

AN ABSTRACT OF THE THESIS OF

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Title Hydrogenation of Solvent Extracted Douglas Fir
Lignin

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The apparatus was designed and constructed for the hydrogenation of solvent extracted Douglas Fir lignin. The lignin obtained from Professor E. F. Kurth of the Oregon Forest Products Laboratory and extracted by him with hot benzene, was originally obtained from the Springfield, Oregon Alcohol Plant.

The lignin was subjected to hydrogenations under various conditions using tetralin and water as the solvents with Shell 105 dehydrogenation catalyst. Also a specially prepared nickel catalyst was employed.

The investigation was undertaken with the purpose of obtaining n-propyl benzene from the lignin by hydrogenation. However, no such results were obtained. Evidence of hydrogenation was obtained but the products exhibited unsaturated side chains which would seem to indicate thermal cracking rather than hydrogenolysis.

Various compounds were isolated; none were identified. Fractionation was employed as a method of separation of the neutral compounds whereas the phenols and acids were removed by chemical means.

In the effluent gases large amounts of methane were discovered which would indicate a breaking of the methoxy group between the methyl radical and the oxygen atom. Perhaps some methane was also formed from hydrogenolysis of methyl side chains.

Tables of operating data, photographs of equipment, a flowsheet and a detailed drawing of the bomb are included.

HYDROGENATION OF SOLVENT EXTRACTED
DOUGLAS FIR LIGNIN

by

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TABLE OF CONTENTS

Section	Page
I Introduction	1
II Apparatus Design	10
A. Detailed Drawing, Hydrogenation Bomb	13
B. Flowsheet of Apparatus	14
C. Photographs of Equipment	15
III Selection of Conditions	17
IV Operating Procedure	21
V Method of Analysis	23
VI Results	26
A. Table No. I - Fractionation of Neutrals	34
B. Table No. II - Physical Data of Different Fractions	35
C. Table No. III - Gas Analyses	36
D. Distillation Curve Run No. 6 ...	37
VII Conclusions	38
VIII Recommendations	40
IX Bibliography	42

Section	Page
X Appendix	44
A. Operational Data	45
B. Nickel Catalyst Preparation ..	53
C. Thermocouple Calibration Curve	54

HYDROGENATION OF SOLVENT EXTRACTED DOUGLAS FIR LIGNIN

INTRODUCTION

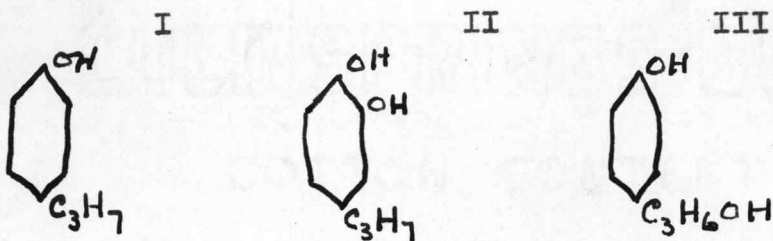
The present investigation was undertaken with the purpose of obtaining n-propyl benzene from lignin obtained from the Springfield, Oregon alcohol plant. The lignin used in this work was first extracted with hot benzene to remove waxes by Dr. E. F. Kurth of the Oregon Forest Products Laboratory. If n-propyl benzene could be obtained in sufficient yield and at a low cost, it would then be possible to consider isomerization of the n-propyl to isopropyl benzene. Isopropyl benzene is an important additive to high octane aviation gasoline.

It is difficult to determine from the literature who was the first to attempt to hydrogenate lignin. One of the earliest investigations listed by the Chemical Abstracts in which hydrogenation of lignin was deliberately planned was reported by Fierz-David in a study of the liquefaction of wood and cellulose (2). When cotton cellulose in the presence of nickel was heated to 450-70°C. under a pressure of 150-220 atmospheres of hydrogen, a yellow liquid was obtained by distillation which contained aldehydes, ketones, phenols, alkylfurans, and fatty acids. M. Phillips

(14 and 15) and M. J. Goss (15) distilled alkali lignin, isolated from corn cobs, with zinc dust in an atmosphere of hydrogen. The distillate consisted of an aqueous portion and an oil. The aqueous distillate contained methanol, acetone and an acid (determined as acetic acid) to the extent of 1.48, 0.36 and 0.24%, respectively calculated on the basis of the weight of lignin used. Catechol was shown to be present in the aqueous distillate. The yield of oil obtained amounted to 16% of the weight of the lignin used. Fifty-five percent of the oil was alkali soluble, and in this fraction guaiacol was definitely identified. A phenol containing the methoxy group and yielding a 3, 5-dinitrobenzoyl derivative melting at 110°C . was also obtained but not further identified. In later work (15) these same researchers under similar conditions separated and identified 1-propyl-3-methoxy-4-hydroxy benzene. Moldavskii and Vainshtein hydrogenated lignin containing 75% moisture and considerable amount of H_2SO_4 in a horizontally rotating autoclave, electrically heated to $400\text{--}450^{\circ}\text{C}$., with a cold hydrogen pressure of 50-70 atmospheres, and in the presences of various catalysts such as MoS_2 (12). The yield of tar was very small. Further experiments were also performed

under the same conditions with phenols or lignin tar as the solvent and MoS_2 as the catalyst. A complete transformation of the lignin into liquid (44%) and gaseous (56%) products was accomplished. The tar obtained was fractionated into 3 fractions: 24.2% boiling below 200°C ., 35.6% between 200° and 300°C ., above 300°C ., and losses 40.2%. Oxidation yielded m-phthalic acid.

In 1938, Harris, D'Ianni and Adkins (8) and Harris and Adkins (7) hydrogenated various lignin preparations in dioxane at a temperature of $250\text{--}60^\circ\text{C}$. and pressure of 170-400 atmospheres in the presence of copper-chromium oxide catalyst. From 80 grams methanol-lignin from aspen wood there were isolated 22 grams of methyl alcohol, 9 grams of 4-n-propyl cyclohexan-1-ol (Formula I), 3 grams of 4-n-propyl cyclohexane-1,2-diol (Formula II), 18 grams of a mixture boiling, $130\text{--}260^\circ\text{C}$., 4 grams of intermediate fractions and 5 grams boiling above 260°C . In further work 3-(4-hydroxycyclohexyl)-1-propanol (Formula III) was separated and identified.



Other lignin preparations yielded varying quantities of the same compounds.

Hatihama, Zyodai and Umezu hydrogenated HCl lignin prepared from Picea Jezoensis at 260-70°C. and a maximum pressure of 230 atmospheres (10). They used various catalysts and solvents but obtained the best results with nickel oxide and dioxane. One mol of hydrogen was absorbed by 40-44 grams lignin in 35-55 hours. The ether-soluble portion of the products amounted to 46.7% of the weight of lignin and contained dihydroeugenol, protocatechuic acid, pyrocatechol and p-hydroxy benzoic acid. Aldehydes and other neutral compounds were also found in the ether-soluble portion.

Hydrogenation of various lignin preparations has been conducted with different hydrocarbon solvents such as dioxane, phenols, alcohols and naphthalenes, also Harris, Saeman, and Sherrard (9) hydrogenated lignin, in aqueous or 1% alkaline solutions or suspensions using Raney nickel as a catalyst. They obtained their lignin from various sources, such as methanol lignin, cellosolve lignin, lignin from wood after treatment with H_2SO_4 , and lignin from pulping liquor. At 1500-2500 pounds pressure and 225-50°C. the hydrogenation was completed in 6-10 hours;

approximately 35 mols hydrogen were absorbed by each equivalent weight of lignin (900 grams). The hydrogenation products insoluble in water were fractionally distilled. The products were divided at 1 mm pressure as follows: fraction I, below 55°C.; fraction II, 55° to 90°C.; fraction III, 90° to 170°C.; fraction IV above 170°C. The amounts of each fraction varied with the starting material and were identified as being similar to those obtained when methanol lignin was hydrogenated in dioxane in the presence of copper chromite catalysts.

