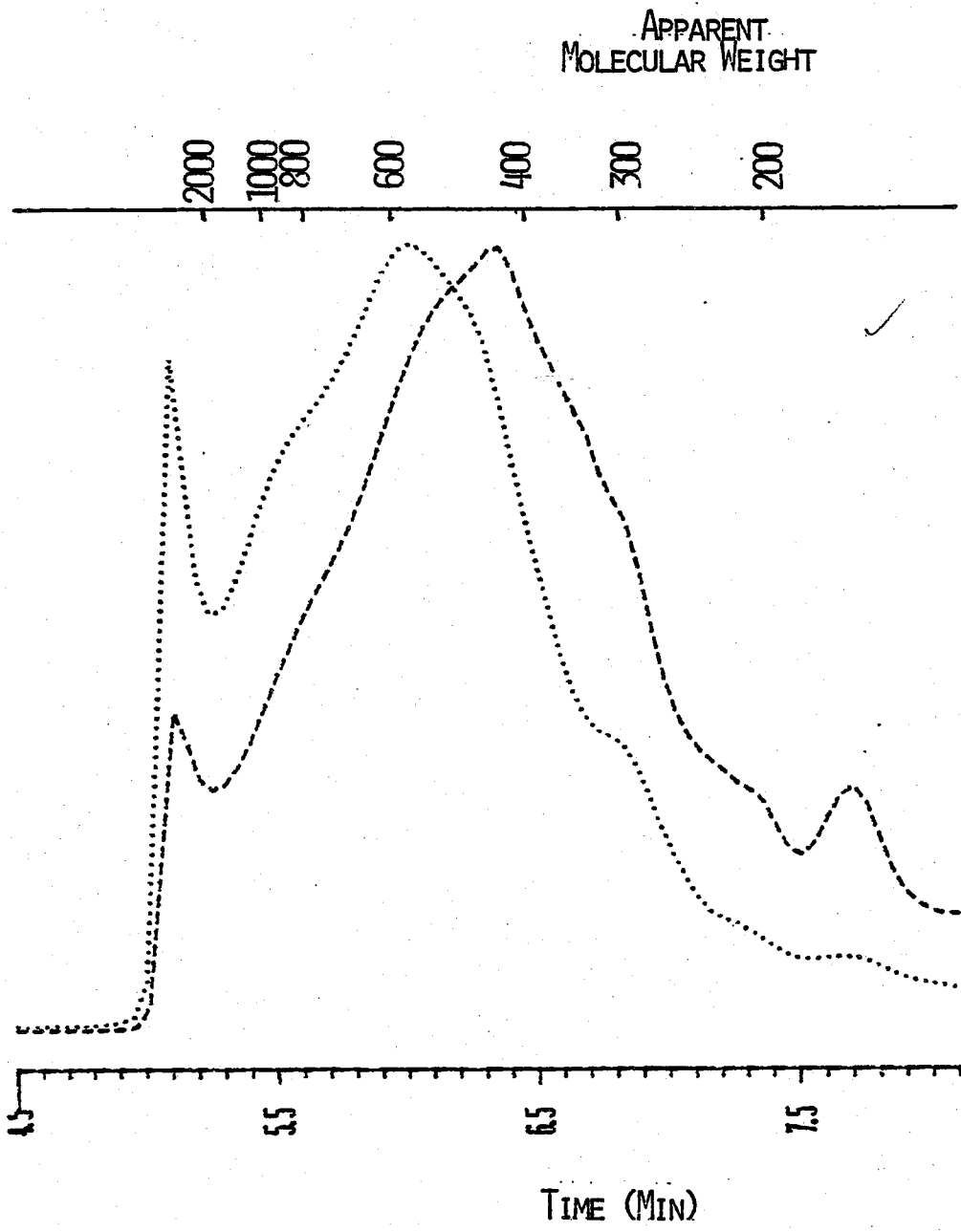


Figure 4-8. Effect of reactor temperature on THF-soluble residue (Batch experiments after 5 minutes, no catalyst added.)

..... 405°C  
 ----- 450°C

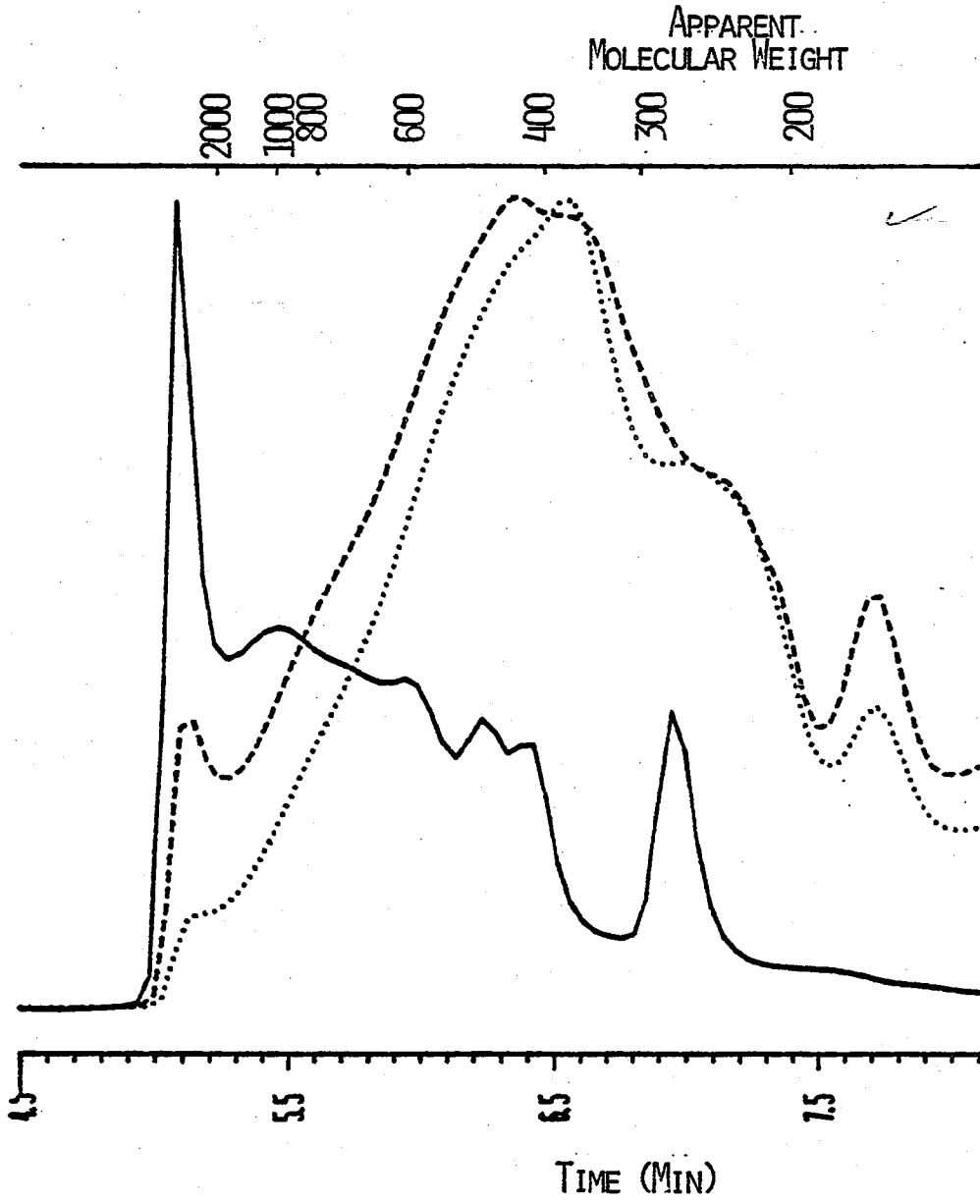


Figure 4-9. Comparison of THF-soluble residues obtained in the flow reactor.

- Untreated lignin
- - - No catalyst, 418°C
- . . . . . Co/Mo catalyst, 428°C

Figure 4-10 compares the molecular weight distributions of the hexane-soluble and hexane-insoluble fractions with the THF-soluble residue obtained from the flow reactor experiment. As expected the higher molecular weights are contained in the insoluble fraction.

In conclusion, these results, although preliminary, indicate that the best yields of monophenols will be obtained using a reactor configured to allow their removal from the reactor as they are formed. The use of a catalyst also appears important although more work remains to be done to find the best catalyst.

#### IV.3.2 4-Propylguaiacol Results and Discussion

The reactions of 4-propylguaiacol were studied over the limited range of conditions listed in Table 4-2. The results are preliminary but qualitatively reflect the results of Bredenberg and Vuori (1984) with a few exceptions. Direct comparison is difficult because they used lower temperatures 200-325°C and lower space velocities (LHSV-0.25h<sup>-1</sup>). Additionally we chose to use a sulfided Mo on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst with the hope of inhibiting complete deoxygenation to hydrocarbons whereas Bredenberg used sulfided Co/Mo on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> which is believed to be more reactive for hydrodeoxygenation.

##### Effect of reaction temperature.

In accordance with Bredenberg's results, increasing temperatures increased the selectivity of the reactions to hydrocarbons. At the space velocities studied conversion is essentially complete at 350°C. The maximum selectivity for the combined hydrocarbons propylcyclohexane, propylbenzene and methylpropyl benzenes was ~40% from 350°-400°C and LHSV = 1.4 h<sup>-1</sup>. The maximum selectivity for 4-propylphenol was 31.7% at 350°C and LHSV = 2.7 h<sup>-1</sup> (see Table 4-3 and Fig. 4-11).

##### Effect of hydrogen pressure.

Decreasing the pressure from (1000 to 500 psig) 69 to 35 atm of H<sub>2</sub> did not significantly effect conversion but did effect the selectivities of the major products. For example, 4-propylphenol selectivity increased by 89%, propylbenzene selectivity increased by 14%, propylcyclohexane selectivity decreased by 20% and the methylpropylbenzenes increased by 25% (see Table 4-3 and Fig. 4-11). The large changes in selectivities are quite contrary to what

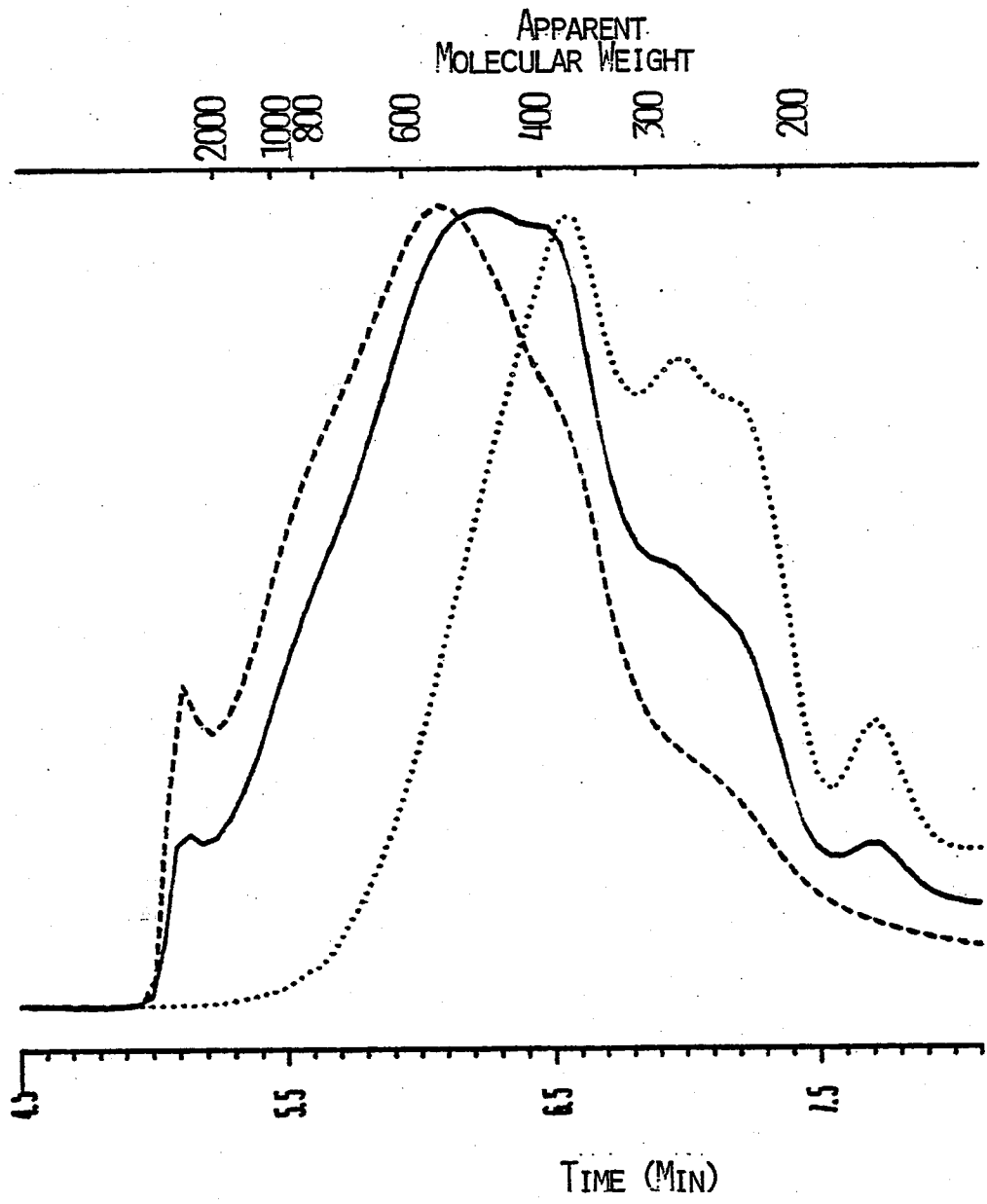


Figure 4-10. Comparison of molecular weight distributions of hexane-soluble (. . . . .) and hexane-insoluble (- - - - -) with the THF-soluble residue (————) from which they were produced. (Flow reactor at 405°C with Co/Mo catalyst).

Table 4-2. Reaction Parameters

| <u>Experiment</u> | <u>LHSV</u> | <u>Temp °C</u> | <u>P(psig)</u> |
|-------------------|-------------|----------------|----------------|
| HDO2              | 1.4         | 350            | 1000           |
| HDO3              | 1.4         | 300            | 1000           |
| HDO4              | 1.4         | 400            | 1000           |
| HDO5              | 1.4         | 400            | 500            |
| HDO6              | 2.7         | 350            | 1000           |
| HDO7              | 2.7         | 400            | 1000           |

LHSV = ml Feed/ml Catalyst . h

Table 4-3. Conversion of 4-propylguaiacol into phenolics and neutrals as a function of temperature at 1000 psig of hydrogen on Mo on  $\gamma$ -alumina.

|                         |     |                      | Propyl-<br>cyclohexane | Propyl-<br>benzene | Methyl-<br>propyl-<br>benzene | 4-Propyl-<br>phenol | Phenol       | Methyl-<br>propyl-<br>phenol |
|-------------------------|-----|----------------------|------------------------|--------------------|-------------------------------|---------------------|--------------|------------------------------|
|                         | T°C | Conver-<br>sion<br>% | Select.<br>%           | Select.<br>%       | Select.<br>%                  | Select.<br>%        | Select.<br>% | Select.<br>%                 |
| IDO 2 #4 <sup>a</sup>   | 350 | 99.7                 | 14.2                   | 18.2               | 9.0                           | 20.5                | 2.7          | 2.4                          |
| IDO 3 #4 <sup>a</sup>   | 300 | 82.1                 | 1.2                    | 0.7                | 0.3                           | 23.6                | 0.7          | 2.7                          |
| IDO 4 #4 <sup>a</sup>   | 400 | 98.4                 | 15.2                   | 16.1               | 8.7                           | 14.3                | 2.9          | 2.1                          |
| IDO 5 #4 <sup>a,b</sup> | 400 | 99.3                 | 12.1                   | 18.4               | 10.9                          | 27.0                | 3.4          | 4.0                          |
| IDO 6 #3 <sup>c</sup>   | 350 | 99.6                 | 2.2                    | 2.8                | 0.8                           | 32.7                | 0.6          | --                           |
| IDO 7 #4 <sup>c</sup>   | 400 | 99.4                 | 5.6                    | 0.9                | 4.2                           | 26.6                | 1.4          | 3.6                          |