Adkins, Frank and Bloom hydrogenated hardwood lignin, obtained from soda black liquors, over Cu-Cr in dioxane at 250-300°C., to give saturated colorless products (1). The amount of hydrogen absorbed per gram of lignin and the general behavior on hydrogenation were very similar to those results obtained using lignin extracted with methanol from hardwood aspen. However, the products from soda lignin differed in several respects from those obtained from methanol lignin. There was no predominance of 9 carbon atom compounds produced from soda lignin and in fact cyclic compounds containing from 6 to at least 70 carbon atoms were found among the products. Cyclohexanol and at least 4 different alkyl cyclohexanols were produced by

hydrogenation but by far the greater part of the soda lignin was converted to alcohols and glycols related to polycyclic hydrocarbons having 20-70 or more carbon atoms in the molecule. Compounds of high molecular weight were obtained from methanol lignin but they were much less in amount and were more oxygenated than were the products of similar physical properties obtained from soda lignin. The high boiling products from methanol lignin carry 1 oxygen atom for each 6 carbon atoms, whereas the products from soda lignin have 1 oxygen for an average of 13.5 carbon atoms. All of these facts are in harmony with the concept that in methanol lignin units related to propyl benzene are joined in chains, while in soda lignin cyclization has taken place during the process of isolation. Hydrogenation using Cu-Cr catalyst cleaves the bond between successive C_9 units in methanol lignin, whereas with soda lignin the action of hydrogen is largely limited to hydrogenation of unsaturated rings and the hydrogenolysis of HO, MeO and cyclic ether linkages, since the rings are stable towards hydrogenolysis.

W. Lautsch (11) hydrogenated lignin and lignosulfonates in dilute alkalies at 250-65°C. in the presence of a catalyst or at 340-50°C. With and

without a catalyst. At the lower temperature range it was possible to obtain either mainly phenols or ring-hydrogenated products. At the higher temperature range, a more pronounced cracking of the side chains and ring hydrogenations took place. HCl-lignin and similar products gave higher yields of low molecular weight compounds than lignosulfonates. Black liquor from alkali cooks of pine wood gave no useful results on hydrogenation at 260°C. but at 340-50°C. about a 60% yield of hydroaromatic alcohols was obtained. Lignin prepared from wood of 150 year old Picea Jezoensis by the HCl method was hydrogenated in dioxane solution with addition of 10-12% nickel as a catalyst (6). The mixture was kept at 260-70°C. for 22-25 hours. The pressure of hydrogen, initially charged under 100 atmospheres, rose to a maximum of 230 atmospheres then dropped to 100 atmospheres. From the final products of hydrogenation, 70% ether-soluble portion was extracted which contained 7, 3, 37 and 25% of carbonyl, carboxyl, phenolic, and neutral compounds respectively.

Bailey (3) hydrogenated lignin obtained from western hemlock by digesting the chips with equal

volumes of butyl alcohol and water at 100°C. The lignin sirup in butyl alcohol was reduced with hydrogen over Raney nickel at 260°C. under pressure of 2500-6000 pounds per square inch for 1 hour. This was followed by heating and stirring for 23 hours. Each 28 grams of lignin absorbed 1 mol of hydrogen. The fraction of products boiling below butyl alcohol contained water 17.9%; 2, 3-dimethyl butane 0.6%; methyl alcohol 0.2%; tetrahydro furfuryl alcohol 1.2%; sec. butyl alcohol 1.2% and methylisopropyl carbinol 0.3%. The use of a Cu-Chromite catalyst produced lower yields and a completely different series of products from lignin than did Raney nickel, water as a solvent produced lower yields and different products than did butyl alcohol and dioxane. The solvent seemed to effect the kind of products formed instead of merely influencing the rate and extent of formation.

Saeman and Harris (16) recently hydrogenated 1 kilogram of lignin prepared from extractive-free green aspen wood with methyl alcohol containing 2% HCl in 100 gram batches in 1000 ml. water with 1:1 Raney nickel : lignin ratio, at 250°C. and 3000 pounds per square inch, hydrogen pressure; the reaction was interrupted at the end of 5 hours when the rate of

pressure drop was 75 pounds or less per hour. One mol of hydrogen was absorbed for each 33 grams of lignin. A yield of 24% volatile products was obtained which was separated into H_2O -soluble and insoluble fractions. The H_2O -insoluble products consisted of 4-ethyl-cyclohexanol, 4-n-propyl cyclohexanol and 2-methoxy-4 ethyl-cyclohexanol. The water soluble fraction consisted of $(CH_2OH)_2$, $(C_2H_4OH)_2O$ and 3-(4-hydroxy cyclohexyl)-1-propanol. The presence of other ethers as impurities in the various fractions was also indicated by MeO and HO analysis.

APPARATUS DESIGN

The hydrogenation apparatus consisted of a high pressure hydrogen booster pump, a high pressure storage cylinder and the hydrogenation bomb. The bomb was constructed by the Mater Machine Works of Corvallis. (See detailed drawing Page 13). The bomb was wrapped with 33 feet of $1/8 \times 0.008$ " Chromel A resistance ribbon. A layer of alundum cement covered the ribbon to hold it in place. The bomb was lagged with 85% magnesia insulation $1"$ to $1\frac{1}{4}"$ thick around the body and $1"$ thick on each flange. The insulation was held in place on the body of the bomb by a galvanized sheet metal cover. Galvanized sheet metal head coverings held the insulation in place on both flanges.

The bomb was rocked suspended between $1"$ oil lubricated bearings by means of a collar and shaft arrangement. The collar was made from $2" \times 3/16"$ hot rolled metal strip with $1"$ steel rods welded in place to form a shaft. The fulcrum supporting the bearings was made from $2" \times 3/16"$ metal strip and bolted to a heavy wooden base. The rocking mechanism consisted of a $\frac{1}{4}$ h.p. geared head motor (counter shaft speed 36 R.P.M.), a $47"$ V belt and a $12"$ pulley.

A 10" shaft was welded $3\frac{1}{2}$ " off center of the pulley. To the free end of this shaft was connected an arm attached to a hook welded on the body of the bomb. As the pulley rotated the bomb rocked back and forth about 45° from the horizontal. (See flow sheet and photographs Pages 14, 15 and 16.)

The power to the heating coils was controlled by a 7.5 KVA Powerstat and measured by a volt meter and ammeter connected in the circuit.

The temperature was measured by an iron-constantan thermocouple inserted in a well made from $1/8$ " Shelby seamless steel tubing in one end of the bomb. The thermocouple was calibrated using U. S. Bureau of Standards lead, tin and zinc melting at 327.5° , 231.85° , and 419.4°C. , respectively. The calibration curve is included in the appendix, Page 54.

The pressure gauges used were calibrated using an Ashcroft high pressure dead weight tester.

All connections between booster pumps, storage cylinder and bomb were made with Shelby seamless steel tubing $1/8$ " O.D. and $1/16$ " I.D.

The gaskets used in sealing the ends of the bomb were made from copper sheet $1/32$ " thick. The gaskets

were cut on a lathe by bolting a piece of copper sheet to a wooden form. The center was cut first and then the outer edge. The dimensions of the gaskets found most satisfactory were $5 \frac{1}{4}$ " I.D. and $5 \frac{3}{4}$ " O.D.

For safety reasons a sandbag and sheet metal wall was built between the instrument table and the bomb.

HYDROGENATION BOMB

SCALE: $\frac{1}{4}$ IN. = 1 IN. 8/29/48

J. K. OLSEN

HYDROGENATION BOMB

SCALE: $\frac{1}{4}$ IN. = 1 IN. 8/29/48

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HYDROGENATION BOMB

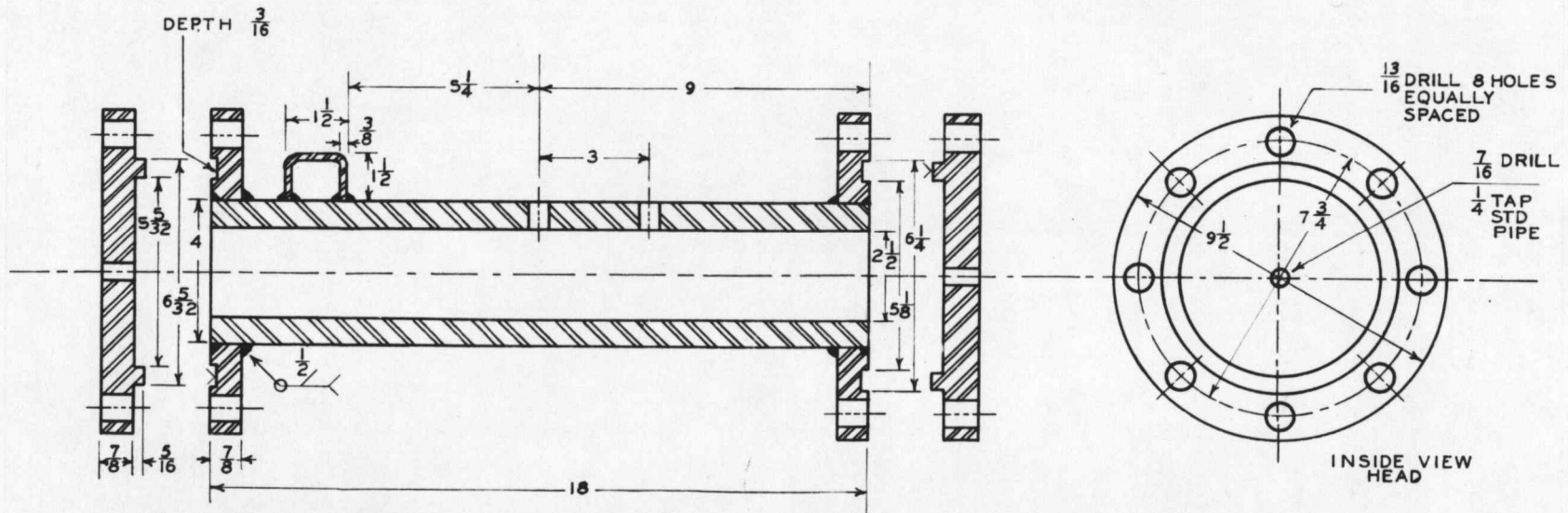
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HYDROGENATION BOMB

SCALE: $\frac{1}{4}$ IN. = 1 IN. 8/29/48

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MATERIALS

BODY	SHELBY SEAMLESS STEEL TUBING
FLANGES	$\frac{1}{2}$ IN. STEEL PLATE-MACHINED TO SIZE
HEAD BOLTS	16-3X $\frac{3}{4}$ AM. STD.
GASKETS	COPPER 2-5 $\frac{1}{2}$ IN. I.D. & 6 IN. O.D.

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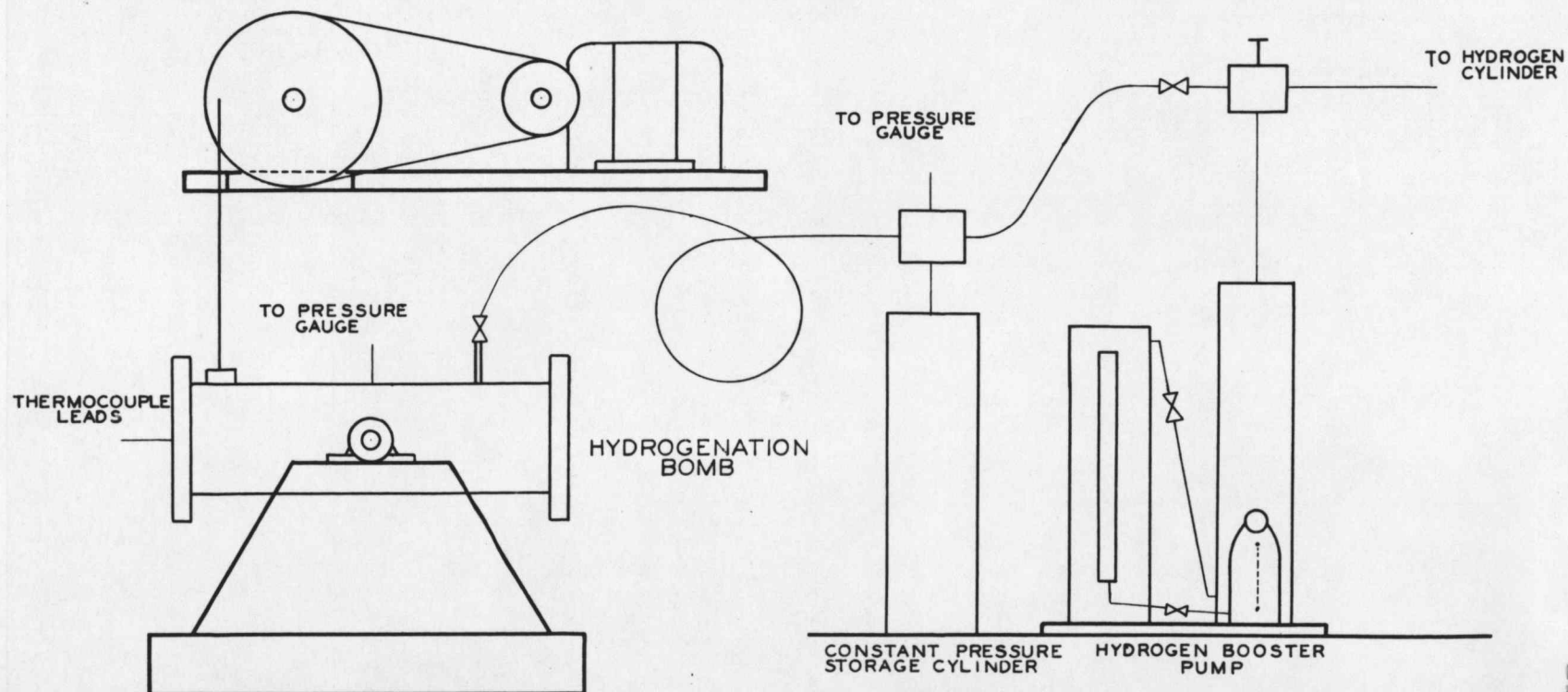
FLOWSHEET - HYDROGENATION APPARATUS