a) LHSV = 1.4 ml Feed/ml Catalyst .h

b) 500 psig of hydrogen

c) LHSV = 2.7 ml Feed/ml Catalyst .h

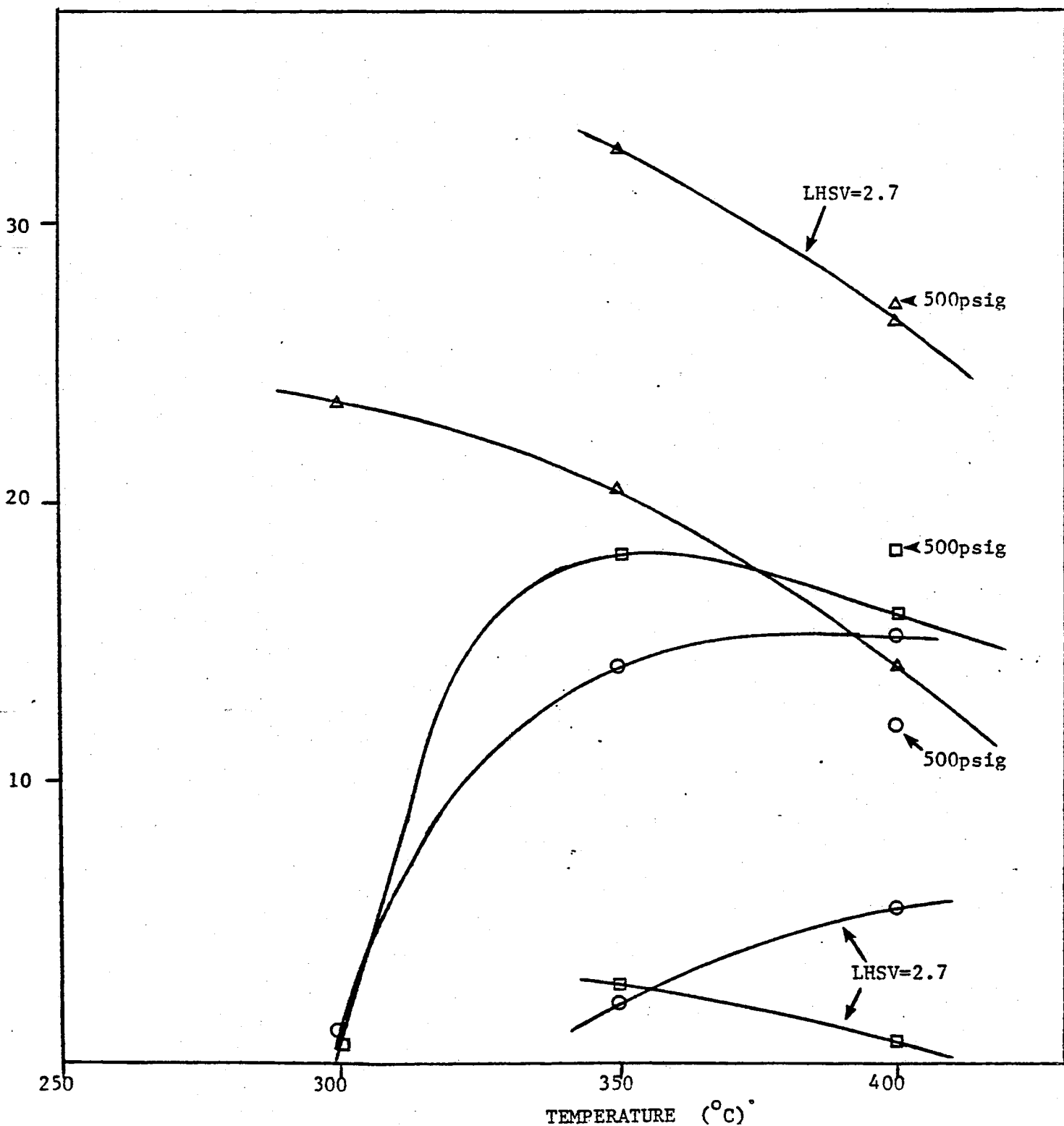


Fig. 4-11. Hydrodeoxygenation of 4-propylguaiacol. Selectivity (%) for 4-propylphenol ( $\Delta$ ), for propylbenzene ( $\square$ ), and for propylcyclohexane ( $\circ$ ) as a function of temperature. Selectivity (%) =  $\frac{\text{mmole desired product}}{\text{mmole 4-propylguaiacol}} \times 100$ . LHSV = 1.4 ml feed/ ml catalysts h.



Bredenberg and Vuori found using sulfided Co/Mo on  $\gamma\text{-Al}_2\text{O}_3$  at 275°C, LHSV = 0.25  $\text{h}^{-1}$ , and varying hydrogen pressure from 25.5 to 99.6 atm (360-1450 psig). They found only slight increases in hydrogenation at higher pressures.

#### Effect of space velocity.

Increasing space velocity within the limits of these experiments dramatically improved the yields of phenolics. This is to be expected as the removal of the second hydroxyl group is much more difficult than the first (Bredenberg et al. 1982). As mentioned earlier, the highest yield of 4-propylphenol was achieved at 350°C and a LHSV = 2.7  $\text{h}^{-1}$ . The improvement was 60% over the experiment at LHSV = 1.4  $\text{h}^{-1}$ . There is an interesting crossover of selectivities for propylcyclohexane and propylbenzene that occurs at 355°C (see Fig. 4-11) and at the higher space velocity. There appears to be a similar crossover using the lower space velocity but not until about 410°C. This behavior suggests that there are two independent reaction paths to propylcyclohexane as has been postulated by Klein and Hurff. One path is the hydrogenation of the intermediate 4-propylphenol to 4-propylcyclohexanol followed by dehydration to propylcyclohexene then hydrogenation to propylcyclohexane. The second path is the direct hydrogenation of the intermediate propylbenzene to propylcyclohexane (see Fig. 3-11). The latter reaction route appears to be favored at higher temperatures and higher space velocities.

#### Gaseous Products.

The only major product of the decomposition of 4-propylguaiacol found in the gas stream was methane. This is in agreement with the liquid product analysis which shows that very little phenol is formed (see Table 4-3). Quantitation was not possible in these early experiments because of air contamination in the gas samples. This problem has been corrected in the new system.

#### Conclusions and Forecast.

The major phenolic product from these studies was 4-propylphenol. The neutral products formed also contained propyl-side chains indicating that very little dealkylation was occurring. This is not surprising as the support  $\gamma\text{-Al}_2\text{O}_3$  is not very acidic.

In contrast to Bredenberg's work, all three experimental parameters i.e., temperature, pressure, and space velocity influenced selectivities of the

products. Our preliminary results suggest that 350°C, an LHSV = 2.7 h<sup>-1</sup> and a lower hydrogen pressure -500 psig will be close to optimum conditions for the formation of 4-propylphenol.

The preferred products from lignin for derivatization to methyl ethers as gasoline blending stocks are the phenols, cresols and xylenols. To accomplish these conversions requires a more acidic catalyst e.g. SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, to crack the propyl-side chains. Experiments are now in progress to increase systematically the acidity of the catalyst and measure its effect on the selectivities for phenols and cresols. Additionally a different model compound, one with β- or α- and β-hydroxyl groups would be investigated because we believe they are more representative of the structures in lignin or thermally depolymerized lignin. Future studies will concentrate on both of these aspects. In addition, we will use the continuous differential plug flow reactor to investigate dilute solutions of lignins in solvents.

We have chosen to operate at higher temperatures than other workers in the field because we believe that temperatures in the range of 350-450°C will be necessary to achieve a high degree of thermal depolymerization of lignin. This step is crucial and prerequisite to catalytic hydrodeoxygenation.

## SECTION V.0

### BIBLIOGRAPHY

- Adkins, H., 1937, REACTIONS OF HYDROGEN WITH ORGANIC COMPOUNDS OVER COPPER CHROMIUM OXIDE AND NICKEL CATALYSTS, University of Wisconsin Press, pp. 12-14.
- Adkins, H., 5 Oct. 1944, HYDROGENATION OF LIGNIN, U.S. Pat. 2,331,154, CA 38.1366(5).
- Adkins, H.; Frank, R. L.; and Bloom, E. S., 1941, PRODUCTS OF THE HYDROGENATION OF LIGNIN, J. Am. Chem Soc., Vol. 63, pp. 549-555, CA 35, 1988(4).
- Akhmina, E. I.; Benzmozgin, E. S.; Nemchenko, A. G.; Podgornaya, T. A.; Sukhanovskii, S. I.; & Yudkevich, Yu. D., 1965, CONTACT PYROLYSIS OF LIGNIN SETTLING TAR TO OBTAIN DEMETHYLATED PHENOLS, Khim. i Tekhnol. Topliva i Produktov ego Perera botki, Sb. (Moscow-Leningrad: Khimiya), Vol. 1965, pp. 12-16 (Russ.).
- Albright; and Tai, 1983. In PYROLYSIS: THEORY AND INDUSTRIAL PRACTICE. Albright, Crynes, & Corcoran, editors, NY: Academic Press.
- Alpert, S. B.; & Schuman, S. C., 15 Sept. 1970, PRODUCTION OF CHEMICALS FROM LIGNIN. (CC Number Kind Date Week) CA 851708 A 7038. (Basic) Priority Data (CC, No, Date): CA 17512 (680416)., Patent assignee: HYDROCARBON RES, INC.
- Alpert, S. B.; & Schuman, S. C., 23 May 1972, LIGNIN SULPHONATE CONVERSION - BY TREATMENT WITH HYDROGEN-RICH GAS IN A LIQUID HYDROCARBON, (CC Number Kind Date Week) CA 900973 A 7223 (Basic) Priority Data (CC, No, Date): US 22056 (700323), Patent assignee: HYDROCARBON RESEARCH INC.
- Arakin, I. E., 1973, NEW METHODS OF WOOD DELIGNIFICATION. Bumazh. Prom. No. 4, pp. 8-9, (Russ.).
- Arlt, H. G.; Gross, S. K.; & Schuerch, C., 1958, THE LIGNIN FRACTION OBTAINED FROM THE ALKALINE HYDROGENATION OF MAPLE WOOD, Tappi, pp. 64-70, CA 52.11410f.
- Babicki, R.; & Piotrowski, Z., 1973, LABORATORY THERMOLYSIS OF HEMICYCLIA SEPIARIA WOOD FROM CEYLON. Pr. Inst. Technol. Drewna, Vol. 20, No. 3/4, pp. 3-10, (Pol.; Russ. & Engl. sum).
- Bailey, A. J., 1940, THE INDUSTRIAL HYDROGENATION OF LIGNIN. Pacific Chem. Met. Inds., Vol. 4, pp. 13-14, 16. CA 34.1845(3).
- Bailey, A. J., 1943, VOLATILE HYDROGENATION DERIVATIVES OF LIGNIN, J. Am. Chem. Soc., Vol. 65, pp. 1165-1168. CA 37.4568(5).

- Balandin, A. A.; Vasyunina, N. A.; Chepigo, S. V.; & Barysheva, G.S., 1959, HYDROLYTIC HYDROGENATION OF CELLULOSE, Doklady Akad. Nauk S.S.S.R., Vol. 128, pp. 941-94. In Russian.
- Belorizky-Perret, N., 1965, SUBSTITUTED DERIVATIVES AND HYDROGENATION OF BENZOFURANS, LIGNIN MODEL COMPOUNDS, Ph.D. Thesis, Universite de Grenoble, 61 p. + 15 plates. (Fr.).
- Benigni, J. D.; & Goldstein, I. S., 1971, HYDROGENATION OF KRAFT LIGNIN, J. Polymer Sci. (C. Polymer Symp.) Vol. 36, pp. 477-88.
- Bergstrom, H. O. V.; & Cederquist, K. N., 19 Feb. 1935, TREATING LIGNIN-CONTAINING MATERIALS SUCH AS WOOD, PEAT, BOG-MOSS AND LIGNITE OR LIGNIN, Swed. Pat. 82,615, CA 31.7230(9).
- Beri, R. M., Feb./March 1977, WOOD AS RAW MATERIAL FOR CHEMICAL INDUSTRIES, Indian Pulp Paper 31, Vol. 5, pp. 3-5.
- Bhaskaran, T. A.; & Schuerch, C., Oct. 1969, STUDY OF NONVOLATILE HYDROGENATED MAPLE WOOD LIGNIN, Tappi 52, Vol. 10, pp. 1948-52.
- Bhattacharya, A.; Sondheimer, E.; & Schuerch, C., 1959, LIGNIN FROM THE ALKALINE HYDROGENATION OF SUGAR MAPLEWOOD. II. THE ACIDIC AND WATER-SOLUBLE FRACTIONS, Tappi, Vol. 42, pp. 446-448. CA 53.19384f.
- Bhattacharyas, A.; & Schuerch, C., 1960, LIGNIN FROM THE ALKALINE HYDROGENATION OF SUGAR MAPLEWOOD. III. CHROMATOGRAPHIC SEPARATION OF HIGHER-MOLECULAR-WEIGHT FRACTION AND A STRUCTURAL STUDY, Tappi, Vol. 43, pp. 840-844. CA 55.10880g.
- Bisenietse, S. K.; Riikuris, A. V.; & Sergeeva, V. N., 1974, COMPOSITION AND PROPERTIES OF TAR FORMED DURING THERMOLYSIS OF LIGNOCELLULOSE. (2). STUDY OF THE ETHER-SOLUBLE FRACTION OF TAR FORMED DURING VACUUM THERMOLYSIS OF CORNCOB AND BIRCHWOOD LIGNOCELLULOSE, Khim. Drev. (Riga), Vol. 15, pp. 130-4, (Russ.) cf. ABIPC 41: abstr. 10630.
- Bisenietse, S. K.; Stendzenietse, M. L.; & Riikuris, A. V., Nov./Dec. 1978, COMPOSITION AND PROPERTIES OF TAR FORMED DURING THERMOLYSIS OF LIGNOCELLULOSE. (9). OLIGOMERIC COMPOUNDS IN ETHER-SOLUBLE FRACTION OF TARS FROM BIRCHWOOD LIGNOCELLULOSE PYROLYSIS, Khim. Drev. (Riga), Vol. 6, pp. 87-90 Russ. cf. ABIPC 47:abstr. 4750.
- Bjorkman, A., 1950, STUDIES ON HYDROGENATION OF SULFITE WASTE LIQUOR, Trans. Roy. Inst. Technol., Stockholm., 40, pp. CA 87.5630m.
- Bolker, H. I.; & Li, C. M., 1973, DELIGNIFICATION OF WOOD BY HYDROGENOLYSIS WITH A SOLUBLE CATALYST, Can. Wood Chem. Symp. (Chem. Inst. Can./CPPA, Chateau Frontenac), Extended Abstrs. Papers Presented Vol. 4, pp. 39-41.

- Bond, G.C., 1974, "HETEROGENEOUS CATALYSIS, PRINCIPLES AND APPLICATIONS", Oxford University Press.
- Boocock, D. G. B.; Mackay, D.; McPherson, M.; Nadeau, S.; & Thurier, R., 1979, DIRECT HYDROGENATION OF HYBRID POPLAR WOOD TO LIQUID AND GASEOUS FUELS, Can. J. Chem. Eng., Vol. 57, No. 1, pp. 98-101, (Fr. sum.).
- Borchers, B.; Fischer, F.; & Schiene, R., 5 Oct. 1975, APPARATUS AND METHOD FOR MANUFACTURING PHENOLS FROM LIGNIN AND LIGNINIZED MATERIALS BY CONTINUOUS PRESSURE HYDROGENATION IN A CONTACT TUBE, Ger. (East) Pat. 115,482, 5 pp. CA 87.5630m, East German patent.
- Bowen, A. R.; & Nash, A. W., 1926, THE THERMAL DECOMPOSITION OF CELLULOSE AND LIGNIN IN PRESENCE OF CATALYSTS AND HYDROGEN UNDER PRESSURE, Fuel in Science and Practice, Vol. 5, pp. 138-42, CA 20.2241.
- Bower, J. R.; Cooke, L. M.; & Hibbert, H. LXX., 1943, HYDROGENOLYSIS AND HYDROGENATION OF MAPLE WOOD, J. Am. Chem. Soc., Vol. 65, pp. 1192-1195, CA 37.4568(1).
- Bower, J. R.; McCarthy, J. L.; & Hibbert, H., 1941, LIGNIN AND RELATED COMPOUNDS. LXIII. HYDROGENATION OF WOOD, 2. J. Am. Chem. Soc., Vol. 63, pp. 3066-3068, CA 36.265(6).
- Brauns, F. E.; & Brauns, D. A., 1960, The Chemistry of Lignin, NY: Academic Press.
- Bredenberg, J. B.; Huuska, M.; & Toropainen, P., 1984. HYDROGENOLYSIS AND HYDROCRACKING OF THE CARBON-OXYGEN BOND. 6. CATALYTIC HYDROGENOLYSIS OF METHOXYPHENOLS. Proceedings of the 9th Iberoamerican Symposium on Catalysis, Lisbon, Vol. 1, 8 pages.
- Bredenberg, J. B.; Huuski, M.; Rätty, J.; & Korpio, M., 1982. HYDROGENOLYSIS AND HYDROCRACKING OF THE CARBON-OXYGEN BOND. 1. HYDROCRACKING OF SOME SIMPLE AROMATIC O-COMPOUNDS. J. of Catalysis, Vol. 77, pp. 242-247.
- Bredenberg, J. B.; & Ceylan, R., March 1983, HYDROGENOLYSIS AND HYDROCRACKING OF THE CARBON-OXYGEN BOND. 3. THERMOLYSIS IN TETRALIN OF SUBSTITUTED ANISOLES, Fuel, Vol. 62, pp. 342-344.
- Brezny, R.; Mihalov, V.; and Kovacik, V., 1983, LOW-TEMPERATURE THERMOLYSIS OF LIGNINS. (1). REACTIONS OF BETA-O-4 MODEL COMPOUNDS, Holzforschung, Vol. 37, No. 4, pp. 199-204, [Engl.; Ger. sum.].
- Bridger, G. L., 1938, PHENOLS FROM CORNSTALK ALKALI LIGNIN. PREPARATION BY DESTRUCTIVE DISTILLATION AND SEPARATION BY FRACTIONAL DISTILLATION, Ind. Eng. Chem., Vol. 30, pp. 1174-80.

- Bronovitskii, V. E.; & Kalinskaya, L. L., 1967a, BEHAVIOR OF (LIGNIN) MODEL COMPOUNDS DURING HYDROGENOLYSIS, Uzbek. Khim. Zh., Vol. 11, No. 5, pp. 79-81, (Russ.; Uzbek sum.) cf. ABIPC 38: abstr. 6673.
- Bronovitskii, V. E.; & Kalinskaya, L. L., 1967b, THE COMPOSITION OF PHENOLIC FRACTION FROM HYDROGENOLYSIS PRODUCTS OF COTTON AND SPRUCE LIGNINS, Uzbek. Khim. Zh. Vol. 11, No. 2, pp. 31-4, (Original in Russ.; cf. ABIPC 38: abstr. 6673. National Lending Library transl. in Engl. (8 p.) available from IPC.
- Bronovitskii, V. E.; & Kalinskaya, L. L., 1970, OXIDATION OF LIGNIN IN AQUEOUS ALKALI SOLUTION, Khim. Prirod. Soed. Vol. 6, No. 5, pp. 512-17, (Russ.), CA 74.100735q.
- Bronovitskii, V. E.; & Kalinskaya, L. L., 1972, HYDROGENOLYSIS OF WILLSTATTER'S LIGNIN, Khim. Prirod. Soed. Vol. 8, No. 1, pp. 106-12, (Russ.).
- Bronovitskii, V. E.; & Nam, A., 1973, ACTION OF ALKALIES ON LIGNIN, Deposited Publ., VINITI 5735-73, 9 pp. CA 85.65058z.
- Bronovitskii, V. E.; & Nam, A., 1973, ACTION OF ALKALIES ON LIGNIN. I., Khimiya i tekhnol. tsellyulozy i volokna, (Vyp. 6), pp. 372-8. CA 83.30163m.
- Bronovitskii, V. E.; & Nam, A., 1973, ACTION OF ALKALIES ON LIGNIN. II., Khimiya i tekhnol. tsellyulozy i volokna, (Vyp. 6), pp. 379-86, CA 83.30163n.
- Bronovitskii, V. E.; & Sharipdzhanov, A., 1967, STABILIZATION OF LOW-DENSITY POLYETHYLENE WITH RESINS FROM LIGNIN HYDROGENOLYSIS, Uzbek. Khim. Zh., Vol. 11, No. 6, pp. 76-8, (Russ.; Uzbek sum.).
- Bronovitskii, V. E.; & Sharipdzhanov, A., 1971, STABILIZATION OF POLYETHYLENE WITH HYDROGENOLYSIS PRODUCTS OF LIGNIN, Plas. Massy, No. 1, pp. 34-6, (Russ.).
- Bronovitskii, V. E.; Cheremukhin, I. K.; Volochkovich, M. A.; & Kalinskaya, L. L., 1967, METHOD OF OBTAINING LOW MOLECULAR PRODUCTS FROM HYDROLYSIS LIGNIN, U.S.S.R. pat. 198,906, filed June 1, 1966, Publ. Izobret. No. 14, p. 165, [Russ.], PATENT.
- Bronovitskii, V. E.; Ikramova, D. R.; & Kalinskaya, L. L., 1973, HYDROGENOLYSIS OF LIGNIN AND MODEL COMPOUNDS IN THE PRESENCE OF ETHANOLAMINE AS AN INHIBITOR, Khim. Tekhnol. Tsellyulozy Volokna, No. 6, pp. 345-71, (Russ.).
- Bronovitskii, V. E.; Kalinskaya, L. L.; & Ikramova, D. I., 1968, COMPOSITION OF THE ACID FRACTIONS OF HYDROGENOLYSIS PRODUCTS OF LIGNIN AND ITS MODEL COMPOUNDS, Uzbek. Khim. Zh., Vol. 12, No. 1, pp. 67-9, (Russ.; Uzbek sum.), CA 69.26934g.

- Bronovitskii, V. E.; Kalinskaya, L. L.; & Ikramova, D. R., 1971a, HYDROGENOLYSIS OF LIGNIN, Gidroliz. Lesokhim. Prom., Vol. 24, No. 8, p. 14, (Russ.)
- Bronovitskii, V. E.; Kalinskaya, L. L.; & Ikramova, D. R., 1971b, NATURE OF NEUTRAL PRODUCTS IN HYDROGENOLYZATES OF ACID LIGNINS AND MODEL COMPOUNDS, Izv. VUZ, Lesnoi Zh., Vol. 14, No. 6, pp. 165-8, (Russ.).
- Bronovitskii, V. E.; Kalinskaya, L. L.; & Kuznetsova, L. G., 1966, BEHAVIOR OF LIGNIN MODEL COMPOUNDS DURING THE PROCESS OF HYDROGENOLYSIS, Struktura i Modifik. Khlopk. Tsellyulozy No. 3, pp. 353-64, (Russ.).
- Bronovitskii, V. E.; Salyamova, F. Kh.; & Volochkovich, M. A., 1968, METHOD OF PREPARATION OF A CATION EXCHANGER, USSR. pat. 228,943, filed March 9, 1965, Izobret. No. 32, p. 75.
- Bronovitskii, V. E.; Salyamova, F.; & Volochkovich, M. A., 1967, CATION EXCHANGE RESINS FROM PRODUCTS OF LIGNIN HYDROGENOLYSIS, Uzbek. Khim. Zh., Vol. 11, No. 4, pp. 68-70, (Russ.; Uzbek sum.), CA 67.109793v.
- Bronovitskii, V. E.; Volochkovich, M. A.; Kalinskaya, L. L.; & Nam, A., 1968, LOW MOLECULAR WEIGHT COMPOUNDS FROM LIGNIN, Uzbek. Khim. Zh., Vol. 12, No. 3, pp. 71-4, (Original in Russ.; cf. ABIPC 39: abstr. 8533. National Lending Library transl. in Engl. (9 p.) available from IPC.
- Browning, B. L., 1967, Methods of Wood Chemistry, Vols. I and II, NY: Interscience.
- Bungay, H. R., 1981, Energy: The Biomass Option, NY: Wiley-Interscience.
- Ceylan, R.; & Bredenberg, J. B., 1982, HYDROGENOLYSIS AND HYDROCRACKING OF THE CARBON-OXYGEN BOND. (2). THERMAL CLEAVAGE OF THE CARBON-OXYGEN BOND IN GUAIACOL, Fuel, Vol. 61, pp. 377-382, [Engl.].
- Chem Systems, Inc., 1984, TECHNICAL AND ECONOMIC ASSESSMENT OF PROCESSES FOR THE PRODUCTION OF BUTANOL AND ACETONE-PHASE TWO: ANALYSIS OF RESEARCH ADVANCES, Final Report for Contract No. AI01-81CS66001. DOE/CS/66001-5.
- Chervenak, M. C.; & Comolli, A.G., 17 Jan. 1980, CATALYTIC HYDROGENATION IN FLUIDISED BED REACTORS - WITH IMPROVED SEPN. OF VAPOUR AND LIQ. PHASES, (CC Number Kind Date Week) DE 2916695 A 8004, (Basic) US 4221653 A 800909 8039, CA 1119535 A 820309 8214, CA 1122554 A 820427 8220, Priority Data (CC, No, Date): US 920825 (780630), Patent Assignee: HYDROCARBON RES INC.
- Chudakov, M. I., 1968, INDUSTRIAL UTILIZATION OF LIGNIN, Khim. Drev. (Riga) No. 1, pp. 311-22, (Russ.).
- Chum, H. L.; Parker, S. K.; Feinberg, D. A.; Wright, J. D.; Rice, P.A.; Sinclair, S. A.; & Glasser, W. G., 1985a, The Economic Contribution of Lignins to Ethanol Production from Biomass. TR-231-2488, Golden, CO: Solar Energy Research Institute.

- Chum, H. L.; Douglas, L. J.; Feinberg, D. A.; & Schroeder, A. A., 1985b, Evaluation of Pretreatments of Biomass for Enzymatic Hydrolysis of Cellulose, TR-231-2183, Golden, CO: Solar Energy Research Institute.
- Chum, H. L.; Johnson, D. K.; Ratcliff, M.; Black, S.; Schroeder, H. A.; & Wallace, K., 1985c. Comparison Between Lignins Produced by Steam Explosion and Organosolv Pretreatments, in Proc. 1985 International Symposium on Wood and Pulping Chemistry, Preprints published by Canadian Pulp and Paper Association, pp. 223-6.
- Chum, H. L.; Johnson, D. K.; Ratcliff, M.; Black, S.; Schroeder, H. A.; Wallace, K.; Robert, D.; & Sarkanen, K. V., 1985d, "Lignin Characterization Research: A Progress Report", in Biochemical Conversion Program Semi Annual Report, SERI/CP 231-2726, Golden, CO: Solar Energy Research Institute.
- Clark, E. L., Feb. 1970, NOVEL HYDROREFINING TECHNIQUE COULD GIVE PULP YIELDS AS HIGH AS 90%, Pulp Paper, Vol. 44, No. 2, pp. 107-8.
- Clark, I. T.; & Green, J., 1968, PRODUCTION OF PHENOLS BY COOKING KRAFT LIGNIN IN ALKALINE SOLUTIONS, Tappi, Vol. 51, No. 1, pp. 44-8.
- Clark, I.T., & Hicks, J.R.; Harris, E.E., 1951, HYDROGENATION OF DOUGLAS FIR LIGNIN, Tappi, Vol. 34, pp. 6-11. CA 45.4445f.
- Clayton, D. W., & Fleming, B. I., 1981, REDUCTIVE DELIGNIFICATION: PAST EXPERIENCE AND CURRENT CONCEPTS, Paperi Puu, Vol. 63, No. 4a, pp. 275-278, 281-282, 287-288, (Engl.;Finn. sum.).
- Connors, W.J., & Johanson, L.N.; Sarkanen, K.V.; Winslow, P., 1980, THERMAL DEGRADATION OF KRAFT LIGNIN IN TETRALIN, Holzforschung, Vol. 34, pp. 29-37, CA 92.199992c.
- Cooke, L.M., & McCarthy, J.L.; Hibbert, H., 1941, LIGNIN AND RELATED COMPOUNDS. LXI. HYDROGENATION OF ETHANOLYSIS FRACTION FROM MAPLE WOOD. 2, J. Am. Chem. Soc., Vol. 63, pp. 3056-3061, CA 36.264(9).
- Cooke, L.M., & McCarthy, J.L.; Hibbert, H., 1941, LIGNINS AND RELATED COMPOUNDS. LX. HYDROGENATION STUDIES ON MAPLE ETHANOLYSIS PRODUCTS. 1, J. Am. Chem. Soc., Vol. 63, pp. 3052-3061. CA 36.264(6).
- Coscia, C.J., & Schubert, W.J.; Nord, F.F., 1961, INVESTIGATION ON LIGNINS AND LIGNIFICATION. XXIV. APPLICATION OF HYDROGENATION, HYDROGENOLYSIS, AND VAPOR PHASE CHROMATOGRAPHY IN THE STUDY OF LIGNIN STRUCTURE, J. Org. Chem., Vol. 26, pp. 5085-5091. CA 56.14139i.
- Coscia, C.J., & Schubert, W.J.; Nord, F.F., 1961, LIGNINS AND LIGNIFICATION. XXIII. HYDROGENATION AND HYDROGENOLYSIS OF NATIVE AND MILLED-WOOD LIGNINS, Tappi, Vol. 44, pp. 360-363, CA 55.19321b.



- Coughlin, R. W., & Sundstrom, D. W.; Klei, H. E.; Avni, E., 1984, CONVERSION OF LIGNIN TO USEFUL CHEMICAL PRODUCTS, Bioconversion Systems (Wise, D. L., ed.) pp. 41-58 CRC Press: Boca Raton, Fl.
- Coughlin, R. W.; & Avni, 1984, Chemical Processing of Renewable Materials, Biotechnol. Bioeng. Symp. No. 14/Simp./ Biotechnol. for Fuels and Chemicals (Gatlinburg) 6th: 21-35 (May 15-18, 1984).
- Coughlin, R. W.; & Davoudzadeh, F., 1983, LIGNIN DEPOLYMERIZES COAL AT 300°C, Nature, Vol. 303, No. 5920, pp. 789-791.
- Cowley, S., 1985, Heterogeneous Catalysis Course at SERI, Summer 1985.
- Davoudzadeh, F.; Smith, B.; Avni, E.; & Coughlin, R. W., 1985, DEPOLYMERIZATION OF LIGNIN AT LOW PRESSURES USING LEWIS ACID CATALYSIS AND UNDER HIGH PRESSURE USING HYDROGEN DONOR SOLVENTS, Holzforschung, Vol. 39, No. 3, pp. 159-166.
- Domburgs, G. E., & Sergeeva, V. N.; Salna, L. Ya., 1967, POSSIBILITY OF STUDYING LIGNIN THERMOLYSIS BY ELECTRON PARAMAGNETIC RESONANCE, Izv. Akad. Nauk Latv. SSR, Ser. Khim. No. 4, pp. 509-10; (Original in Russ.; cf. ABIPC 39: abstr. 6555. National Lending Library transl. in Engl. (2 p.)).
- Domburgs, E.; Kirshbaums, I.; & Sergeeva, V. N., 1971, RAPID PYROLYSIS OF ALKALI LIGNIN IN VACUO, Khim. Drev., No. 7, pp. 51-4 (Russ.).
- Domburgs, G.; & Sergeeva, V. N., 1967, EFFECT OF THE DEGREE OF SAMPLE DILUTION WITH ALUMINUM OXIDE ON THE DISPLAY OF LIGNIN THERMAL EFFECTS, Khim. Drev., No. 3, pp. 377-81 (Russ.).
- Domburgs, G.; Kirshbaums, I. Z.; & Sergeeva, V. N., 1969, RAPID THERMAL DECOMPOSITION OF ASPEN ALKALI LIGNIN IN AIR AT NORMAL PRESSURE, Khim. Drev., No. 3, pp. 133-37 (Russ.).
- Domburgs, G.; Kirshbaums, I.; & Segeeva, V. N., 1971, PYROLYSIS OF ALKALI LIGNIN IN A GAS FLOW, Khim. Drev., No. 7, pp. 43-50 (Russ.).
- Domburgs, G.; Sergeeva, V. N.; & Zeibe, G., 1971, THERMOGRAPHIC STUDY OF MODEL COMPOUNDS OF LIGNIN. I. THERMAL DECOMPOSITION OF PHENYLPROPANOIC MONOMERS WITH A SIDE CHAIN OF DIFFERENT STRUCTURES, Khim. Drev., No. 7, pp. 59-65 (Russ.).
- Donath, E. E., Issued April 24, 1967, HYDROREFINING PROCESS FOR VEGETABLE FIBERS AND STABILIZED PRODUCTS OBTAINED, Fr. pat. 1,483,142, 3 claims, 11 p. (Fr.), PATENT.
- Donath, E. E., Issued Sept. 24, 1969, HYDROGENATION PROCESS FOR TREATING A LIGNIN-CONTAINING MATERIAL, Brit. pat. 1,165,141, 11 claims, 7 p.
- Dzhon, L. S.; & Dobrev, S., 1970, EFFECT OF SOME FACTORS ON THE DESTRUCTIVE HYDROGENATION OF HYDROLYSIS LIGNIN IN THE PRESENCE OF LIMONITE CONCENTRATE AS CATALYST, Tseluloza, Vol. 1, No. 2, pp. 19-23, (Bulg., Russ., Ger., & Engl. sum.).

- Eachus, S. W., & Dence, C. W., 1975, HYDROGENATION OF LIGNIN MODEL COMPOUNDS IN THE PRESENCE OF A HOMOGENEOUS CATALYST, Holzforschung, Vol. 29, No. 2, pp. 41-48, (Engl.; Ger. sum.).
- Efendieva, N. F., & Shorygina, N. N., 1974, HYDROGENOLYSIS OF THE LIGNOCARBOHYDRATE COMPLEX ISOLATED FROM MILLED SPRUCEWOOD, Izv. Akad. Nauk SSSR, Ser. Khim. No. 2, pp. 458-61, (Russ.) cf. ABIPC 45: abstr. 6912.
- Emmett, P.H., 1965, "CATALYSIS THEN AND NOW", Franklin Publishing Co.
- Enkvist, T., 1975, PHENOLICS AND OTHER ORGANIC CHEMICALS FROM KRAFT BLACK LIQUORS BY DISPROPORTIONATION AND CRACKING REACTIONS, J. Appl. Polymer Sci. (Appl. Polymer Symp.) Vol. 28, pp. 285-295.
- Enkvist, T.; Turunen, J.; & Ashorn, T., 1962, THE DEMETHYLATION AND DEGRADATION OF LIGNIN OR SPENT LIQUORS BY HEATING WITH ALKALINE REAGENTS, Tappi, Vol. 45, pp. 128-35.
- Evans, R. J.; Milne, T. A.; & Soltys, M. N., 1986, "DIRECT MASS-SPECTROMETRIC STUDIES OF THE PYROLYSIS OF CARBONACEOUS FUELS III. PRIMARY PYROLYSIS OF LIGNIN". To appear in J. Analyt. and Applied Pyrolysis.
- Faix, O., & Schweers, W., 1975, COMPARATIVE STUDIES DEALING WITH POLYMERIC MODELS OF LIGNIN (DHP's) HAVING DIFFERENT COMPOSITIONS. (6). ETHANOLYSIS, NITROBENZENE OXIDATION, AND HYDROGENOLYSIS, Holzforschung, Vol. 29, No. 2, pp. 48-55, (Ger.; Engl. sum.) cf. ABIPC 45: abstr. 9130.3.
- Faix, O., 1973, COMPARATIVE STUDIES ON SYNTHETIC LIGNINS (DHP) OF VARIOUS COMPOSITION WITH THE AID OF ISOTOPE AND SPECTROSCOPIC METHODS AS WELL AS THROUGH CHEMICAL DECOMPOSITION, Mitt. Bundesforsch. Reinbek/Hamburg, Vol. 92, 205 p., (Ger.).
- Fengel, D.; & Wegener, G., 1983, WOOD: CHEMISTRY, ULTRA-STRUCTURE, REACTIONS. de Gruyter:New York.
- Fierz-David, H. E.; & Hannig, M., 1925, THE DISTILLATION OF CELLULOSE, WOOD AND SIMILAR SUBSTANCES UNDER HYDROGEN PRESSURE WITH CATALYSTS, Helvetica Chim. Acta, Vol. 8, pp. 900-23 (Ger.).
- Fischer, F., 1980, LIGNIN CHEMISTRY (MAKES) CONTRIBUTIONS TO THE USE OF A SECONDARY RAW MATERIAL; Zellstoff Papier, Vol. 29, No. 1, pp. 13-18, [Ger.].
- Fischer, F.; & Schrader, H., 1920, THE DRY DISTILLATION OF LIGNIN AND CELLULOSE, Ges. Abh. Kenntnis Kohle, No. 5, pp. 106-16 (Ger.).
- Fischer, F.; & Wienhaus, O., 1980 DIFFERENTIAL THERMAL ANALYSIS OF SPRUCE LIGNINS, Wiss. Z. Tech. Univ. Dresden, Vol. 29, No. 3/4, pp. 923-927, [Ger.].CA 94.5076e.