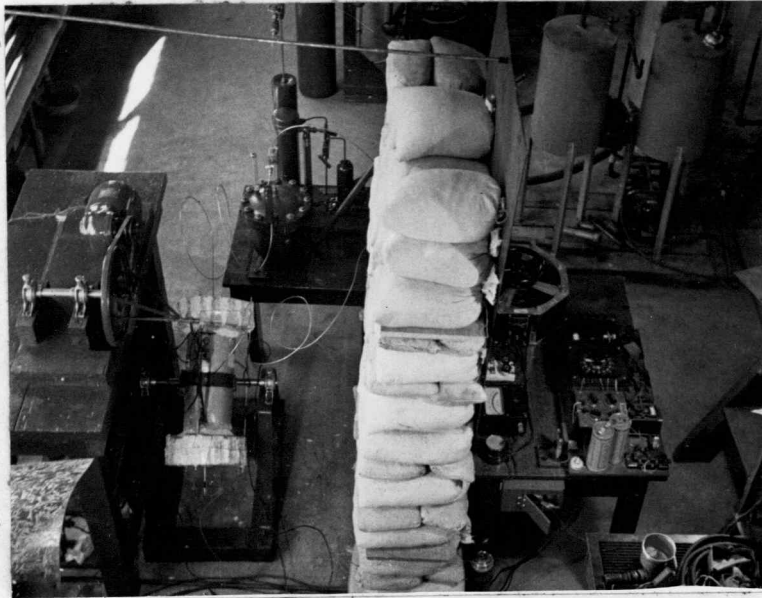
HYDROGENATION OF LIGNIN

J. K. OLSEN

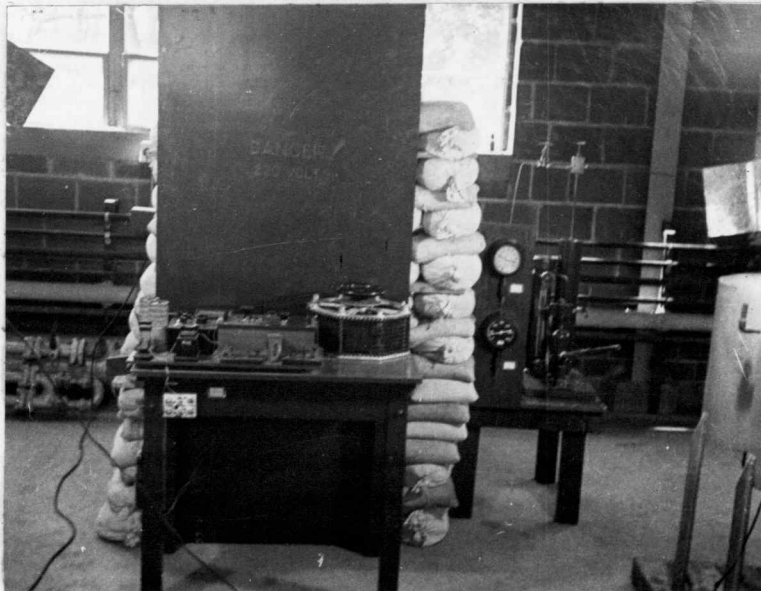
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GEARED HEAD MOTOR
COUNTER-SHAFT SPEED 36 R.P.M.





General View - Hydrogenation Equipment



Front View - Hydrogenation Equipment



Instrument Table



Hydrogen Booster Pump

SELECTION OF CONDITIONS

It has been shown in a number of instances that the lignin molecule consists of nine carbon atom units which are easily separated by hydrogenation; however, in most cases it was the intent of the researchers occupied in this field in the past to completely saturate the degradation products obtained. For this reason Raney nickel and copper chromite were most generally used as catalysts. Both of these are very vigorous catalysts, easily hydrogenating the benzene ring. Dioxane was found to be the best solvent in which to conduct the hydrogenation of lignin; however, it was not used in this work, because it has been shown to decompose explosively in the presence of hydrogen when the temperature is raised much above 210°C . (5). Since the temperature used in this work was considerably above this figure it was necessary to find another solvent which would be stable at higher temperatures. Tetralin was chosen.

Boomer, Edwards and Argue (4) describe various hydrogenations using tetralin as the solvent. They point out that an ideal solvent must also act as a hydrogen carrier by maintaining a supply of combined hydrogen greatly in excess of that possible in true

solution. Such ideal substances should themselves be capable of rapid reversible hydrogenations. Tetralin is typical of such a substance. Tetralin is readily prepared from naphthalene and hydrogen even on a commercial scale. Hall and others (4) have examined the reaction between hydrogen, naphthalene and tetralin at temperatures as high as $500^{\circ}\text{C}.$, or higher, and have found that a catalyst is essential. Tetralin is the principal constituent of the equilibrium mixture at $400^{\circ}\text{C}.$, while decalin appears in small quantities at higher temperatures. Both tetralin and decalin are fairly stable at $400^{\circ}\text{C}.$, while naphthalene is stable at higher temperatures. Cracking of tetralin to benzene and related compounds is slight at $400^{\circ}\text{C}.$ and extensive at $450^{\circ}\text{C}.$ and is independent of the presence of the catalyst. The hydrogen atoms in the 1, 2, 3, 4 positions in tetralin are in a highly active state and represent a concentration of two gram molecules of available hydrogen per gram molecule of medium.

The catalyst used in most of these runs was the commercial Shell 105 dehydrogenation catalyst. The composition of this catalyst is as follows:

Fe_2O_3 - 70%

Cr_2O_3 - 30%

CuSO_4 - 1%

KNO_3 - 0.5%

It was hoped that under the conditions chosen for the hydrogenations this catalyst would become a hydrogenation catalyst. The catalyst was used in pellet form.

For the sixth run a nickel catalyst was prepared by dissolving nickel nitrate in distilled water and precipitating nickel hydroxide on powdered pumice using dilute NH_4OH . The $\text{Ni}(\text{OH})_2$ was dehydrated in a furnace at 800°F . - 1000°F . for 6 hours and then the nickel oxide reduced using H_2 at 700 pounds per square inch and 850°F . for 6 hours.

The temperature and pressure conditions chosen for the runs were controlled to a large extent by the limitations of the equipment. This was especially true of the pressure. It was found that the maximum pressure obtainable using the copper gaskets was about 1450 pounds per square inch. When the pressure was raised much above this figure serious leaks occurred about both flanges.

The temperature used, of course, limited the initial cold H_2 pressure. It was found that temperatures up to $850^{\circ}F.$ could be obtained using the insulation and resistance ribbon described previously in this paper under "Apparatus Design." The temperature used was also limited by the solvent. As pointed out above tetralin undergoes very little decomposition to benzene or related compounds at temperatures below $400^{\circ}C.$ or $752^{\circ}F.$, however, decomposition is extensive at $450^{\circ}C.$ The maximum temperature used, therefore, was about $750^{\circ}F.$

OPERATING PROCEDURE

A weighed quantity of lignin which had been reduced to small particles by a Knapp-Monarch liquidizer was introduced into the bomb as well as a weighed quantity of catalyst. The bomb was then sealed and tested for leaks using the Curtis 3 stage air compressors on the liquid air plant at the Industrial Building. The pressure was raised to between 850 and 900 pounds per square inch. A soap suds solution was used to test all fittings and openings. If there was no pressure drop over a period of time, say fifteen minutes, the bomb was assumed sealed.

The bomb was next placed in position, and the heads insulated. The heating coil leads were attached and taped into position so that the resistance ribbon would not fail due to fatigue as the bomb was rocked. The hydrogen feed line was attached to a high pressure valve which in turn was fastened to a 4" piece of 1/4" steel pipe attached to the top of the bomb. The pressure gauge line was attached and also the thermocouple fitted into place. The equipment was then ready for use.

The initial cold hydrogen pressure was raised to an approximate calculated value. The valve on top

of the bomb was then closed and no further hydrogen admitted during the run. The bomb was once again checked for leaks using the soap suds solution.

The rocking mechanism was started and the current turned on. The voltage was raised to approximately 200 volts for the heating period. As the temperature approached the desired operating conditions the voltage was adjusted so as to maintain this temperature.

Readings were taken at $1/2$ hour intervals during the run. After about 6 to 12 hours the current was turned off and the bomb allowed to cool over night. The following day the pressure was noted as well as the gas temperature. Gas samples were obtained through the valve on top of the bomb. The bomb was then opened and the liquid and solid material removed for analysis.

METHOD OF ANALYSIS

The method of separation used in the analysis of the liquid products recovered from the bomb was essentially that given by Shriner and Fuson (17, p 294-295).

1. Liquid was filtered, and the volume measured.
A 30 ml. sample was set aside as representative of that particular run.
2. The remaining liquid was extracted with 100 ml. portions of 5% NaOH solution. Larger or smaller aliquots were used depending on the volume of original solution.

It was found to be true in all runs that this separation was very difficult to make. The NaOH solution was immiscible in the product solution; however, it had a tendency to form an emulsion which could be broken by centrifuging at 1500-2000 R.P.M. The two layers were then separated by decanting the upper layer.

Another difficulty encountered during this separation was the formation of a black tarry residue which stuck to the glassware and defied removal. It was finally removed with 95% ethanol.

3. The NaOH layer should contain all phenols and

acids, the other layer or "neutral" layer should contain alcohols, aldehydes, hydrocarbons both aliphatic and aromatic and also any other neutral compounds. No separations were attempted for nitrogen or halogen compounds for it is known that lignin does not contain these elements.

4. The "neutral" solution from step No. 2 was next washed with 5% HCl until the solution was acid to litmus and then washed with water to remove excess acid. This washed neutral solution was then subjected to a simple distillation.
5. The distillate from step No. 4 was fractionally distilled in a spiral packed 15 plate column. Different fractions were taken as listed in the results.
6. The NaOH layer from step No. 2 was filtered to remove any suspended tarry material from this solution. It was then saturated with CO_2 . According to Shriner and Fuson (17) this should precipitate compounds in solubility class A_2 which include phenols. The NaHCO_3 solution was next filtered. The precipitate was allowed to air dry.
7. The NaHCO_3 solution was warmed and stirred on a

steam bath to remove any dissolved ether. It was then cooled and acidified with 5% HCl solution. This should precipitate compounds in solubility class A₁ which include negatively substituted phenols and high-molecular weight acids. The acid solution was filtered and the precipitate allowed to air dry.

8. For the fractions from step No. 5 which from their boiling range appear to be pure, various physical constants such as density and refractive index were recorded.
9. The solid material which was removed from the bomb was allowed to air dry and it was then weighed. After the weight of catalyst is subtracted, the remaining weight of solid was used to calculate the percent conversion to liquid products of the original lignin charged.
10. The gas samples which were withdrawn at the end of each run before the bomb was opened were analyzed using a Fischer "Unitized" gas analysis apparatus. The analyses can be found in the results.

RESULTS

Only runs No. 2, 4 and 6 can be considered successful in producing liquid products. In run No. 1 the amount of lignin subjected to hydrogenation was so small, only 25 grams, that the amount of products formed and separated was of necessity small. However, solubility tests on run No. 1 indicated the presence of weak acidic compounds, probably phenols.

In run No. 3 no liquid solvent was added to the bomb for the hydrogenation. It was thought that possibly in this way the effect of the solvent could be determined. There were no liquid products. The solid material removed had lost 32 grams in weight indicating a destructive decomposition to gaseous products. This was proven to be correct when the effluent gases from run No. 3 were analyzed. The large amount of methane indicated that the methoxy groups and possibly the aromatic ring structures themselves were decomposed by the high temperature of the run. The solid material was black and charred, somewhat like charcoal.

For run No. 5 distilled water was used as the solvent. According to Harris, Saeman and Sherrard (9)

this should give similar results to that obtained with a hydrocarbon solvent, however, in this case very little hydrogenation was accomplished. The material removed was black and charred, but no liquid products could be recovered. The solution removed was neutral to litmus; when acidified there was no indication of reaction; when made alkaline no noticeable reaction occurred; when distilled the water was removed at 100°C. leaving a black residue. When the original solution was extracted with ether, the ether layer was slightly yellow. No liquid products could be obtained from this layer when the ether was distilled.

For run No. 2 tetralin was used as the solvent with Shell 105 catalyst. Seventy-five grams of lignin were charged and 33.3 grams of solid material were recovered after allowing for the weight of catalyst employed. This would indicate a percentage conversion of solid to liquid or gaseous products of 55.6. A black tarry material weighing approximately 10.5 grams was precipitated when the solution was extracted with 5 percent sodium hydroxide solution. This material was soluble in 95 percent ethanol and only slightly soluble in ether. When the sodium hydroxide layer was saturated with carbon dioxide a dark brown precipitate

was formed which weighed approximately 6.0 grams after air drying. This material smelled very much like phenol and decomposed at some temperature less than 95°C .

When the sodium bicarbonate solution was acidified a light brown precipitate was formed which weighed approximately 1.3 grams after air drying. This should consist of a mixture of acids. The neutral solution remaining after the sodium hydroxide extraction was steam distilled. From 346 milliliters 260 milliliters were recovered. This distillate was then subjected to a fractionation at atmospheric pressure with three fractions being recovered as indicated in Tables I and II. Fractions 2 and 3 were principally tetralin and thus no further work was done on them. Fraction 1 had a sweet aromatic odor. A picrate derivative stable in air and melting at $113-115^{\circ}\text{C}$. was prepared. The crystals were small light yellow flat plates. An aroyl benzoic acid derivative was also prepared, melting between $147-152^{\circ}\text{C}$. An attempt to purify this derivative further by recrystallization failed. Upon nitrating this fraction a red gummy oil was formed, but no crystallization could be induced using different solvents.

For run No. 4 tetralin was used as the solvent but no catalyst was employed. According to Boomer, Edwards and Argue (4) tetralin itself should act as a hydrogen carrier because of the highly active hydrogen atoms in the 1, 2, 3, 4 positions. Seventy-five grams of lignin were charged and 19.5 grams of solid were removed after hydrogenation. This would indicate a percentage conversion of solid to liquid or gaseous products of 74. The previously described method of separation was followed with 3 grams of phenolic material precipitating from the sodium hydroxide solution when saturated with carbon dioxide. One and six-tenths grams of mixed acids were recovered from the acidified sodium bicarbonate solution. The neutral solution was subjected to a simple distillation and then fractionated in a 15 theoretical plate spiral packed column. Four fractions were recovered as shown in Tables I and II.

For run No. 6 a specially prepared nickel catalyst was employed. The preparation of this catalyst has been described previously under "Selection of Conditions". Tetralin was used as the solvent. Seventy-five grams of lignin were charged but the amount of solid remaining after hydrogenation could not be determined because the amount of nickel catalyst deposited on pumice was not

determined. In this run small round pebbles were introduced into the bomb to promote better mixing. When the sodium hydroxide solution was saturated with carbon dioxide a black gummy precipitate was formed. An attempt to remove this material from the solution by ether extraction partly succeeded, however, 3.3 grams of solid was removed by filtration after ether extraction which was not soluble in ether, but was soluble in slightly alkaline solution. The sodium bicarbonate solution was acidified with 2.8 grams of mixed acids recovered by filtration. The ether solution was dried over sodium sulfate and distilled. Thirty milliliters of a black oil was left after the ether was removed. This oil was subjected to a vacuum distillation at 12 millimeters pressure. Ten milliliters of a colorless liquid was recovered boiling between 95-105°C. at this pressure. The normal boiling point of this liquid at 760 millimeters should be between 220-230°C. as determined from a Cox chart. The method of separation employed on this liquid would denote phenols, and various tests were applied to substantiate this hypothesis. The ceric ammonium nitrate test gave a red coloration in dioxane which according to Shriner and Fuson (17, p 96) indicates

phenols. Tests for unsaturation were made using bromine in carbon tetrachloride and aqueous potassium permanganate. Both of these tests gave positive results for unsaturation. An interesting result was obtained with the bromine. When the bromine was added the color disappeared immediately at first with no noticeable gas given off, however, after considerable bromine had been added the disappearance of the color was much slower and it was now accompanied with the release of a white gas presumably hydrogen bromide. This result would indicate addition until the compound was saturated and then substitution. A picrate derivative of this liquid was prepared, melting between 116-119°C. The crystals were flat lemon yellow plates. From the physical properties and the tests for unsaturation it was concluded that this liquid might contain some allyl phenols but no compound was identified definitely.

The neutral fraction after sodium hydroxide extraction was subjected to a simple distillation and then fractionally distilled in the previously described column. Nine fractions were obtained. An approximate distillation curve was constructed for this run. (See Page 37).