- Fisher, J. H.; & Marshall, H. B., 27 Nov. 1951, U.S. Patents 2,576,752-3.
- Fisher, J. H.; & Sankey, C. A., 27 Nov. 1951, U.S. Pat. 2,576,754.
- Foster, N. C., 1979, ADHESIVE FORMULATION VIA THERMOLYTIC MODIFICATION OF LIGNIN, Univ. of Washington, Ph.D. Thesis, 191 p. (Avail. from Univ. Microfilms, Ann Arbor, MI 48106).
- Freundenberg, K.; & Lautsch, W., 1939, Naturwiss., Vol. 27, p. 227.
- Freundenberg, K.; & Lautsch, W., 4 Dec. 1945, PRODUCTS FROM LIGNIN BY HYDROGENATION, U.S. Pat. 2,390,063, CA 40.2985(1).
- Freundenberg, F.; & Lautsch, W.; Piazzolo, G.; Scheffer, A., 1941, LIGNIN. XLII. THE PRESSURE HYDROGENATION OF LIGNIN AND THE LIGNIN-CONTAINING WASTE LIQUORS OF THE SPRUCE, Ber., Vol. 74B, pp. 171-183. CA 35.4197(5).
- Freundenberg, K.; & Lautsch, W.; Piazzolo, G., 1943, LIGNIN. LV. HYDROGENATION OF LIGNIN AND LIGNIN-CONTAINING SUBSTANCES WITH AGENTS WHICH YIELD HYDROGEN, ESPECIALLY ALCOHOLS, Ber., Vol. 76B, pp. 486-498. CA 37.6566(3).
- Fukuzumi, T.; Naito, K.; & Shibamoto, T., 1976, CATALYTIC HYDROGENATION OF LIGNIN-CARBONYL MODEL COMPOUND AT MODERATE TEMPERATURE AND PRESSURE, J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 22, No. 8, pp. 457-460, (Jap.; Engl. sum.).
- Gaslini, F., 2 Aug. 1960, HYDROGENATION OF LIGNIN AND LIGNOCELLULOSIC MATERIALS WITH SEPARATION OF CELLULOSE FIBERS, U.S. Pat. 2,947,739, CA 55.4962g.
- Gates, B. C.; J. R. Katzer; & G. C. A. Schuitt, 1979, "CHEMISTRY OF THE CATALYTIC PROCESS", McGraw-Hill.
- Gendler, J. L.; Huibers, D. T. A.; & Parkhurst, H. J., Jr., 1983, HYDROXY-AROMATICS FROM LIGNIN HYDROGENOLYSIS, Wood & Agr. Residues (Soltes, E. J., ed.) Proc. ACS Conf. (Kansas City) pp. 391-400 (Sept. 12-17, 1982; publ. 1983 Acad. Press). CA 100.8816z.
- Giesen, J., 24 Jan., 1955, DEGRADATION OF LIGNIN AND LIGNIN-CONTAINING MATERIAL, Ger. Pat. 922,710. Also German Pat. 933,988, 6 Oct., 1955. CA 51.13396f. Assigned to Inventa A.-G. für Forschung und Patentverwertung.
- Giesen, J., 16 Mar. 1955, FORMATION OF PHENOLS BY SPLITTING OF SULFITE SPENT LIQUOR LIGNIN. Swiss Pat. 305,712. Also German Pat. 936,270, 7 Dec., 1955; US Pat. 2,809,216, 8 Oct., 1957. Assigned to Inventa A.G. für Forschung und Patentverwertung.

- Giesen, J., 18 Dec. 1956, DEGRADATION OF LIGNIN AND LIGNIN-CONTAINING MATERIAL. U.S. Pat. 2,774,795, CA 51.6154a. Assigned to Inventa A.-G. für Forschung und Patentverwertung. See Swiss Pat. 308,262.
- Giesen, J., 18 Jan, 1956, DECOMPOSITION OF LIGNIN AND LIGNIN-CONTAINING MATERIALS, Brit. Pat. 743,592. US Pat. 2,290,009, 23 Apr., 1957. Assigned to Inventa A.-G. für Forschung und Patentverwertung. CA 50.13442f.
- Giesen, J., 28 Feb. 1957, CLEAVAGE OF LIGNIN, Swiss Pat. 318,446. Also German Pat. 1,039,527, CA 51.15128e. Assigned to Inventa A.-G. für Forschung und Patentverwertung.
- Giesen, J., 15 Mar 1957, ISOLATION OF LIGNIN FROM BLACK LIQUOR, Swiss Pat. 318,820, Patent assigned to Inventa A.-G. für Forschung und Patentverwertung Luzern.
- Giesen, J., 4 July 1961, PROCESS FOR CLEAVAGE OF LIGNIN TO PRODUCE PHENOLS, U.S. Pat. 2,991,314, Assigned to Inventa A.-G. für Forschung und Patentverwertung.
- Giesen, J., Jan. 20, 1959, MAKING PHENOLS BY CATALYTIC HYDROGENATION OF LIGNIN, U.S. Pat. 2,870,133, CA 53.9672d. Pat. assigned to Inventa Akt.-Ges. für Forschung und Patentverwertung Luzern.
- Godard, H. P.; McCarthy, J. L.; & Hibbert, H., 1940, HYDROGENATION OF WOOD, J. Am. Chem. Soc., Vol. 62, p. 988, CA 34.3912(9).
- Godard, H. P.; McCarthy, J. L.; & Hibbert, H., 1941, LIGNIN AND RELATED COMPOUNDS. LXII. HIGH-PRESSURE HYDROGENATION OF WOOD USING COPPER CHROMITE CATALYST. 1, J. Am. Chem. Soc., Vol. 63, pp. 3061-3066, CA 36.265(4).
- Goheen, D. W., 1966, HYDROGENATION OF LIGNIN BY THE NOGUCHI PROCESS, Advan. Chem. Ser. Vol. 59, pp. 205-225. CA 66.20091w.
- Goheen, D. W., 1971, LOW MOLECULAR WEIGHT CHEMICALS (FROM LIGNIN), In Lignins (Wiley-Interscience), pp. 797-831.
- Goheen, D. W., 24 May 1966, HYDROGENATION SULFONATED LIGNIN TO PHENOLIC SUBSTANCES, U.S. Pat. 3,253,044, 4 pp. Assigned to Crown Zellerbach Corp. CA 65.5661f.
- Goldstein, I. S., 1975, PERSPECTIVES ON PRODUCTION OF PHENOLS AND PHENOLIC ACIDS FROM LIGNIN AND BARK, J. Appl. Polymer Sci. (Appl. Polymer Symp.) Vol. 28, pp. 259-267.
- Goldstein, I. S., ed., 1981, Organic Chemicals from Biomass, Boca Raton, FL: CRC Press, Inc.
- Goldstein, I. S.; & Benigni, J. D., 4 Dec. 1969, HYDROLYSIS OF LIGNIN, Ger. Offen., 1,926,673, 15 pp.

- Gromovs, V., & Pormale, M., 1961, HYDROTROPIC AND ALKALINE PULPING OF DECIDUOUS WOODS WITH SIMULTANEOUS HYDROGENATION OF LIGNIN. II. FRACTIONATION OF THE PRODUCTS OF HYDROGENATION OF LIGNIN AND SEPARATION OF PHENOLS, Latvijas PSR Zinatnu Akad. Vestis, pp. 85-92. CA 58.658e. In Russian.
- Gugnin, Yu. A., 1970, THE ACCELERATING EFFECT OF POLYSULFIDES AND HYDRAZINE ON (WOOD) PULPING, Izv. VUZ, Lesnoi Zh., Vol. 13, No. 2, pp. 115-18. (Russ.).
- Hachihama, Y., & Jodai, S., 1942, CATALYTIC HYDROGENATION OF LIGNIN. IV. CATALYTIC HYDROGENATION OF SOFTWOOD LIGNIN, J. Soc. Chem. Ind. Japan, Vol. 45, pp. 302-303. CA 43.8674i.
- Hachihama, Y., & Jodai, S., 1943, STUDIES ON LIGNIN AND RELATED COMPOUNDS. IX. CARBONYL AND NEUTRAL CONSTITUENTS OF THE HYDROGENATION PRODUCTS OF SOFTWOOD LIGNIN, J. Soc. Chem. Ind., Japan, Vol. 46, pp. 507-509. CA 43.2427h.
- Hachihama, Y.; & Jodai, S., 1943, STUDIES ON LIGNIN AND RELATED COMPOUNDS. VI-VIII. VI. COMPARISON OF BEHAVIOURS OF LIGNINS ISOLATED FROM SOFTWOOD, HARDWOOD AND GRASS IN COURSE OF HYDROGENATION. VII. PHENOLS IN THE HYDROGENATION PRODUCTS OF HARDWOOD AND GRASS LIGNINS. VIII. PHENOLS IN HYDROGENATION PRODUCTS OF LIGNIN, J. Soc. Chem. Ind., Japan, Vol. 46, pp. 132-139. CA 43.2427h.
- Hachihama, Y.; & Jodai, S., 1950, BUILDING STONE OF LIGNIN, Mem. Inst. Sci. Ind. Research Osaka Univ., Vol. 7, pp. 165-166, CA 45.6837d.
- Hachihama, Y.; Jodai, S.; & Umezu, M., 1940, LIGNIN AND RELATED COMPOUNDS. I. HYDROGENATION OF SOFT WOOD LIGNIN, J. Soc. Chem. Ind., Japan, Vol. 43, p. 127. CA 34.5655(8).
- Hachihama, Y; & Jodai, S., 1941, CATALYTIC HYDROGENATION OF LIGNIN, J. Soc. Chem. Ind. Japan, Vol. 44, pp. 773-776. CA 42.2427h.
- Halmeroski, J.; & Enkvist, T., 1956, SOME COMPARATIVE PRESSURE HYDROGENATIONS OF SULFATE LIGNINS, Suomen Kemistilehti, Vol. 29B, pp. 53-58. CA 50.13437i.
- Harris, E. E.; D'Ianni, J.; & Adkins, H., 1938, REACTION OF HARD WOOD LIGNIN WITH HYDROGEN, J. Am. Chem. Soc., Vol. 60, pp. 1467-1470. CA 32.5794(4).
- Harris, E. E.; Saeman, J.; & Sherrard, E.C., 1940, HYDROGENATION OF LIGNIN IN AQUEOUS SOLUTIONS, Ind. Eng. Chem., Vol. 32, pp. 440-441. CA 34.2589(6).
- Harris, E.E., & Adkins, H., 1938, REACTIONS OF LIGNIN WITH HYDROGEN, Paper Trade J., Vol. 107, pp. 38-40. CA 33.854(9).
- Harris, E.E., & Saeman, J.F.; Bergstrom, C.B., 1949, LIGNIN HYDROGENATION PRODUCTS, Ind. Eng. Chem., Vol. 41, pp. 2063-2067. CA 44.326a.

- Harris, E.E., 1940, HYDROGENATION OF LIGNIN, Paper Trade J., Vol. 111, pp. 27-28. CA 35.1223(1).
- Hastbacka, K.; & Bredenbergh, J. B., March 1973, HYDROCRACKING OF LIGNIN TAR AND LIGNIN MODEL COMPOUNDS, Paperi Puu, Vol. 55, No. 3, pp. 129-31, 133-4. (Engl.; Finn. sum.).
- Heitz, M., & Massoussa, B.; Loubinoux, B., Sept. 20-22, 1982, PREPARATION OF CHEMICAL PRODUCTS FROM LIGNINS, Colloque Sci. Ind. Bois (Grenoble) 3 (Transform. Biol. Chim.) pp. 185-212, [Fr.].
- Heuser, E.; & Herrmann, F., 1924, FUSION OF LIGNIN, CELLULOSE AND WOOD WITH CAUSTIC POTASH, Celluloschemie, Vol. 5, pp. 1-6.
- Heuser, E.; & Skiöldebrand, C., 1919, RESEARCHES ON THE LIGNIN OF WOOD. I. DESTRUCTIVE DISTILLATION OF LIGNIN, Z. angew. Chem., Vol. 32, No. 1, pp. 41-5; J. Soc. Chem. Ind., Vol. 38, p. 215A.
- Hoffmann, P.; & Schweers, W., 1975, HYDROGENOLYSIS OF LIGNIN. (6). USE OF A SEMIMICRO PROCESS IN STUDIES ON THE HYDROGENOLYSIS SYSTEM, Holzforschung, Vol. 29, No. 1, pp. 18-24, (Ger.; Engl. sum.) cf. ABIPC 45: abstr. 1358.
- Hoffmann, P.; & Schweers, W., 1975, HYDROGENOLYSIS OF LIGNIN. (7). COMPARISON OF SOME SOLVENTS AND CATALYSTS FOR HYDROGENOLYSIS OF SPRUCE LIGNIN, Holzforschung, Vol. 29, No. 3, pp. 73-79, (Ger.; Engl. sum.) cf. ABIPC 43: abstr. 11566.
- Hoffmann, P.; & Schweers, W., 1975, HYDROGENOLYSIS OF LIGNIN. (9). COMPARATIVE HYDROGENOLYSIS OF DIFFERENT LIGNIN PREPARATIONS FROM SOME SPECIES, Paperi Puu, Vol. 57, No. 11, pp. 771-774, 777-778, 783-785, (Engl.; Finn. sum.) cf. ABIPC 46: abstr. 7944.
- Hoffmann, P.; & Schweers, W., 1975, HYDROGENOLYSIS OF LIGNIN. (8). COMPARATIVE HYDROGENOLYSES OF MONOMERIC MODEL COMPOUNDS OF LIGNIN AND LIGNOSULFONATE, Paperi Puu, Vol. 57, No. 9, pp. 581-584, 589-592, (Engl.; Finn. sum.) cf. ABIPC 46: abstr. 4637.
- Hoffmann, P.; & Schweers, W., Special Issue, 1976, HYDROGENOLYSIS OF LIGNIN. (10). COMPARATIVE HYDROGENOLYSES OF LIGNINS, LIGNOSULFONIC ACID, AND LIGNOSULFONATE MODEL COMPOUNDS UNDER IRRADIATION WITH GAMMA-RAYS, Paperi Puu, Vol. 58, No. 4a, pp. 227-230, 233-234, 237-238, 243-244, (Engl.; Finn. sum.) cf. ABIPC 46: abstr. 9995.
- Hrutfjord, B. F., 1971, REDUCTION AND HYDROGENOLYSIS (OF LIGNIN), In Lignin (Wiley-Interscience), pp. 487-509.

- Huibers, D T A; PARKHURST H J (inventor), 9 Mar. 1983, PHENOL PRODN. FROM LIGNIN - BY HYDROCRACKING IN EBULLATED CATALYST BED, (CC Number Kind Date Week) GB 2104545 A, 8310 (Basic) DE 3228897 A 830317 8312, FR 2511697 A 830225 8313, SE 8204813 A 830328 8315, JP 58043932 A 830314 8316, NO 8202840 A 830321 8318, FI 8202896 A 830429 8323, ZA 8205692 A 830518 8336, US 4420644 A 831213 8401, CA 1179374 A 841211 8503, GB 2104545 B 850116 8503, Priority Data (CC, No, Date): US 295459 (810824) Applications (CC, No, Date): GB 8222421 (820803), Patent Assignee: HYDROCARBON RES INC.
- Huibers, D. T. A., & Jones, M. W., 1980, FUELS AND CHEMICAL FEEDSTOCK FROM LIGNOCELLULOSIC BIOMASS, Can. J. Chem., Vol. 58, No. 6, pp. 718-722, (Engl.; Fr. sum.).
- Hurff, S. J., & Klein, M. T., 1983, REACTION PATHWAY ANALYSIS OF THERMAL AND CATALYTIC LIGNIN FRAGMENTATION BY USE OF MODEL COMPOUNDS. I&EC Fundam., Vol. 2, No. 4, pp. 426-430, [Engl.], CA 99,141733x.
- Hwang, B. H., & Sakakibara, A., 1981, HYDROGENOLYSIS OF PROTOLIGNIN. (18). ISOLATION OF A NEW DIMERIC COMPOUND WITH A HEREROCYCLE INVOLVING ALPHA- BETA-DIETHER, Holzforschung, Vol. 35, No. 6, pp. 297-300, [Engl.; Ger. sum.] cf. ABIPC 52: abstr. 10829, CA 96.87252n.
- Hwang, B. H., & Sakakibara, A., 1980, DIMERIC HYDROGENOLYSIS PRODUCT FROM PROTOLIGNIN OF FRAXINUS MANDSHURICA RUPR. VAR. JAPONICA MAX, J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 26, No. 5, pp. 363-364, (Engl.).
- Hwang, B. H., & Sakakibara, A., 1979, HYDROGENOLYSIS OF PROTOLIGNIN. (15). FURTHER ISOLATION OF SOME COMPOUNDS FROM HARDWOOD LIGNIN, J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 25, No. 10, pp. 647-652, (Engl.; Jap. sum.) cf. ABIPC 50: abstr. 4289, CA 92.43460s.
- Hwang, B. H., & Sakakibara, A.; Miki, K., 1981, HYDROGENOLYSIS OF PROTOLIGNIN. (17). ISOLATION OF THREE DIMERIC COMPOUNDS WITH GAMMA-O-4, BETA-1 AND BETA- O-4 LINKAGES FROM HARDWOOD LIGNIN, Holzforschung, Vol. 35, No. 5, pp. 229-232, (Engl.; Ger. sum.) cf. ABIPC 51: abstr. 9502, CA 96.21493k.
- Hwang, B. H., 1981, CHEMICAL STRUCTURES OF PROTOLIGNIN. (1). ISOLATION OF A NEW DIMERIC COMPOUND WITH BETA-ARYL ETHER LINKAGE, J. Tappik, Vol. 13, No. 2, pp. 10-18, [Engl.; Korean sum.], CA 96.124739x.
- Hwang, B. H., 1981, STUDY ON HYDROGENOLYSIS OF PROTOLIGNIN OF FRAXINUS MANDSHURICA, J. Tappik, Vol. 13, No. 1, pp. 27-28, (Korean).
- Hwang, B. H., 1983, CHEMICAL STRUCTURES OF NEW LIGNOLS WITH ETHER LINKAGE, Int. Symp. Wood & Pulping Chem. (Japan), Vol. 1, pp. 95-100, [Engl.].

- Hydrocarbon Research, Inc., COAL HYDROGENATION - IN TWO STAGES USING EBULLATED BED CATALYST, (CC Number Kind Date Week) CA 902529 A 000000 7226 (Basic) Priority Data (CC, No, Date): CA 17208 (680410), HYDROCARBON RESEARCH INC. Drying of carbonaceous solids. (CC Number Kind Date Week) US 3519552 A 000000 7027 (Basic). Priority Data (CC, No, Date): US 707061 (680221).
- Hydrocarbon Research, Inc., 12 Oct. 1976, PASSIVATING PARTICULATE LOW-RANK COALS - BY DRYING AND COATING WITH HEAVY HYDROCARBON OIL. (CC Number Kind Date Week) US 3985516 A, 7643 (Basic). Priority Data (CC, No, Date): US 606256 (750820), HYDROCARBON RES INC. Pharmaceuticals prepd from lignin - by oxygenating and then selectively hydrogenating the lignin (deriv). (CC Number Kind Date Week) JP 75002501 B 27 Jan., 1975, 7508 (Basic). Priority Data (CC, No, Date): JP 6962249 (690806).
- Ikramova, D. R.; Bronovitskii, V. E.; & Kalinskaya, L. L., 1970, HYDROGENOLYSIS OF LIGNIN IN THE PRESENCE OF MONOETHANOLAMINE, Uzbek. Khim. Zh., Vol. 14, No. 5, pp. 97-100, (Russ.; Uzbek sum.) cf. ABIPC 39: abstr. 8532-3, CA 74.100736r.
- International Hydrogenation Patents Co. Ltd., 16 Nov. 1938, UTILIZING SULFITE CELLULOSE WASTE LIQUOR, Fr. Pat. 834,204, CA 53.4011(9). In French.
- Inventa A.-G. für Forschung und Patentverwertung, 16 Sept. 1955, DEGRADATION OF LIGNIN AND LIGNIN-CONTAINING MATERIAL, Swiss Pat. 308,262, CA 51.3142c.
- Inventa A.-G. für Forschung und Patentverwertung, 1 Oct. 1955, DEGRADATION OF LIGNIN AND LIGNIN-CONTAINING MATERIAL, Swiss Pat. 308,560, CA 51.3142c.
- Inventa A.-G. für Forschung und Patentverwertung, 24 Oct. 1956, DECOMPOSING LIGNIN. Brit. Pat. 759,811, CA 51.7718f.
- Iotech Corporation Ltd., 1982, OPTIMIZATION OF STEAM EXPLOSION PRETREATMENT, Final Report for Contract No. DE-AC02-79ET3050.
- Iotech Corporation Ltd., 1982, STEAM EXPLOSION AS A PRETREATMENT FOR BIOMASS CONVERSION, Final Report For Contract No. IB-1-9343-1.
- John, L. S., & Dobrev, S. T., 1973, INFRARED SPECTROSCOPY AND GAS CHROMATOGRAPHIC STUDY OF PHENOLS AND NEUTRAL SUBSTANCES IN THE PRODUCTS OF HYDROLYSIS LIGNIN HYDROGENATION, Tseluloza Khartiya, Vol. 4, No. 4, pp. 22-6, .
- Karavaev, N. M., & Karaseva, E. Z., 1975, THERMOLYSIS OF WOOD IN A FURNACE WITH REPEATED CIRCULATION OF THE HEAT CARRIER, Khim. Tverd. Topliva (Moscow) No. 5, pp. 93-97, (Russ.) cf. ABIPC 40:abstr. 9149.
- Karig, F., & Stahl, E., 1974, INFLUENCE OF THERMOLYSIS CONDITIONS ON FUNCTIONAL GROUPS DURING THERMOFRAC TOGRAPHY OF LIGNINS, Holzforschung, Vol. 28, No. 6, pp. 201-3, (Ger.; Engl. sum.).



- Karpunin, I. I., 1981, TRANSFORMATIONS OF LIGNIN DURING ALKALINE DELIGNIFICATION AND HYDROGENATION OF WOOD IN AQUEOUS MEDIA, Zh. Prikl. Khim., Vol. 54, No. 10, pp. 2282-2289, [Russ.], CA 96.37120x.
- Kashima, K., & Osada, T., 1961, HYDROCRACKING OF LIGNIN, THE, Kogyo Kagaku Zasshi, Vol. 64, pp. 916-919, CA 57.3669b. Noguchi Inst., Tokyo.
- Kashima, K., & Osada, T.; Tabata, H.; Watanabe, H.; Kubo, T., 1963, STUDIES ON THE HYDRO-CRACKING OF LIGNIN BY THE CONTINUOUS PROCESS, J. Jap. Tappi, Vol. 17, No. 1, pp. 25-34, (Original in Jap.; cf. ABIPC 34: abstr. 3678. Engl. transl. available from NTC).
- Kashima, K., & Tabata, H; Watanabe, H., 1961, DECOMPOSITION OF LIGNIN BY HIGH PRESSURE HYDROGEN ADDITION. II. ACIDIC CONSTITUENTS OF LIGNIN LIQUEFIED, Kogyo Kagaku Zasshi, Vol. 64, pp. 919-921, CA 57.7489f.
- Kashima, H, & Tabata, H.; Watanabe, H; Kubo, T., 1962, HYDROCRACKING OF LIGNIN, THE, Kami-pa Gikyoshi, Vol. 16, 901-905, CA 61.12186b.
- Kato, Y., & Sugino, K.-i., 13 June 1939, UTILIZATION OF LIGNIN. Japan. Pat. 130,526, CA 35.1992(8), In Japanese.
- Kirshbums, I. Z.; & Domburga, G., 1970, YIELD AND COMPOSITION OF MONOHYDRIC PHENOLS DURING ACCELERATED PYROLYSIS OF ALKALI LIGNIN, Latv. PSR Zinat. Akad. Vestis, Vol. 1970, No. 2, pp. 43-7 (Russ.).
- Kislitsyn, A. N., & Rodionova, Z. M.; Savinykh, V. I., 1971, CHARACTER OF BOND RUPTURE DURING THERMOLYSIS OF LIGNIN, Sb. Tr. Tsent. Nauch.-Issled. Proekt. Inst. Lesokhim. Prom. Vol. 21, pp. 11-18, (Russ.).
- Klein, M. T., & Virk, P. S., 1981, MODELING OF LIGNIN THERMOLYSIS, ACS Div. Fuel Chem. Preprints of Papers, Vol. 26, No. 3, pp. 77-88, [Engl.].
- Klein, M. T., & Virk, P. S., Feb. 1981, MODEL PATHWAYS IN LIGNIN THERMOLYSIS, Massachusetts Inst. Technol. Energy Lab. Rept. MIT-EL 81-005: 96 p.
- Klein, M. T., & Virk, P. S., 1983, MODEL PATHWAYS IN LIGNIN THERMOLYSIS. (1). PHENETHYL PHENYL ETHER, I&EC Fundam., Vol. 22, No. 2, pp. 35-45, [Engl.].
- Kleinert, Th., 1952, HYDROGENATION OF LIGNIN WITH CYCLOHEXANOL, Monatsh, Vol. 83, pp. 623-628, CA 56.11673t.
- Klemola, A., & Pepper, J. M., 1969, 2-(2-METHOXY-4-n-PROPYLPHENOXY)PROPAN-1-OL AS A NEW SPRUCE LIGNIN HYDROGENOLYSIS PRODUCT. Chem. Commun., No. 18, p. 1048.
- Klemola, A., 1970, HYDROGENATION OF LIGNIN, Soum. Kemistilehti A, Vol. 43, pp. 265-71, CA 74.100702b, in Finnish.

- Kosyukova, L. V., 1975, GAS CHROMATOGRAPHIC ANALYSIS OF PHENOLS OF WOOD THERMOLYSIS TARs, Khromat. Anal. Khim. Drev. pp. 256-260. (Russ.).
- Kringstad, K., 1978, CHALLENGE OF LIGNIN, Future Sources Org. Raw Mats. (St.-Pierre, L. E., & Brown, G. R., eds.)/Invited Lectures IUPAC World Conf. (Toronto)/CHEMRAWN I: 627-636 (c1980 Pergamon Press).
- Kurschner, K., June, Sept., Dec., 1967, NEW RESULTS IN BASIC RESEARCH ON WOOD, Holztechnol., Vol. 8, No. 2, pp. 99-103; No. 3, pp. 153-7; No. 4, pp. 233-6, [Ger.; Russ. & Engl. sum.].
- Lai, Y. Z.; & Sarkanen, K. V., 1971, ISOLATION AND STRUCTURAL STUDIES IN LIGNINS. OCCURRENCE, FORMATION, STRUCTURE AND REACTIONS (Sarkanen, K. V. and Ludwig, C. H., Eds), New York: Wiley - Interscience.
- Lautsch, W., & Freudenberg, K., 30 Sept. 1943, PHENOL OR ITS DERIVATIVES FROM LIGNIN OR LIGNEOUS MATERIALS, Ger. Pat. 741,686, CA 39.2516(4). Deutsche Revisions- und Truhand A.-G. W.
- Lautsch, W., 1941, OXIDATIVE AND HYDROGENATING DEGRADATION OF WOOD, LIGNIN AND SULFUR-CONTAINING WASTE LIQUOR FROM SPRUCE, Cellulosechem., Vol. 19, pp. 69-87, CA 36.6796(5).
- Leary, R., March-June, Aug., Sept., 1967, THE SILVICHEMICAL FILE, Can. Pulp Paper Ind., Vol. 20, No. 3, pp. 25-7; No. 4, pp. 132-3, 135; No. 5, pp. 35-6; No. 6, pp. 36-7; No. 8, pp. 68; No. 9, pp. 64-5.
- Lee, Y. W., & Pepper, J. M., 1978, LIGNIN AND RELATED COMPOUNDS. (7). ISOLATION OF A TRIMERIC LIGNIN COMPOUND BY HYDROGENOLYSIS OF SPRUCE WOOD, Tetrahedron Letters No. 51: 5061-5062, CA 91.56521s.
- Leger, F.; & Hibbert, H., 1938, J. Am. Chem. Soc., Vol. 60, p. 565.
- Leopold, B., 1952, Acta Chem. Scand., Vol. 6, p. 38.
- Levin, E. D., & Rachinskii, A. V.; Repyakh, S. M., 1975, HYDROCRACKING WITH RESIDUELESS PROCESSING OF RESINOUS WASTES FROM THE SILVICHEMICAL INDUSTRY, Izv. VUZ, Lesnoi Zh., Vol. 18, No. 6, pp. 105-108, (Russ.) cf. ABIPC 45:abstr. 8311.
- Lin, S. Y., & Kringstad, K. P., 1970, STABILIZATION OF LIGNIN AND LIGNIN MODEL COMPOUNDS TO PHOTODEGRADATION, Tappi, Vol. 53, No. 9, pp. 1675-7.
- Lin, S. Y.; 1983, "LIGNIN UTILIZATION: POTENTIAL AND CHALLENGE," Progress in Biomass Conversion, Vol. 4, NY: Academic Press, pp. 33-78.
- Loubinoux, B., & Heitz, M.; Coudert, G.; Guillaumet, G., 1980, HYDROGENOLYSIS OF LIGNINS (WITH) NICKEL BORIDE CATALYST, Tetrahedron Letters, Vol. 21, No. 51, pp. 4991-4994, CA 95.24421a.

- Loubinoux, B., 15 Jan. 1982, LIGNIN HYDROGENOLYSIS AND ITS USE IN THE PRODUCTION OF 4-ETHYL-2-METHOXYPHENOL AND 2,6-DIMETHOXY-4-ETHYLPHENOL, Fr.Damande FR 2,486,524(CL C07C43/23), 15 pp. 97.5971e.
- Lundquist, K., 1970, ACID DEGRADATION OF LIGNIN. II. SEPARATION AND IDENTIFICATION OF LOW-MOLECULAR-WEIGHT PHENOLS, Acta Chem. Scand., Vol. 24, No. 3, pp. 889-907 (Eng.).
- Madan, R. N., & Upadhyaya, J. S., 1982, PLANTS AND SILVICHEMICALS AND THEIR IMPORTANCE IN HUMAN AFFAIRS, Pulp Paper World, Vol. 2, No. 5-6, pp. 21-27, [Engl.].
- Manville, J. F., & Pepper, J. M., July 4-6, 1973, HYDROGENOLYSIS PULPING, Can. Wood Chem. Symp. (Chem. Inst. Can./CPPA, Chateau Frontenac), Extended Abstrs. Papers Presented 4, pp. 31-7.
- Matsukura, M., & Sakakibara, A., 1973, HYDROGENOLYSIS OF PROTOLIGNIN. (8). ISOLATION OF A DIMER WITH BETA-BETA PRIME C-C LINKAGE AND A BIPHENYL, J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 19, No. 4, pp. 171-6, (Engl.; Jap. sum.) cf. ABIPC 44: abstr. 3756.
- Matsukura, M., & Sakakibara, A., 1971 ISOLATION OF NEW DIMERIC AND TRIMERIC COMPOUNDS WITH CARBON-TO-CARBON LINKAGES FROM HYDROGENOLYSIS PRODUCTS OF PROTOLIGNIN, J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 17, No. 6, pp. 263-4, (Engl.) cf. ABIPC 40: abstr. 7794.
- Matsukura, M., & Sakakibara, A., 1971, ISOLATION OF FURTHER DIMERIC COMPOUNDS WITH CARBON-TO-CARBON LINKAGE FROM HYDROGENOLYSIS PRODUCTS OF PROTOLIGNIN, J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 17, No. 6, pp. 265-6, (Engl.) cf. ABIPC 42: abstr. 8967.
- Matsukura, M., & Sakakibara, A., 1973, HYDROGENOLYSIS OF PROTOLIGNIN. (5). ISOLATION OF SOME DIMERIC COMPOUNDS WITH CARBON-TO-CARBON LINKAGE. (6). ISOLATION OF A NEW TRIMERIC COMPOUND WITH CARBON-TO-CARBON LINKAGE, J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 19, No. 3, pp. 131-5, 137-40, (Engl.; Jap. sum.) cf. ABIPC 40: abstr. 7794; 42: abstr. 8966-7.
- Matsukura, M., & Sakakibara, A., 1969, HYDROGENOLYSIS OF PROTOLIGNIN. IV. ISOLATION OF A DIMERIC MATERIAL OF THE "CONDENSED TYPE", J. Japan Wood Res. Soc., Vol. 15, No. 7, pp. 297-302, (Engl.; Jap. sum.) cf. ABIPC 40: abstr. 7796, .
- Meier, D., & Schweers, W., 1981, PROPERTIES AND DECOMPOSITION OF LIGNINS ISOLATED BY MEANS OF ALCOHOLIC WATER MIXTURES. (4). PRODUCTION OF MONOMERIC PHENOLS BY CATALYTIC HYDROGENOLYSIS, Holzforschung, Vol. 35, No. 2, pp. 81-85, (Ger.; Eng. sum.) cf. ABIPC 51: abstr. 4506, CA 95.99542z.