Samples from runs No. 1, 2 and 4 were combined and subjected to a simple distillation. The distillate was then fractionated and six fractions were collected as shown in Tables I and II.

The characterization factor as defined by Nelson (13, p 102) was determined for the different fractions of each run. This factor is calculated by the following equation.

$$K = \sqrt[3]{T_b/s}$$

where K = characterization factor

T_b = average boiling point, degrees

R. = degrees F. $\neq$ 460

s = specific gravity at 60° F.

This factor is useful in determining the paraffinicity of the various fractions. The values for this factor vary from 12.5 for straight chain aliphatic compounds to 9.5 for aromatic compounds. From Table II it is evident that all fractions obtained were definitely aromatic in nature. The higher values of the characterization factor obtained were probably influenced in part by aliphatic side chains.

Gas samples were removed from each run before the bomb was opened. They were obtained by displacing water from standard gas sampling bulbs. The analyses were conducted with a Fischer "Unitized" gas analysis apparatus.

The carbon dioxide was determined by absorption in KOH, illuminants were absorbed in fuming H_2SO_4 and oxygen absorbed in alkaline pyrogallol. The hydrogen and carbon monoxide were determined by oxidation over copper oxide maintained at 300°C . Methane and ethane were determined by slow combustion in an atmosphere of oxygen.

The results of these analyses are listed in Table III.

Table I
Results of Fractionation of Neutrals

<u>Run No.</u>	<u>Fraction No.</u>	<u>Volume ml.</u>	<u>Boiling Point Range °C.</u>
2	1	13	197-200
	2	10	200-202
	3	13	202-204
4	1	5	175-197
	2	5	197-202
	3	10	202-202
	4	20	202-202
6	1	1.0	114-154
	2	1.0	157-175
	3	2.4	177-182
	4	3.0	182-187
	5	2.8	187-194
	6	6.6	194-198
	7	3.6	197.5-198
	8	4.6	198-199.5
	9	160.0	199.5-204
Combined 1, 2 & 4	1	1.7	156-180
	2	3.0	180-190
	3	4.0	190-200
	4	3.5	198-200
	5	10.0	200-202
	6	26.0	202-203
Mixed Phenols Run No.6	1	10	95-105° @ 12 mm

Table II

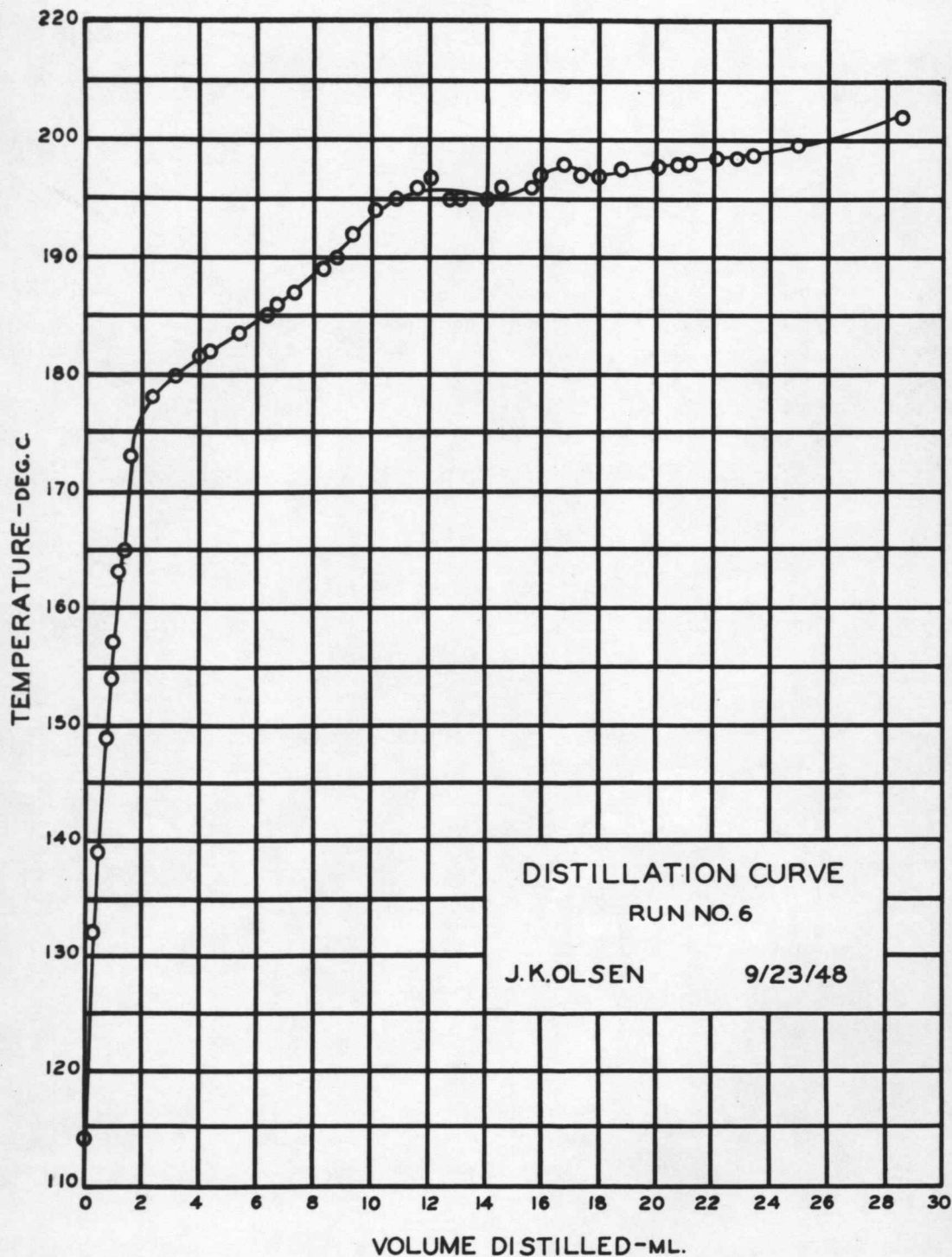
Physical Properties of Different Fractions

<u>Run No.</u>	<u>Fraction No.</u>	<u>Average Boiling Point °C.</u>	<u>Specific Gravity 60°F.</u>	<u>Refractive Index</u>	<u>Charac-terization Factor</u>
2	1	199	0.947	1.5358	9.66
	2	201	0.960	1.5426	9.62
	3	203	0.970	1.5486	9.62
4	1	187	0.905	1.4976	9.70
	2	200	0.955	1.5308	9.62
	3	202	0.960	1.5375	9.62
	4	202	0.963	1.5378	9.62
6	1	134	-	1.4500	-
	2	166	-	1.4675	-
	3	180	0.890	1.4895	9.72
	4	185	0.905	1.4985	9.68
	5	191	0.915	1.5092	9.68
	6	196	0.935	1.5225	9.66
	7	198	0.940	1.5225	9.66
	8	198.5	0.950	1.5310	9.62
	9	202	0.968	1.5412	9.60
Combined 1, 2 & 4	1	178	0.895	1.4848	9.68
	2	185	0.910	1.4994	9.68
	3	195	0.940	1.5195	9.65
	4	199	0.955	1.5300	9.62
	5	201	0.960	1.5350	9.62
	6	202	0.968	1.5385	9.60
Mixed Phenols Run No. 6	1	225	0.976	1.5430	9.70

Table No. III

Results of Gas Analyses

<u>Component</u>	<u>Run #2</u>	<u>Run #3</u>	<u>Run #4</u>	<u>Run #5</u>	<u>Run # 6</u>
Carbon Dioxide	7.3	9.0	5.0	8.4	12.9
Illuminants	0.2	0.2	Neg.	0.2	0.3
Oxygen	0.8	0.6	1.2	0.4	0.9
Hydrogen	65.2	35.0	78.5	85.5	48.3
Carbon Monoxide	0.4	1.3	1.8	0.4	5.4
Ethane	3.0	7.0	0.9	Neg.	Neg.
Methane	15.4	36.3	6.6	1.3	26.0
Nitrogen (By Diff.)	7.7	10.6	6.0	3.8	6.2



CONCLUSIONS

Although no evidence was found that n-propyl benzene had been obtained, definite indication of some hydrogenation having taken place was obtained. The fact that unsaturation was found in some of the liquid products would indicate that part of the reaction was one of thermal cracking rather than hydrogenolysis of the lignin molecule. The relatively large amount of methane obtained in the effluent gases indicates a cracking between methoxy group and ring structure to form methanol. No methanol was isolated from these runs. The possibility of some methane having been obtained from hydrogenolysis of methyl side chains can not be overlooked.