- Melms, F., & Schwenzon, K., 1967, APPLICATIONS OF SPENT SULFITE LIQUOR, (Verwertungsgebiete fur Sulfitablauge). Leipzig, Deutscher Verlag fur Grundstoffindustrie, 541 p. (Ger.).
- Merewether, J. W. T., & Samsuzzaman, L. A. M.; Cooke, R. G., 1972, STUDIES ON A LIGNIN-CARBOHYDRATE COMPLEX. (3). NATURE OF THE COMPLEX, Holzforschung, Vol. 26, No. 6, pp. 193-7, (Engl.; Ger. sum.) cf. ABIPC 43: abstr. 11863.
- Miller, J. G., & Schuerch, C., 1968, SYNTHESIS OF 2,4'-DIHYDROXY-3,5'-DIMETHOXY-5-ETHYLBIBENZYL AND ITS FORMATION IN LIGNIN HYDROGENATION, Tappi, Vol. 51, No. 6, pp. 273-7.
- Miyazaki, M., & Oda, K.; Ishihara, T.; Tanaka, J.; Furuya, N.; Yamaguchi, A.; Takahashi, S.; Hiroi, T.; Shimizu, K.; Sakakibara, A., 1966, STUDIES ON HYDROGENATION OF LIGNIN IN CONTINUOUS EQUIPMENT, Bull. Govt. Forest Expt. Sta. (Tokyo) Vol. 195, pp. 57-159, (Jap.; Engl. sum.).
- Moldavskii, B. L.; & Vainshtein, K., 1935, HYDROGENATION OF A LIGNIN, Khim. Tverdogo Topliva, Vol. 6, pp. 656-662, CA 30.8570(2).
- Monsanto Chemical Co., 5 Aug. 1953, Brit. Pat. 695,301.
- Moore, R.G.D., & Hibbert, H., 1936, LIGNIN AND RELATED COMPOUNDS. XXVIII. THE BEHAVIOR OF LIGNIN TOWARD ACTIVATED HYDROGEN, Can. J. Research, Vol. 14, pp. 404-407, CA 31.1199(9).
- Morgen, L. M., 1966, PHENOLS AS THERMOLYSIS PRODUCTS OF COTTON HULL LIGNIN, Struktura i Modifik. Khlopk. Tsellyulozy, No. 3, pp. 365-73, (Russ.), .
- Morikawa, K., & Kimoto, T.; Ryonosuke, A., 1941, DIRECT DETERMINATION OF OXYGEN IN ORGANIC COMPOUNDS BY HYDROGENATION. III. REDUCTION MECHANISM ON THE NICKEL- THORIA CATALYST, Bull. Chem. Soc. Japan, Vol. 16, pp. 229-232, CA 36.722(2).
- Morita, M., & Sato, S., Feb. 15, 1980, LIQUEFACTION OF COAL AND LIGNIN, Jap. pat. Kokai 21,478/80. 6 p. Cl.C10G1/06. Filed: Jap. appln. 84,440/79 (July 4, 1977), CA 93.10659f.
- Morohoshi, N., & Sakakibara, A., 1971, DISTRIBUTION OF CONDENSED TYPE (STRUCTURES) IN LIGNIN: COMPARISON OF LIGNIN FRACTIONS IN HYDROGENOLYSIS PRODUCTS OF MWL, LCC (LIGNIN-CARBOHYDRATE COMPLEX), AND WOOD RESIDUE. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 17, No. 8, pp. 354-61. (Original in Jap.; cf. ABIPC 42: abstr. 8970. Engl. transl. available from IPC).
- Morohoshi, N., & Sakakibara, A., 1971, STUDIES ON HYDROGENOLYSIS OF MILLED WOOD LIGNIN: PROPERTIES OF FRACTIONS SEPARATED BY GEL FILTRATION. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 17, No. 8, pp. 347-53. (Jap.; Engl. sum.).

- Murashkevich, T. V.; Runtso, A. P.; & Skrigan, A. I., 1970, SYNTHESIS OF RESINS FROM TOTAL PHENOLS ISOLATED DURING PYROLYSIS OF WOOD HYDROLYSIS LIGNIN, Issled. Prir. Sn. Polim Mater. Ikh Ispol'z, pp. 176-79 (Russ.).
- Murashkevich, T. V.; Skrigan, A. I.; & Khat'ko, A. I., 1970, PYROLYTIC DECOMPOSITION OF HYDROLYSIS LIGNIN, Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk, No. 1, pp. 80-4 (Russ.).
- Naham, L.S., 1965, DELIGNIFICATION OF WOOD BY HYDROGENATION IN THE PRESENCE OF DICOBALT OCTACARBONYL. Ind. Eng. Chem., Prod. Res. Develop. No. 4, pp. 71-74. CA 63.1983f.
- Naham, L. S. April 1969, ESTIMATION OF DOUBLE BOND CONTENT IN LIGNIN FROM RESULTS OF THE OXO REACTION OF WOOD AND LIGNIN MODEL COMPOUNDS. Tappi, Vol. 52, No. 4, pp. 712-14.
- Nakatsubo, F., & Higuchi, T., 1975, SYNTHESIS OF 1,2-DIARYLPROPANE-1,3-DIOLS AND DETERMINATION OF THEIR CONFIGURATIONS. Holzforschung, Vol. 29, No. 6, pp. 193-198, (Engl.; Ger. sum.).
- Nakatsubo, F., & Sato, K.; Higuchi, T., 1975, SYNTHESIS OF GUAIACYLGLYCEROL- BETA-GUAIACYL ETHER. Holzforschung, Vol. 29, No. 5, pp. 165-168. (Engl.; Ger. sum.).
- Nimz, H.; Das, K.; & Minemur, N., 1971, LOW-MOLECULAR-WEIGHT DEGRADATION PRODUCTS OF LIGNIN. I. DEGRADATION OF BEECHWOOD LIGNIN WITH THIOACETIC ACID, Chem. Ber., Vol. 104, No. 6, pp. 1871-6 (Ger.).
- Nippon Kaihatsu Consultant K.K., April 10, 1981, CATALYTIC CRACKING OF HEAVY OIL AND THE CATALYST. Jpn. Patent Kokai Tokkyo Koho 81 37,046. 4 pp. CA 95.83493q.
- Nippon Kaihatsu Kogyo KK., January 12, 1981, CATALYTIC CRACKING OF HEAVY PETROLEUM OILS. Jap. pat. Kokai 2,389/81. 5 p. Cl.C10G11/02. Filed: Jap. appln. 77,546/79 (June 21, 1979) CA 94.142526.
- Noguchi Research Foundation, September 4, 1963, LIQUEFACTION OF LIGNIN. Japan. Pat. 17,018 ('63). 2 pp. CA 59.13012f. M. Oshima, Y. Maeda, and H. Kajima were the inventors.
- O'Neil, D. J., 1978, INTEGRATED CHEMICAL SYSTEM FOR WHOLE-TREE UTILIZATION OF PARAQUAT-TREATED PINES. Lightwood Res. Coord. Council Proc. Ann. Mtg. (Atlantic Beach, FL): 54-65 (Jan. 10-11, 1978). [Avail. from SE Forest Expt. Sta., Box 2570, Asheville, NC 28802].
- Oelert, H. H., & El Saied, H., 1977, CONVERSION OF AGRICULTURAL WASTE PRODUCTS TO OIL. Erdol Kohle Erdgas Petrochemie, Vol. 30, No. 3, pp. 138, (Ger.), .

- Ohta, M., & Sakakibara, A., October 1969, HYDROGENOLYSIS OF PROTOLIGNIN. III. ISOLATION OF DIGUAIACYLPROPANOL, AND CHROMATOGRAPHIC DETECTION OF SOME MONOMERS. J. Japan Wood Res. Soc., Vol. 15, No. 6 pp. 247-50, (Engl.; Jap. sum.) cf. ABIPC 40: abstr. 7804.
- Oiwa, S., & Kashima, H.; Fukushima, M.; Morita, M., September 8, 1959, LIQUEFATION OF LIGNIN. Japan. Pat. 7920('59), CA 54.3952g. Assigned to Noguchi Research Institute, Inc.
- Olcay, A., 1962, LIGNIN AND LIGNIFICATION. XXV. HYDROGENATION OF MILLED-WOOD LIGNINS FROM WHITE PINE AND BLUE SPRUCE. J. Org. Chem., Vol. 27, pp. 1783-1786. CA 57.4907i.
- Olcay, A., 1963, INVESTIGATIONS OF LIGNINS AND LIGNIFICATION. XXIX. HYDROGENATION PRODUCTS OF SPRUCE MILLED-WOOD LIGNIN AND OF RELATED MODEL COMPOUNDS. Holzforschung, Vol. 17, pp. 105-110. CA 60.756a. In English.
- Oshima, M., & Kashima, K.; Kubo, T.; Tabata, H.; Watanabe, H., 1966, STUDIES OF THE HYDROCRACKING OF LIGNIN. (1) THE HYDROCRACKING OF DESULFONATED SULFITE WASTE LIGNIN. (2) COMPONENTS OF LIGNIN HYDROCRACKING PRODUCTS. (3) HYDROCRACKING OF VARIOUS TYPES OF LIGNIN. (4) EVALUATION OF CATALYSTS. Bull. Chem. Soc. Japan, Vol. 39, No. 12, pp. 2750-67 (1966). (Engl.), CA 66.56775m.
- Oshima, M.; Maeda, Y.; & Kashima, K., 14 Dec. 1965, LIQUEFYING LIGNIN, U.S. Pat. 3,223,698, 9 pp. (Noguchi Institute).
- Oshima, M.; Maeda, Y.; & Kajima, H., 4 Sept. 1963, LIQUEFACTION OF LIGNIN, Japan. Pat. 17,018('63), 2 pp. (Noguchi Institute).
- Oshima, M.; Maeda, Y.; & Kajima, H., 1 Aug. 1963, LIQUEFACTION OF LIGNIN, Japan. Pat. 13,864('63), 3 pp. (Noguchi Institute).
- Oshimo, M., & Maeda, Y.; Kashima, K., 26 Oct., 1961, LIQUEFACTION OF LIGNIN COMPOUNDS. Ger. Pat. 1,115,737. 6 pp. CA 57.11436. Noguchi Inst., Tokyo.
- Oshimo, M.; Maeda, Y.; & Kashima, K., 26 Oct. 1961, LIQUEFACTION OF LIGNIN COMPOUNDS, Ger. Pat., 1,115,737, 6 pp. (Noguchi Institute).
- Osuskii, A., & Kubin, (J.) Yu., 1965, HYDROLYSIS LIGNIN, ITS ACTIVATION WITH ALKALI UNDER PRESSURE AND ITS USES. Perspekt. Grundlagenforsch. Holzes, Bratislava, 1963, pp. 221-4. (Russ.; Slovak. & Ger. sum.).
- Panasyuk, V. G., 1957, THERMAL TREATMENT OF HYDROLYTIC LIGNIN. IV. MECHANISM OF VACUUM-THERMAL PROCESS OF LIQUID-PHASE DECOMPOSITION OF LIGNIN AND THE EFFECT OF PHYSICAL FACTORS, J. Appl. Chem. USSR, Vol. 30, pp. 1258-65 (English translation).

- Panasyuk, V. G., 1957, THERMAL TREATMENT OF HYDROLYTIC LIGNIN. III. PHENOLS FROM THE DECOMPOSITION OF HYDROLYTIC LIGNIN, J. Appl. Chem. USSR, Vol. 30, pp. 1114-20 (English translation).
- Panasyuk, V. G., 1957, THERMAL TREATMENT OF HYDROLYTIC LIGNIN. I. VACUUM-THERMAL DECOMPOSITION OF WOOD HYDROLYTIC LIGNIN IN A LIQUID PHASE, Zhur. Priklad. Khim., Vol. 30, pp. 598-603.
- Panasyuk, V. G.; Panasyuk, L. V.; Marksimenko, N. S.; & Lapshin, F. S., 1959, THERMAL DECOMPOSITION OF HYDROLYTIC LIGNIN UNDER VACUUM, Gidrolis i Lesokhim. Prom., Vol. 12, No. 7, pp. 16-17.
- Panasyuk, V. G., 1958, THERMAL TREATMENT OF HYDROLYTIC LIGNIN. VI. COMPARISON OF DIFFERENT METHODS OF THERMAL DECOMPOSITION OF HYDROLYTIC LIGNIN, Zhur. Priklad. Khim., Vol. 31, pp. 1605-07.
- Panasyuk, V. G., 1958, THERMAL SOLUTION OF COTTON-SEED-HULL LIGNIN, Zhur. Priklad. Khim., Vol 31, pp. 1409-14.
- Panasyuk, V. G.; & Maksimenko, N. S., 1958, THERMAL DECOMPOSITON OF HYDROLYTIC LIGNIN FROM COTTON-SEED HULLS, Gidrolz i Lesokhim Prom., Vol. 11, No. 1, pp. 16-17.
- Parker, P. E., 1967, ALKALINE HYDROGENATION OF LIGNIN IN MAPLEWOOD. Ph.D. Thesis. State Univ. College of Forestry at Syracuse Univ., 131 p., Diss. Abstr. 27, Vol. 9 pp. 3044B (March, 1967).
- Parkhurst, H. J., & Jr.; Huibers, D. T. A.; Jones, M. W., 1980, PRODUCTION OF PHENOL FROM LIGNIN. ACS Div. Petroleum Chem. Preprints, Vol. 25, No. 3, pp. 657-667.
- Pearl, I. A., 1942, J. Am. Chem. Soc., Vol. 64, p. 1429.
- Pearl, I. A., 1944, J. Org. Chem., Vol. 9, p. 429.
- Pearl, I. A., 1950, J. Am. Chem. Soc., Vol. 72, p. 2309.
- Pearl, I. A., 4 Oct., 1949, U.S. Pat. 2,483,559.
- Pearl, I. A., March 1974, ANNUAL REVIEW OF LIGNIN CHEMISTRY. IPC (Appleton, Wis.), 90 p.
- Pepper, J. M., & Fleming, R. W., 1978, LIGNIN AND RELATED COMPOUNDS. (5). HYDROGENOLYSIS OF ASPEN WOOD LIGNIN USING RHODIUM-ON-CHARCOAL AS CATALYST. Can. J. Chem., Vol. 56, No. 7, pp. 896-898, (Fr. sum.) cf. ABIPC 43: abstr. 6050, CA 89.112850w. This citation is also contained in HYDROG.
- Pepper, J. M., & Lee, Y. W., 1970, LIGNIN AND RELATED COMPOUNDS. II. STUDIES USING RUTHENIUM AND RANEY NICKEL AS CATALYSTS FOR LIGNIN HYDROGENOLYSIS. Can. J. Chem., Vol. 48, No. 3, pp. 477-9; cf. ABIPC 40: abstr. 231.

- Pepper, J. M., & Lee, Y. W., 1969, LIGNIN AND RELATED COMPOUNDS. (1). COMPARATIVE STUDY OF CATALYSTS FOR LIGNIN HYDROGENOLYSIS. Can. J. Chem., Vol. 47, No. 5, pp. 723-7. CA 70.88972x.
- Pepper, J. M., & Supathna, P., 1978, LIGNIN AND RELATED COMPOUNDS. (6). STUDY OF VARIABLES AFFECTING THE HYDROGENOLYSIS OF SPRUCE WOOD LIGNIN USING A RHODIUM-ON-CHARCOAL CATALYST. Can. J. Chem., Vol. 56, No. 7, pp. 899-902. CA 89.26259d.
- Pepper, J. M., & Brounstein, C. J.; Shearer, D. A., 1951, STUDIES ON LIGNIN BY MEANS OF CATALYTIC HYDROGENATION OF ASPENWOOD AND WHEAT STRAW. J. Am. Chem. Soc., Vol. 73, pp. 3316-3319. CA 46.1253f.
- Pepper, J. M., & Steck, W., 1963, THE EFFECT OF TIME AND TEMPERATURE ON THE HYDROGENATION OF ASPEN LIGNIN. Can. J. Chem. Vol. 41, pp. 2857-2875. CA 59.14189c.
- Pepper, J. M., & Steck, W. F.; Swaboda, R.; Karapally, J. C., 1966, HYDROGENATION OF LIGNIN BY USING NICKEL AND PALLADIUM CATALYSTS. Advan. Chem. Ser., Vol. 59, pp. 238-248. CA 66.20090v.
- Phillips, 1929, Chemistry of Lignin. II. DESTRUCTIVE DISTILLATION OF LIGNIN FROM CORN COBS, J. Am. Chem. Soc., Vol. 51, pp. 2420-26.
- Phillips, M., & Goss, M.J., 1932, LIGNIN. VI. DISTILLATION OF ALKALI LIGNIN WITH ZINC DUST IN AN ATMOSPHERE OF HYDROGEN. J. Am. Chem. Soc. Vol. 54, pp. 1518-1521. CA 26.2711.
- Phillips, M., 1933, DRY DISTILLATION OF RESIDUE OF WASTE SULFITE LIQUOR, Ind. Eng. Chem., Vol. 25, pp. 991-3.
- Phillips, M., 1931, CHEMISTRY OF LIGNIN. V. DISTILLATION OF ALKALI LIGNIN WITH ZINC DUST IN AN ATMOSPHERE OF HYDROGEN. J. Am. Chem. Soc. Vol. 53, pp. 768-774. CA 25.1230.
- Phillips, M.; & Goss, M. J., 1932, CHEMISTRY OF LIGNIN. VII. DISTILLATION OF ALKALI LIGNIN IN REDUCED ATMOSPHERE OF CARBONDIOXIDE, Ind. Eng. Chem., Vol. 24, pp. 1436-41.
- Pines, H., 1981, "THE CHEMISTRY OF CATALYTIC HYDROCARBON CONVERSIONS", McGraw-Hill.
- Ploetz, T., & Richtzenhain, H.; Deiters, W.; Giesen, J., January 1963, LOW-BOILING CLEAVAGE PRODUCT PREPARATION FROM LIGNIN. German Pat. 1,142,853, 31 6 pp. Assigned to Reldmuehie A.-G. CA 58.8137h.
- Ploetz, T.; Richtzenhain, H.; Dieters, W.; & Giesen, T., 31 Jan. 1963, LOW-BOILING CLEAVAGE PRODUCT PREPARATION FROM LIGNIN, Ger. Pat. 1,142,853, 6 pp.



- Pressure Chemical Co., 1968, NEW "SELECTIVE" HYDROGENATION PULPING PROCESS. Pulp Paper Mag. Can., Vol. 69, No. 15, p. 30.
- Prosinski, S., & Czechowski, Z.; Kielczewski, M., 1970, THERMOLYSIS OF OAKWOOD LIGNIN AND SOME PROPERTIES OF THE PRODUCTS OBTAINED. Koks. Smola. Gaz, Vol. 15, No. 11, pp. 322-3, (Pol.; Russ., Engl.; Fr. & Ger. sum.).
- Rachinskii, A. V., & Dorzet, N. M.; Levina, L. M.; Chuprova, N. A.; Belikova, Z. P.; Repyakh, S. M.; Nikolaeva, G. V.; Tikhomirova, G. V.; Levin, E. D., 1975, CHROMATOGRAPHIC ANALYSIS OF CONDENSING PRODUCTS OF WOOD PYROLYSIS. Khromat. Anal. Khim. Drev., pp. 249-255. (Russ.).
- Rachinskii, A. V., & Levin, E. D., 1974, COMPOSITION OF HYDROCRACKING PRODUCTS OF THE OIL FROM LIGNIN PYROLYSIS TAR. Izv. VUZ, Lesnoi Zh., Vol. 17, No. 1, pp. 111-13, (Russ.).
- Rachinskii, A. V., & Levin, E. D., 1975, EFFECT OF TECHNOLOGICAL FACTORS ON PRODUCT YIELD FROM THE HYDROCRACKING OF THE TOTAL OIL OBTAINED FROM LIGNIN PYROLYSIS TAR. Izv. VUZ, Khim. i Khim. Tekhnol., Vol. 18, No. 4, pp. 645-648, (Russ.).
- Reale, M.J., & Clarke, D.D.; Schubert, W.J.; Nord, F.F., 1966, LIGNINS AND LIQNIFICATION. XXXI. CHARACTERIZATION OF METASEQUOIA MILLED WOOD LIGNIN. Holzforschung, Vol. 20, pp. 31-36. CA 65.5650g (Engl.).
- Richterova, V., May 15, 1982, SEMICHEMICAL PULP AND LIGNIN. Czechosl. pat. 195,751. Issued May 15, 1982. 3pp. Cl.D213C3/00. Filed: Czechosl. appln. 2,646/67 (April 11,1967).
- Rieche, A., & Redinger, L.; Lindenhayn, K., 1964, HYDROGENOLYSIS OF LIGNIN AND ANALYSIS OF PHENOLIC PRODUCTS. Monatsber. Deut. Akad. Wiss. Berlin, Vol. 6, pp. 430-439. GERMAN. CA 62.7991a.
- Rieche, A., & Redinger, L.; Lindenhayn, K., 1966, HYDROGENATION OF LIGNIN. Brennst. Chem., Vol. 47, pp. 326-330. In German. CA 66.77125q.
- Riikuris, A. V., & Bisenietse, S. K., 1974, COMPOSITION AND PROPERTIES OF TAR FORMED DURING THERMOLYSIS OF LIGNOCELLULOSE. (3). POTENTIOMETRIC TITRATION IN A NON-AQUEOUS MEDIUM OF LIGNIN AND OF PRODUCTS OF THERMAL DEGRADATION OF CORNCOB AND BIRCHWOOD LIGNOCELLULOSE. Khim. Drev. (Riga) Vol. 15, pp. 135-43, (Russ.) cf. ABIPC 45: abstr. 10820.
- Riikuris, A. V., & Bisenietse, S. K., 1976, COMPOSITION AND PROPERTIES OF TAR FORMED DURING THERMOLYSIS OF LIGNOCELLULOSE. (7). DETERMINATION OF ACID GROUPS IN COMPOUNDS ISOLATED FROM TAR FORMED DURING THE THERMOLYSIS OF BIRCHWOOD AND IN MODEL AROMATIC HYDROXY ACIDS. Khim. Drev. (Riga) No. 1, pp. 78-83, (Russ.) cf. ABIPC 47:abstr. 507.

- Rudnick, L.R., October 11, 1983, COAL LIQUEFACTION AND RESID. PROCESSING WITH LIGNIN. U.S. Pat. 4,409,089. 5 pp. CA 100.9896n. Assigned to Mobil Oil Corp.
- Rydholm, S. A., 1965, Pulping Processes, NY: Wiley.
- Sakakibara, A., & Edashige, Y.; Uematsu, T.; Takeyama, H., 1983, HYDROGENOLYSIS PULPING. Japan Tappi, Vol. 37, No. 4, pp. 343-348, [Jap.; Engl. sum.].
- Sakakibara, A., & Ohta, M.; Wada, I.; Matsukura, M., 1969, HYDROGENOLYSIS OF PROTOLIGNIN. J. Japan Wood Res. Soc., Vol. 15, No. 2, p. 84, (Engl.), CA 71.82805u.
- Sakakibara, A., & Sudo, K.; Kishi, M.; Aoyama, M.; Hwang, B. H., 1980, HYDROGENOLYSIS OF PROTOLIGNIN. (16). ISOLATION OF beta-O-4 AND beta-beta TYPE COMPOUNDS. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 26, No. 9, pp. 628-632, (Engl.; Jap. sum.) cf. ABIPC 50: abstr. 10145, CA 94.5064z.
- Sakakibara, A., & Tadasi, A., 1961, PRESSURE HYDROGENOLYSIS OF LIGNIN. III. SELECTION OF CATALYSTS FOR OBTAINING PHENOLS. Nippon Mokuzai Gakkaishi, Vol. 7, pp. 19-23. CA 55.20421f.
- Sakakibara, A., & Tanaka, J; Furuya, N., 1966, STUDIES ON HYDROGENOLYSIS OF LIGNIN. (6) FACTORS AFFECTING HYDROGENOLYSIS OF LIGNOSULFONIC ACIDS WITH IRON PENTACARBONYL CATALYST. J. Japan Wood Res. Soc., Vol. 12, No. 5, pp. 245-50, [Jap.; Engl. sum.] cf. A.B.I.P.C. 36: abstr. 7885.
- Sakakibara, A., 1976, DEGRADATION PRODUCTS OF PROTOLIGNIN AND THE STRUCTURE OF LIGNIN. Recent Adv. Phytochem., 11 (Proc. 16th Ann. Mtg. Phytochem. Soc. N.Am., Aug. 1976 Vancouver) pp. 117-139 (Plenum Press 1977).
- Sakakibara, A., 1980, STRUCTURAL MODEL OF SOFTWOOD LIGNIN. Wood Sci. Technol. (NY), Vol. 14, No. 2, pp. 89-100.
- Sakakibara, A., 1983, CHEMICAL STRUCTURE OF LIGNIN RELATED MAINLY TO DEGRADATION PRODUCTS. Recent Adv. Lignin Biodegradation Res. (T. Higuchi, H.-M. Chang & T. K. Kirk, eds.) pp. 12-33 (c1983, Uni Publ. Co., Tokyo). [Engl.].
- Sakakibara, A., December 23, 1963, PHENOLS FROM LIGNIN OR LIGNIN-CONTAINING MATERIAL. Japan. Pat. 26,668. 23 Dec., 1963. 3 pp. CA 60.10920b. Japanese patent issued to the Forestry Institute.
- Sakakibara, A., 1981, HYDROGENOLYSIS OF LIGNIN. IUFRO 17th World Congress (Kyoto), September 6- 12, Vol. 5, pp. 367-375.
- Salyamova, F., & Bronovitskii, V. E., 1970, CATION-EXCHANGE RESINS FROM LIGNIN. Uzbek Khim. Zh., Vol. 14, No. 3, pp. 72-3, (Russ.; Uzbek sum.).

- Sangalova, N. A., & Kravchenko, M. I.; Uvarov, I. P., 1968, SEDIMENTATION TARS FROM THERMOLYSIS OF HYDROLYSIS LIGNIN. Sb. Tr. TNII Lesokhim. Prom. Vol. 19, pp. 46-51, (Russ.).
- Sano, Y., & Sakakibara, A., 1980, HYDROGENOLYSIS OF LIGNIN WITH MIXTURE OF ALCOHOL, SODIUM HYDROXIDE, AND WATER. Res. Bull. Coll. Expt. Forest Hokkaido Univ., Vol. 37, No. 1, pp. 241-259, (Jap.; Engl. sum.), CA 93.74120f.
- Sarkanen, K. V., & Ludwig, C. H., Editors, 1971, LIGNINS: OCCURRENCE, FORMATION, STRUCTURE, AND REACTIONS. Wiley-Interscience (N.Y., London, Sydney, Toronto), c1971, 916 p.
- Sarkanen, K. V., 1980, "ACID-CATALYZED DELIGNIFICATION OF LIGNOCELLULOSICS IN ORGANIC SOLVENTS", Progress in Biomass Conversion, Vol. 2, pp. 127-44.
- Sarkanen, K. V., 1979, LIGNIN AND PHENOLIC POLYMERS. IUPAC Intern. Cong. (27th) Pure Appl. Chem., pp. 299-306 (Aug. 27-31, 1979; c1980), .
- Satterfield, R.N., 1981, "HETEROGENEOUS CATALYSIS, IN PRACTICE", McGraw-Hill.
- Saur, M., & Medonos, V.; Ruzicka, V., 1983, PYROLYSIS OF A SODIUM SALT OF KRAFT LIGNIN IN HYDROGEN ATMOSPHERE. Chem. Prumysl, Vol. 33, No. 12, pp. 652-655, [Czech].
- Schultz, L., 16 Jan., 1940, U.S. Pat. 2,187,366.
- Schultz, T. P., & Chen, C. L.; Goldstein, I. S.; Scaringelli, F. P. 1981, ANALYSIS OF LIGNIN HYDROGENATION PRODUCTS BY GAS CHROMATOGRAPHY. J. Chromat. Sci., Vol. 19, No. 5, pp. 235-237, CA 95.63952u.
- Schultz, T. P., & Chen, C.-L.; Goldstein, I. S., 1982, ATTEMPTED DEPOLYMERIZATION OF HCL LIGNIN BY CATALYTIC HYDROGENOLYSIS. J. Wood Chem. Technol., Vol. 2, No. 1, pp. 33-46, CA 97.7889r.
- Schultz, T. P., 1981, SYSTEMATIC STUDY OF REDUCTIVE DEGRADATION OF HCL LIGNIN INTO USEFUL CHEMICALS. North Carolina State Univ. (Raleigh), Ph.D. thesis: 135 p. [Avail. from Univ. Microfilms, Ann Arbor, MI 48106; no. 8128503.], .
- Schultz, T.P., & Preto, R.J.; Pittman, J.L.; Goldstein, I.S., 1982, HYDROTREATING OF HYDROCHLORIC ACID LIGNIN IN A HYDROGEN-DONOR SOLVENT. J. Wood Chem. Technol, Vol. 2, No. 1, pp. 17-31. CA 97.7988q.
- Schuman, S. C., & Field, S., September 15, 1970, HYDROGENATION OF SULFITE WASTE LIQUOR. Can. pat. 851,709. Issued Sept. 15, 1970. 30 claims, Assignee: Hydrocarbon Res., Inc.
- Schweers, W., & Beinhoff, O., 1974, HYDROGENATION OF LIGNIN. (5). COMPARATIVE HYDROGENATION OF 4-ALKYLSYRINGOLS. Holzforschung, Vol. 28, No. 1, pp. 20-4, (Ger.; Engl. sum.) cf. ABIPC 43: abstr. 11566.

- Schweers, W., & Lange, W.; Beinhoff, O., 1972, HYDROGENOLYSIS OF LIGNIN. (6). SYNTHESIS AND CHARACTERIZATION OF 3,5-DIMETHOXYALKYLCYCLOHEXANES. Holzforschung, Vol. 26, No. 5, pp. 161-4, (Ger.; Engl. sum.) cf. ABIPC 40: abstr. 4692.
- Schweers, W., 1966, HYDROGENOLYSIS OF LIGNIN. Paperi Puu, Vol. 48, No. 4a, pp. 161-74, (Original in Ger.; cf. ABIPC 37: abstr. 2695. Engl. transl. available from NTC.
- Schweers, W., 1969, HYDROGENOLYSIS OF LIGNIN. (3). COMPARATIVE HYDROGENATIONS OF 4-ALKYLPHENOLS AND OF 4-ALKYLGUAIAICOLS. Holzforschung, Vol. 23, No. 4, pp. 120-7, (Ger.; Engl. sum.) cf. ABIPC 40: abstr. 2006.
- Schweers, W., 1969, HYDROGENOLYSIS OF LIGNIN. (2). HYDROGENATION OF VARIOUS LIGNINS WITH COMPLEX COMPOUNDS OF THE TRANSITION METALS IRON, COBALT, AND NICKEL USED AS CATALYSTS. Holzforschung, Vol. 23, No. 1, pp. 5-9, (Ger.; Engl. sum.) cf. ABIPC 37: abstr. 2695.
- Schweers, W., 1975, RESEARCH PROBLEMS IN WOOD CHEMISTRY IN CONNECTION WITH PROBLEMS OF RAW MATERIAL AND ENERGY. Papier, Vol. 29, No. 1, pp. 1-8, (Ger.; Engl. & Fr. sum.).
- Schweers, W.; & Rechy, M., 1973, REPORT ON THE (LECTURES AND) ROUND-TABLE DISCUSSION ON THE "CHEMISTRY OF WOOD DIGESTION" HELD ON JUNE 25, 1973 IN BADEN-BADEN. (3). PULPING WOOD WITH PHENOLS (III). PULPING PINE- AND BEECH WOOD, Papier, Vol. 27, No. 12, pp. 636-39 (Ger.).
- Seidel, E. M., 1967, NEW DEVELOPMENTS IN SILVICHEMICALS. Econ. Botany, Vol. 21, No. 1, pp. 31-41.
- Sergeeva, V.N., & Surna, J., 1960, THERMAL DECOMPOSITION OF SULFURIC ACID LIGNIN IN A STREAM OF HYDROGEN. Trudy Inst. Lesokhoz. Problem i Khim. Drevesiny, Akad. Nuak Latv. S.S.R. Vol. 21, pp. 107-117. CA 56.6216g. In Russian.
- Sharipdzhanov, A., & Bronovitskii, V. E., 1970, STABILIZATION OF POLYPROPYLENE WITH THE PRODUCTS OF LIGNIN HYDROGENOLYSIS. Uzbek. Khim. Zh., Vol. 14, No. 4, pp. 60 - 1, (Russ.; Uzbek sum.) cf. ABIPC 39: abstr. 6551.
- Sharipdzhanov, A.; Bronovitskii, V. E.; & Usmanov, Kh. U., January 1971, STABILIZER FOR LOW-PRESSURE POLYETHYLENE. USSR Pat. 292,943, CA. 75.37271p. From Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 1971, 48(5), 92.
- Sharipdzhanov, A., & Usmanov, Kh. U., October 24, 1977, SOLUTION FOR FORMING FILMS. USSR pat. 732,307. Issued May 5, 1980. Filed: USSR apln. 2,535,949/23-05.
- Sheppard, E.C., & Harris, E.E.; Saeman, J.P., January 12, 1942, HYDROGENATION AND (OR) HYDROLYSIS OF LIGNIN. Brit. Pat. 542,471. CA 35.4336(3).

- Sherrard, E.C., & Harris, E.E., February 7, 1939, CATALYTIC HYDROGENATION OF LIGNIN, U.S. Pat. 2,146,655. CA 33.3390(9).
- Sherrard, E.C., & Harris, E.E., October 1940, TREATING LIGNIN. Brit. Pat. 528,268. 25, CAL. 35.7712(5).
- Sherrard, E.C., & Harris, E.E., September 7, 1944, SIMULTANEOUS PRODUCTION OF PULP AND HYDROGENATED PRODUCTS FROM LIGNOCELLULOSE. U.S. Pat. 2,328,749. 7 CA 38.1113(6).
- Sherrard, E.C., & Harris, E.E.; Saeman, J.F., November 5, 1941, HYDROGENATION OF LIGNIN AND WASTE PULP LIQUORS. U.S. Pat. 2,220,624. CA 35.1634(3).
- Shimada, M., & Fukuzuka, T.; Higuchi, T., 1971, ESTER LINKAGES OF P-COUMARIC ADID IN BAMBOO AND GRASS LIGNINS. Tappi. Vol. 54, pp. 72-78, (Engl.).
- Shimada, M., 1972, BIOCHEMICAL STUDIES ON BAMBOO LIGNIN AND METHOXYLATION IN HARDWOOD AND SOFTWOOD LIGNINS. Wood Res. (Kyoto) Vol. 53, pp. 19-65, (Engl.).
- Shishkin, V. A., & Yur'ev, Yu. L., 1975, CATALYTIC CRACKING OF SEDIMENTATION TAR OILS FROM PYROLYSIS OF HYDROLYSIS LIGNIN. Izv. VUZ, Lesnoi Zh., Vol. 18, No. 3, pp. 113-116, (Russ.) cf. ABIPC 44:abstr. 1685.
- Shorygina, N. N.; & Kefeli, T. Ya., 1947, THE DECOMPOSITION OF LIGNIN BY METALLIC SODIUM IN LIQUID AMMONIA, J. Gen. Chem. (U.S.S.R.), Vol. 17, pp. 2058-65 (Russ.).
- Shorygina, N. N.; & Kefeli, T. Ya., 1948, REACTION OF LIGNIN WITH METALLIC SODIUM IN LIQUID AMMONIA. II., Zhur. Obshchei Khim., Vol. 18, pp.528-33 (Russ.).
- Shorygina, N. N.; & Kefeli, T. Ya., 1950, CLEAVAGE OF LIGNIN WITH METALLIC SODIUM IN LIQUID AMMONIA. IV., Zhur. Obshchei Khim., Vol. 20, pp. 1199-1208 (Russ.).
- Shorygina, N. N.; Kefeli, T. Ya.; & Semechkina, A. F., 1949, CLEAVAGE OF LIGNIN BY METALLIC SODIUM IN LIQUID AMMONIA, Doklady Akad. Nauk, U.S.S.R., Vol. 64, pp. 689-92 (Russ.).
- Shorygina, N. N.; Kefeli, T.; & Semechkina, 1949, CLEAVAGE OF LIGNIN BY METALLIC SODIUM IN LIQUID AMMONIA III., Zhur. Obshchei Khim., Vol. 19, pp. 1558-66 (English translation).
- Singerman, G. M., 1980, Methyl Aryl Ethers from Coal Liquids as Gasoline Extenders and Octane Improvers, Gulf Research and Development Co., Pittsburgh, PA 15230, report prepared under contract No. DE-AC01-79C50022.
- Sjöström, E., 1981, Wood Chemistry-Fundamentals and Application, NY: Academic Press.