In all runs using tetralin as the solvent no indication of water was obtained. This would indicate that the hydroxyl groups attached to the lignin molecule were not removed to form water.

It can be concluded from the results obtained that cracking of the lignin molecule can be accomplished with the high temperature, however, to insure complete saturation of any side chains attached to ring structures it will be necessary to have a higher pressure than 500 pounds per square inch cold hydrogen pressure.

The characterization factor was practically constant for all fractions from the fractionation of the neutrals for runs No.s 2, 4 and 6. Since this factor depends upon the paraffinicity of the material, the results would indicate aromatic compounds almost exclusively in all fractions.

The distillation curve of run No. 6 (Page 37) would seem to indicate that most of the fractions coming off consisted principally of tetralin which boils at 204° - 207° C. This was not correct, however, since physical data obtained such as specific gravity and refractive index were considerably different from that listed in the literature for tetralin. The odor of these fractions was also different from that of tetralin.

RECOMMENDATIONS

The author would like to offer the following recommendations for future work on this problem:

1. One of the greatest difficulties during these runs was leaks. A more efficient method of sealing the bomb must be obtained so that a large number of runs can be easily and quickly made.

2. The capacity of the bomb is such that only a relatively small amount of material can be handled at one time, therefore, it is suggested that several runs be conducted under exactly the same conditions and that these runs be analyzed collectively.

3. For efficient mixing, a more vigorous method of shaking must be devised. The mixing would probably be increased considerably if small steel balls were introduced into the bomb.

4. To insure complete hydrogenation it will be necessary to obtain higher hydrogen pressures than are now available. A cold hydrogen pressure of at least 1000 pounds per square inch should be possible.

5. A study of the effects of various catalysts and solvents should be undertaken. It has been shown that dioxane is one of the best hydrogenation solvents for lignin, however, until higher pressures are

available its use will have to be omitted because a lower temperature would have to be employed.

6. For the analysis of the products obtained a more efficient fractionating column should be constructed. On the column used, the reflux ratio was difficult to adjust and maintain, thus if some type of automatic control could be introduced, better fractionation would result.

BIBLIOGRAPHY

1. Adkins, Homer, Frank, R. L. and Bloom, E. S., "Products of the Hydrogenation of Lignin", J. Am. Chem. Soc. 63, 549-55 (1941).
2. Bailey, A. J., "The Industrial Hydrogenation of Lignin", Pacific Chem. Met. Ind. 4, No. 1, 13-14, 16 (1940).
3. Bailey, A. J., "Volatile Hydrogenation Derivatives of Lignin", J. Am. Chem. Soc. 65, 1165-8 (1943).
4. Boomer, E. H., Edwards, J. and Argue, G. H. "Hydrogenations in Tetralin Medium", Can. J. Research v 13 n6 sec. B Dec. 1935 p 323-30.
5. Drake, N. L. "Organic Synthesis", v 21 p 16 John Wiley & Sons. New York, New York (1941).
6. Hachihama, Yoshikazu and Jodia, Sho, "Catalytic Hydrogenation of Lignin", J. Soc. Chem. Ind. Japan 44, 773-6 (1941).
7. Harris, E. E. and Adkins, H., "Reactions of Lignin with Hydrogen", Paper Trade J. 107, No. 20, 38-40 (1938).
8. Harris, E. E., D'Ianni, J. and Adkins, H., "Reaction of Hardwood Lignin with Hydrogen", J. Am. Chem. Soc. 60, 1467-70 (1938).
9. Harris, E. E., Saeman, J. and Sherrard, E. C., "Hydrogenation of Lignin in Aqueous Solutions", Ind. Eng. Chem. 32, 440 - 1 (1940).
10. Hatihama, Yosikazu, Zyodai, Syo and Umezu, Masao, "Lignin and Related Compounds. I. Hydrogenation of Softwood Lignin", J. Soc. Chem. Ind., Japan 43, Suppl. binding 127 (1940) (in English).

11. Lautsch, W., "Oxidative and Hydrogenating Degradation of Wood, Lignin and Sulfur-containing Waste Liquor from Spruce", Cellulosechem. 19, 69-87 (1941) Svensk Papperstid 44,440 (1941).
12. Moldavskii, B. L. and Vainshtein, S. M., "Hydrogenation of Lignin" Khim Tverdogo Topliva 6, 656-62 (1935).
13. Nelson, W. L., "Petroleum Refinery Engineering", 2nd. Ed., p 101-105, McGraw-Hill Book Co. New York, New York (1941).
14. Phillips, Max, "Chemistry of Lignin V. Distillation of Alkali Lignin with Zinc Dust in an Atmosphere of Hydrogen", J. Am. Chem. Soc. 53, 768-74 (1931).
15. Phillips, Max and Goss, M. J., "Chemistry of Lignin VI. Distillation of Alkali Lignin with Zinc Dust in an Atmosphere of Hydrogen", J. Am. Chem. Soc. 54, 1518-21 (1932).
16. Saeman, J. F. and Harris, E. E., "Hydrogenation of Lignin over Raney Ni", (Forest Products Lab., Madison, Wis.) J. Am. Chem. Soc. 68, 2507-9 (1946).
17. Shriner, R. L. and Fuson, R. C., "The Systematic Identification of Organic Compounds", 3rd. Ed., John Wiley & Sons, New York, New York (1948).

APPENDIX

OPERATION DATA:

Run No. 1

Date: July 26, 1948

Weight of Lignin - 25 gms.

Weight of Catalyst - 25 gms.

Volume of Tetralin - 650 ml.

Initial H₂ Pressure - 375 lb. per sq. in. @ 20°C

<u>Time</u>	<u>Volts</u>	<u>Amps.</u>	<u>Pressure</u>	<u>Temp.</u> °F
10:47 A.M.	100	12	375 #/sq.in.	68
11:00	130	16	450	
11:15	133	15.8	550	
12:25	170	11.5	650	420
12:55	165	11.5	850	555
1:11 P.M.	165	11.5	950	630
1:22	160	10.0	1035	685
1:30	160	9.0	1050	685
1:45	148	8.0	1050	685
2:00	148	8.0	1050	700
2:15	104	6.8	1050	700
2:45	104	6.8	1040	700
3:15	104	6.8	1030	700
3:45	104	6.8	1025	705
4:15	104	6.8	990	706
4:45	104	6.8	980	720
6:13	80	5.0	840	670
6:45	104	6.8	890	700

Heat turned off at 7:00 P.M.

Volume of Liquid Removed - 520 ml.

Run No. 2

Date: August 7, 1948

Weight of Lignin - 75 gms.

Weight of Catalyst - 75 gms.

Volume of Tetralin - 600 ml.

Initial H₂ Pressure - 400 lb. per sq. in. GaugeTemp. of H₂ at Start - 68°F.Final H₂ Pressure - 200 lb. per sq. in. GaugeTemp. of H₂ at End - 140°F.