- Smilga, A. K., & Erin'sh, P. P.; Zakis, G. F.; Gavars, M. P., 1975, CALCULATION METHOD FOR OBTAINING DIFFERENTIAL INFRARED SPECTRA OF LIGNIN. Khim. Drev. (Riga) No. 1, pp. 50-55, (Russ.).
- Snajberk, K., & Zavarin, E., August 1970, HYDROGENOLYSIS OF WHITE FIR LIGNIN USING METALLIC NICKEL CATALYST GENERATED IN SITU. Tappi, Vol. 53, No. 8, pp. 1507-9, CA 73.89321q.
- Snell, G.J., & Huibers, D.T.A., October 11, 1983, LIGNIN CRACKING USING FAST FLUIDIZED BED REACTIONS. U.S. Pat. 4,409,416. 6 pp. CA 99.214401z.
- Sobolev, I., & Arlt, H.G.; Schuerch, C., 1957, ALKALINE HYDROGENATION PULPING. Ind. Eng. Chem. Vol. 49, pp. 1399-1400. CA 52.7693f.
- Sobolev, I., & Schuerch, C., 1958, ALKALINE HYDROGENATION PULPING. Tappi, Vol. 41, pp. 545-551. CA 53.5670h.
- Sogo, M., & Ishihara, T.; Hata, K., 1966, CHEMICAL STUDIES ON BARK. (13) HYDROGENOLYSIS OF OUTER BARK LIGNIN OF PINUS DENSIFLORA. J. Japan Wood Res. Soc. 12, Vol. 2, pp. 96-101, [Engl.; Jap. sum.] cf. A.B.I.P.C. 35: abstr. 7102,
- Sokolova, I.V., & Nimirovskii, V.D.; Raskin, M.N., 1982, ANIMATED PRODUCTS OF LIGNIN DEGRADATION. Khim. Drev. 54-56. CA 97.25344f. In Russian.
- Soltes, E. J., 1983, HYDROCARBONS FROM LIGNOCELLULOSIC RESIDUES. J. Appl. Polymer Sci. (Appl. Polymer Symp.), Vol. 37, No. 2, pp. 775-786, [Engl.], .
- Soltes, E. J. & Elder, T. J. 1981 in "Organic Chemicals from Biomass", I. S. Goldstein Ed., CRC: Boca Raton, Fla., p.63.
- Sorensen, N. A.; & Mehlum, J., 26 June, 1956, U.S. Pat. 2,752,394.
- Stavitskii, V. D., 1979, LIGNIN-TAR BINDER. Avtomobil'nye Dorogi No. 1, pp. 20-22 (Russ.).
- Stromskaya, G. I., & Chupka, E. I.; Stromskii, S. V., 1977, REDUCTION OF LIGNIN AND LIGNIN MODEL COMPOUNDS WITH AMALGAMS. Khim. Drev. (Riga) No. 1, pp. 78-82, (Russ.) cf. ABIPC 48:abstr. 2321.
- Sudo, K., & Hwang, B. H.; Sakakibara, A., 1978, ISOLATION OF ALPHA-O-GAMMA COMPOUND FROM HYDROGENOLYSIS PRODUCTS OF LIGNIN. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 24, No. 6, pp. 242-425, (Engl.), CA 89.112862b.
- Sudo, K., & Mullord, D. J.; Pepper, J. M., 1981, LIGNIN AND RELATED COMPOUNDS. (8). LIGNIN MONOMERS AND DIMERS FROM HYDROGENOLYSIS OF ASPEN POPLAR WOOD USING RHODIUM-ON-CHARCOAL CATALYST. Can. J. Chem., Vol. 59, No. 7, pp. 1029-1031, (Engl.; Fr. sum.) cf. ABIPC 50: abstr. 9178, CA 95.26818j.

- Sudo, K., & Pepper, J. M., 1982, LIGNIN AND RELATED COMPOUNDS. (9). ISOLATION OF A DIMER WITH A BENZYLISCHROMAN STRUCTURE FROM HYDROGENOLYSIS PRODUCTS OF ASPEN [*POPULUS TREMULOIDES*] LIGNIN. Can. J. Chem., Vol. 60, No. 2, pp. 229-230, [Fr. sum.] cf. ABIPC 52: abstr. 2525, CA 96.159312g.
- Sudo, K., & Sakakibara, A., 1972, ISOLATION OF A NEW TRIMERIC HYDROGENOLYSIS PRODUCT WITH DIPHENYL LINKAGE FROM EZOMATSU (*PICEA JEZOENSIS*) WOOD LIGNIN. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 18, No. 10, pp. 517-18, (Engl.) cf. ABIPC 40: abstr. 7794, 7796, 7799, 7804-5.
- Sudo, K., & Sakakibara, A., 1975, HYDROGENOLYSIS OF PROTOLIGNIN. (12). ISOLATION OF DIMERIC AND TRIMERIC COMPOUNDS WITH CARBON-TO-CARBON LINKAGES. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 21, No. 3, pp. 164-169, (Engl.; Jap. sum.) cf. ABIPC 45: abstr. 5753.
- Sudo, K.-I., & Hwang, B. H.; Sakakibara, A., 1979, HYDROGENOLYSIS OF PROTOLIGNIN. (14). ISOLATION OF A DIMERIC COMPOUND WITH alpha-O-gamma LINKAGE. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 25, No. 1, pp. 61-66, (Engl.; Jap. sum.) cf. ABIPC 48: abstr. 4562; 49: abstr. 4753, CA 89.112862b.
- Sudo, K.-I., & Sakakibara, A., 1973, ISOLATION OF NEW DIMERIC AND TRIMERIC CONDENSED TYPE COMPOUNDS FROM HYDROGENOLYSIS PRODUCTS OF PROTOLIGNIN. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 19, 4, pp. 201-2, (Engl.).
- Sudo, K.-I., & Sakakibara, A., 1973, HYDROGENOLYSIS OF PROTOLIGNIN. (7). ISOLATION OF D,L-SYRINGARESINOL, BIPHENYL, AND DIARYLPROPANE FROM HARDWOOD LIGNIN. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 19, No. 4, pp. 165-9, (Engl.; Jap. sum.) cf. ABIPC 44: abstr. 3751.
- Sudo, K.-I., & Sakakibara, A., 1974, HYDROGENOLYSIS OF PROTOLIGNIN. (11). ISOLATION OF A DIMER WITH C(beta)-C(6) AND A TRIMER WITH TWO C(beta)-C(5) LINKAGES. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 20, No. 8, pp. 396-401, (Engl.; Jap. sum.) cf. ABIPC 45: abstr. 4572.
- Sudo, K.-I., & Sakakibara, A., 1974, HYDROGENOLYSIS OF PROTOLIGNIN. (9). ISOLATION OF A TRIMERIC COMPOUND LINKED WITH BIPHENYL AND C(beta)-C(5) LINKAGES. (10). ISOLATION OF TWO DIMERIC COMPOUNDS WITH BETA-ARYL ETHER LINKAGE. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 20, No. 7, pp. 327-35, (Engl.; Jap. sum.) cf. ABIPC 44: abstr. 3752.
- Sudo, K.-I., & Sakakibara, A., 1977, HYDROGENOLYSIS OF PROTOLIGNIN. (13). ISOLATION OF TRIMERIC BIPHENYL- AND LIGNAN-TYPE COMPOUNDS. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 23, No. 3, pp. 151-155, (Engl.; Jap. sum.) cf. ABIPC 46: abstr. 2443, CA 87.25017v.
- Sugo, M., & Ishihara, T.; Hata, K., 1966, BARK. XIII. HYDROGENOLYSIS OF OUTER BARK LIGNIN OF *PINUS DENSIFLORA*. Nippon Mokuzai Gakkaishi. Vol. 12, pp. 96 - 101. In English. CA65.5651a.

- Sukhanovskii, S. I.; Akhima, E. I.; Evstiteeva, E. I.; Podgornaya, T. A.; Kalvins, A. I.; Abele, K.; Alsups, I.; Kul'kwits, A. I.; & Kiselis, O., 1964, THERMAL DECOMPOSITION OF HYDROLYSIS LIGNIN BY NONCONDENSABLE GASES IN A RETORT WITH INTERNAL HEATING, Khim. Pererabotka i Zashchita Drevesing, Akad. Nauk Latv. SSSR, Inst. Khim. Drevesing, pp. 87-101 (Russ.).
- Sukhanovskii, S. I.; Akhmina, E. I.; Podgornaya, T. A.; Bezinozgin, E. S.; Nemchenko, A. G.; & Yudkevich Yu. D., 1964, CONTACT PYROLYSIS OF THE RESIDUAL RESIN AFTER THERMOLYSIS OF HYDROLYTIC LIGNIN, Gidrolizn. i Lesokhim. Prom., Vol. 17, No. 5, pp. 17-18 (Russ.).
- Sundstrom, D. W.; & Klei, H. E., 1982, USES OF BYPRODUCTS FROM ALCOHOL FUEL PROCESSES, Biotechnol. Bioeng. Symp., No. 12, pp. 45-56.
- Suty, L. & Golis, E., 1972, CHEMICAL STRUCTURE OF BEECH LIGNIN AND ITS CHANGES DURING AQUEOUS HYDROLYSIS. Cellulose chem. Technol., Vol. 6, pp. 485-491.
- Tomlinson, G. H.; & Hibbert, H., 1936, J. Am. Chem. Soc., Vol. 58, p. 345.
- Vasyunina, N.A., & Balandin, A.A.; Chepigo, S.V.; Barysheva, G.S., 1960, CATALYTIC HYDROGENATION OF LIGNIN. Izvest. Akad. Nauk S.S.S.R., Otdel Khim. Nauk, p. 1312. CA 55.1495a.
- Vincent, G. G., 1980, OXYGEN-CONTAINING AROMATIC COMPOUNDS OBTAINED FROM LIGNIN. Proc. Bio-Energy '80 World Cong. (Atlanta), pp. 299-300, [Engl.] [Avail. from Bio-Energy Council, Washington, DC 20006], Crown Zellerbach Corp.
- Vogelzang, M.; Li, C.; Schnit, G.; Gates, B.; & Petrakis, L., 1983. HYDROGENATION OF 1-NAPHTHOL: ACTIVITIES AND STABILITIES OF MOLYBDENA AND RELATED CATALYSTS. J. of Catalysis, Vol. 84, pp. 170-177.
- Voss, W., 1968, USE OF WOOD AS A RAW MATERIAL FOR THE CHEMICAL INDUSTRY. Wiss. Z. Tech. Univ. Dresden, Vol. 17, No. 5, pp. 1405-13 (1968). (Ger.).
- Vuori, A., & Bredenberg, J. B., 1984, HYDROGENOLYSIS AND HYDROCRACKING OF THE CARBON-OXYGEN BOND. (5). HYDROGENOLYSIS OF 4-PROPYLGUAIACOL BY SULFIDED COBALT OXIDE/MOLYBDENUM OXIDE/GAMMA-ALUMINUM OXIDE. Holzforschung, Vol. 38, No. 5, pp. 253-262, [Engl.; Ger. sum.] cf. ABIPC 55: abstr. 5173.
- Vuori, A.; & Bredenberg, J. B., 1984, HYDROGENOLYSIS AND HYDROCRACKING OF THE CARBON-OXYGEN BOND. 4. THERMAL AND CATALYTIC HYDROGENOLYSIS OF 4-PROPYLGUAIACOL, Holzforschung, Vol. 38, No. 3, pp. 133-140, [Engl.; Ger. Sum.].
- Vuori, A.; & Bredenberg, J. J., 1985, THERMOLYSIS OF SUBSTITUTED ANISOLES, Paper presented at ACS Div. of Fuel Chem., Miami Beach, Florida, April 28-May 3, 1985, Preprints Vol. 30, No. 1, pp. 366-378.



- Vuori, A.; Karinen, T.; & Bredenberg, J. B., 1984. THERMOLYSIS OF ANISOLE, Finn. Chem Lett. No. 4-5, pp. 89-94.
- Wada, I., & Ohta, M.; Sakakibara, A., 1969, HYDROGENOLYSIS OF PROTOLIGNIN. II. ISOLATION OF SOME HYDROGENOLYSIS PRODUCTS. J. Japan Wood Res. Soc., Vol. 15, No. 5, pp. 218-21, (Engl.; Jap. sum.) cf. ABIPC 40: abstr. 7805, CA 72.112991s.
- Wada, I., & Sakakibara, A., 1969, HYDROGENOLYSIS OF PROTOLIGNIN. I. HYDROGENOLYSIS PRODUCTS UNDER VARIOUS REACTION CONDITIONS. J. Japan Wood Res. Soc., Vol. 15, No. 5, pp. 214-18, (Engl.; Jap. sum.), CA 72.12310m.
- Weigold, H., 1982, BEHAVIOR OF Co-Mo-Al<sub>2</sub>O<sub>3</sub> CATALYSTS IN THE HYDRODEOXYGENATION OF PHENOLS, Fuel, Vol. 61, pp. 1031-26.
- Weisser, O.; & Landa, S., 1973. SULFIDE CATALYSTS, THEIR PROPERTIES AND APPLICATIONS, Pergamon Press: New York.
- Wenzl, H. F. J., 1970, CHEMICAL TECHNOLOGY OF WOOD. Acad. Press (N.Y. & London), 692 p. (Transl. from Ger. by F. E. & D. A. Brauns).
- Wienhaus, O., & Fischer, F.; Schiene, R., 1976, HYDROGENOLYSIS OF LIGNIN - A PROMISING DEGRADATION PROCESS TO OBTAIN FUNDAMENTAL ORGANIC CHEMICALS. Zellstoff Papier, Vol. 25, No. 4, pp. 109-116, (Ger.).
- Wienhaus, O., & Schiene, R.; Fischer, F., 1980, HYDROGENOLYSIS AND PYROLYSIS OF LIGNINS. Zellstoff Papier, Vol. 29, No. 3, pp. 125-128, (Ger.), CA 93.187941t.
- Yamashina, H., & Sakakibara, A., 1974, HYDROGENOLYSIS OF PROTOLIGNIN. (11). ISOLATION OF DEGRADATION PRODUCTS FROM HARDWOOD LIGNIN. Res. Bull. Coll. Expt. Forests Hokkaido Univ., Vol. 31, No. 1, pp. 51-62, (Jap.; Engl. sum.) cf. ABIPC 45: abstr. 5753.
- Yasuda, S., & Sakakibara, A., 1977, HYDROGENOLYSIS OF PROTOLIGNIN IN COMPRESSION WOOD. (4). ISOLATION OF A DIPHENYL ETHER AND THREE DIMERIC COMPOUNDS WITH CARBON-TO-CARBON LINKAGE. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 23, No. 8, pp. 383-387, (Engl.; Jap. sum.) cf. ABIPC 48: abstr. 1258, CA 87.153596v.
- Yasuda, S., & Sakakibara, A., 1977, HYDROGENOLYSIS OF PROTOLIGNIN IN COMPRESSION WOOD. (3). ISOLATION OF FOUR DIMERIC COMPOUNDS WITH CARBON-TO-CARBON LINKAGE. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 23, No. 2, pp. 114-119, (Engl.; Jap. sum.) cf. ABIPC 47: abstr. 11359, CA 86.191479w.
- Yasuda, S., & Sakakibara, A., 1975, HYDROGENOLYSIS OF PROTOLIGNIN IN COMPRESSION WOOD. (1). ISOLATION OF TWO DIMERS WITH C(beta)-C(5) AND C(beta)-C(3) LINKAGES COMPOSED OF p-HYDROXYPHENYL AND GUAIACYL NUCLEI AND TWO p-HYDROXYPHENYL NUCLEI, RESPECTIVELY. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 21, No. 6, pp. 370-375, (Engl.; Jap. sum.).

- Yasuda, S., & Sakakibara, A., 1975, ISOLATION OF A NEW DIMERIC "CONDENSED TYPE" COMPOUND FROM HYDROGENOLYSIS PRODUCTS OF COMPRESSION WOOD LIGNIN. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 21, No. 11, pp. 639-640 (Engl.) cf. ABIPC 42: abstr. 8970, 11479.
- Yasuda, S., & Sakakibara, A., 1976, HYDROGENOLYSIS OF PROTOLIGNIN IN COMPRESSION WOOD. (2). ISOLATION OF TWO DIMERS WITH BETA-ARYL ETHER LINKAGES AND PHENYLISOCROMAN STRUCTURE. J. Japan Wood Res. Soc. (Mokuzai Gakkaishi), Vol. 22, No. 11, pp. 606-612, (Engl.; Jap. sum.) cf. ABIPC 46: abstr. 11208, CA 86.92053w.
- Yasuda, T., & Sakakibara, A., 1981, HYDROGENOLYSIS OF PROTOLIGNIN IN COMPRESSION WOOD. (5). ISOLATION OF TWO TRIMERIC COMPOUNDS WITH gamma-LACTONE RING. Holzforschung, Vol. 35, No. 4, pp. 183-187, (Engl.; Ger. sum.) cf. ABIPC 48: abstr. 8046, CA 96.3632a.
- Zarubin, M.; & Tishchenko, D. 1960, ALKALI HYDROLYSIS OF SCHOLLER LIGNIN YIELDING LOW-MOLECULAR-WEIGHT SUBSTANCES, Zhur. Priklad. Khim., Vol. 33, pp. 2576-81 (Russ.).
- Zarubin, M.; & Tishchenko, D., 1959, LOW-MOLECULAR SUBSTANCES FROM HIGHLY CONDENSED HYDROLYTIC LIGNIN BY ALKALI HYDROLYSIS, Zhur. Priklad. Khim., Vol. 32, pp. 395-9 (Russ.).
- Ziemelis, U. K., & Dubava, L. K.; Domburg, G. E.; Paicha, V. P.; Luksa, R.V., 1979, RAPID THERMOLYSIS OF HYROLYSIS LIGNIN. Gidroliz. Lesokhim. Prom. Vol. 2 pp. 8-10, (Russ.).