<u>Time</u>	<u>Volts</u>	<u>Amps.</u>	<u>Pressure</u>	<u>Temp. °F.</u>
8:15 A.M.	100	5.2	400 #/sq.in.	68
8:45	200	10.05	515	280
9:15	200	10.05	600	480
9:45	200	10.05	725	627
10:15	160	8.0	795	685
10:45	120	6.0	925	720
11:15	100	5.2	965	730
11:45	100	5.2	965	720
12:15	100	5.2	1000	730
12:45	120	6.0	1000	720
1:00 P.M.	120	6.0	1025	735
2:30	100	5.2	990	715
3:00	110	5.6	1005	720
3:30	110	5.6	1015	733
4:00	110	5.6	1025	733
4:30	110	5.6	1040	737
5:00	110	5.6	1060	739
5:30	105	5.3	1060	737
7:00	100	5.2	1075	670

Heat turned off at 7:00 P.M.

Weight of Solid Removed - 108.3 gms.

Volume of Liquid Removed - 540 ml.

Gas Sample Withdrawn - 8/8/48.

Run No. 3

Date: August 26, 1948

Weight of Lignin - 75 gms.

Weight of Catalyst - 75 gms.

Volume of Tetralin - None

Initial H₂ Pressure - 500 lb. per sq. in. @ 25°C.Final H₂ Pressure - 250 lb. per sq. in. @ 22°C.

<u>Time</u>	<u>Volts</u>	<u>Amps.</u>	<u>Pressure</u>	<u>Temp. °F.</u>
10:45 P.M.	200	10.2	500 #/sq.in.	77
11:30	200	10.2	500	140
12:00	200	10.2	500	200

Leak Noted and Stopped - Run Resumed

2:10 A.M.	200	10.2	675	160
2:30	200	10.1	875	190
3:00	200	10.1	1000	275
3:30	200	10.1	1100	350
4:00	200	10.1	1125	400
4:30	210	10.6	1100	440
5:00	210	10.6	1112	465
5:30	220	11.0	1137	487
6:00	220	11.0	1150	515
6:30	210	10.6	1150	530
7:00	210	10.6	1145	537
7:30	220	11.1	1125	537
8:51	220	11.2	1150	560
9:30	220	11.2	1150	560
10:00	220	11.4	1150	575
10:30	225	11.5	1150	575
11:00	225	11.5	1150	575
11:30	225	11.5	1150	585
12:00	225	11.6	1150	585
12:55 P.M.	225	11.6	1150	620
2:40	225	11.4	1125	595
3:15	235	12.0	1135	600
3:35	230	11.8	1140	610

Run No. 3 (Continued)

Heat turned off at 3:35 P.M.

Weight of Solid Removed - 118 gms.

Gas Sample Withdrawn 8/27/48.

Run No. 4

Date: August 28, 1948

Weight of Lignin - 75 gms.

Weight of Catalyst - None

Volume of Tetralin - 600 ml.

Initial H₂ Pressure - 400 lb. per sq. in. @ 68°F.Final H₂ Pressure - 300 lb. per sq. in. @ 73°F.

<u>Time</u>	<u>Volts</u>	<u>Amps.</u>	<u>Pressure</u>	<u>Temp. °F.</u>
8:20 A.M.	200	10.8	400 #/sq.in.	68
9:00	200	10.0	575	250
9:30	200	10.1	675	360
10:00	200	10.1	725	400
10:30	200	10.1	775	425
11:00	225	11.0	925	510
11:30	225	11.1	1200	610
12:00 Noon	150	7.6	1375	665
1:05	122	6.1	1185	605
1:30	120	6.0	1475	725
2:00	65	4.5	1225	650
2:30	115	6.0	1195	637
3:15	115	6.0	1175	650
3:45	160	7.5	1300	715
4:30	95	5.0	1175	665
5:00	155	8.0	1175	675
8:00 P.M.	-	-	675	400
8:00 A.M.	-	-	300	73

Heat turned off - 5:00 P.M.

Weight of Solid Removed - 19.5 gms.

Volume of Liquid Removed - 450 ml.

Gas Sample Withdrawn 8/29/48.

Run No. 5

Date: August 31, 1948

Weight of Lignin - 100 gms.

Weight of Catalyst - 75 gms.

Volume of H₂O - 700 ml.Initial H₂ Pressure - 775 lb. per sq. in. @ 65°F.Final H₂ Pressure - 325 lb. per sq. in. @ 104°F.

<u>Time</u>	<u>Volts</u>	<u>Amps.</u>	<u>Pressure</u>	<u>Temp. °F.</u>
8:30 A.M.	200	10.3	775 #/sq.in.	65
9:00	200	10.0	1130	257
9:30	200	10.0	1375	347
10:00	220	11.0	1525	383
10:30	225	11.0	1550	446
11:00	-	-	1380	446
11:30	-	-	875	302
2:30 P.M.	-	-	675	176
3:30	-	-	650	158

Leak Noted - Current Turned Off at 10:45 A.M.

Drew Off 50 ml. Sample - Added 300 ml. More H₂O.

Run Resumed - 3:50 P.M.

<u>Time</u>	<u>Volts</u>	<u>Amps.</u>	<u>Pressure</u>	<u>Temp. °F.</u>
3:50 P.M.	220	11.0	350	149
4:30	220	11.0	850	446
4:45	100	5.2	940	464
6:45	110	5.6	1100	464
9:30 P.M.	95	5.0	1075	464
9:15 A.M.	-	-	325	104

Heat Turned Off - 9:30 P.M.

Weight of Solid Removed - 135.8 gms.

Run No. 5 (Continued)

Volume of Liquid Removed - 550 ml.

Gas Sample Withdrawn - 9/1/48.

Run No. 6

Date: September 20, 1948

Weight of Lignin: 75 gms.

Volume of Tetralin - 600 ml.

Nickel Catalyst Suspended on Pumice

Initial H₂ Pressure - 380 lb. per sq. in. @ 66°F.Final H₂ Pressure - 210 lb. per sq. in. @ 95°F.

<u>Time</u>	<u>Volts</u>	<u>Amps.</u>	<u>Pressure</u>	<u>Temp. °F.</u>
10:52 A.M.	200	10.0	380 #/sq.in.	66
11:30	200	11.6	725	410
11:55	200	11.6	940	540
12:40	Lead Burned Out - Amps. Dropped to Zero			
12:57	200	10.0	700	420
1:30	224	11.0	1020	650
2:10	163	7.9	1325	735
2:30	134	6.5	1315	725
3:00	104	5.0	1325	710
3:30	120	5.9	1315	710
4:00	120	5.9	1325	707
5:00	85	4.2	1390	695
6:18	100	5.0	1250	645
6:33	115	5.5	1325	675

Heat Turned off at 6:33 P.M.

Volume of Liquid Removed -

Gas Sample Withdrawn - 9/21/48.

Preparation of Nickel Catalyst for Run No. 6

Approximately 350 grams of nickel nitrate were added to 200 milliliters of distilled water. This solution was stirred for one hour to insure complete solution. At the end of this time the solution was filtered and 100 grams of powdered pumice added. While the solution was being stirred dilute ammonium hydroxide was added until the solution was a definite sky blue color. The solution was again filtered and the residue washed with distilled water. After washing, the residue was placed in a furnace at 900 to 1000°F. for six hours. The solid was then removed, cooled and placed in the hydrogenation bomb. The catalyst was reduced in an atmosphere of hydrogen according to the following data.

<u>Time</u>	<u>Volts</u>	<u>Amps.</u>	<u>Pressure</u>	<u>Temp. °F.</u>
8:15 A.M.	200	10.0	350 #/sq.in.	61
8:30	200	9.8	460	160
9:00	200	9.8	550	300
9:30	212	10.5	610	400
11:20	205	10.1	650	510
11:45	220	10.8	700	600
1:45 P.M.	200	9.6	350	780

New hydrogen admitted with pressure increased to 575 pounds per square inch.

2:00	185	9.0	580	860
2:30	155	7.8	575	860
2:50	-	-	575	845

Heat turned off at 2:50 P.M.

