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SAND2002-1317  
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Printed May 2002

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**Batch Microreactor Studies of Lignin  
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1. Alcohol Solvents**

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# **Batch Microreactor Studies of Lignin Depolymerization by Bases.**

## **1. Alcohol Solvents**

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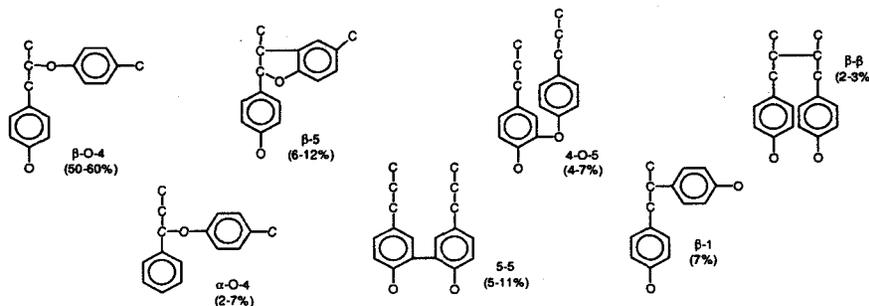
### **Abstract**

Biomass feedstocks contain roughly 10-30% lignin, a substance that can not be converted to fermentable sugars. Hence, most schemes for producing biofuels (ethanol) assume that the lignin coproduct will be utilized as boiler fuel to provide heat and power to the process. However, the chemical structure of lignin suggests that it will make an excellent high value fuel additive, if it can be broken down into smaller molecular units. From fiscal year 1997 through fiscal year 2001, Sandia National Laboratories was a participant in a cooperative effort with the National Renewable Energy Laboratory and the University of Utah to develop and scale a base catalyzed depolymerization (BCD) process for lignin conversion. SNL's primary role in the effort was to utilize rapidly heated batch microreactors to perform kinetic studies, examine the reaction chemistry, and to develop alternate catalyst systems for the BCD process. This report summarizes the work performed at Sandia during FY97 and FY98 with alcohol based systems. More recent work with aqueous based systems will be summarized in a second report.

Batch microreactor studies demonstrated that the conversion of lignin to ether solubles by KOH in methanol or ethanol was rapid at 290 °C, reaching the maximum value (only 7% ether insoluble material remaining) within 10-15 minutes. Model compound studies confirmed that the dominant depolymerization route is the solvolysis of ether linkages. Strong bases (KOH, NaOH, CsOH) were shown to convert more of the lignin to ether soluble material than weaker bases (LiOH, Ca(OH)<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub>). An excess of base relative to lignin monomer units is required for maximum conversion. However, a synergistic interaction between NaOH and Ca(OH)<sub>2</sub> allows reasonable conversions of lignin to be achieved with small amounts of NaOH by coupling it with Ca(OH)<sub>2</sub>. Ethanol and methanol are converted to acetic and formic acid respectively under the reaction conditions with an activation energy of approximately 50 kcal/mol. This results in a loss of solvent, but more importantly neutralizes the base catalyst, halting forward progress of the reaction, and accounting for the excess base requirement.

## 1. Introduction

Lignins are complex polymers found in nature where they provide strength to vascular plants. Chemically, they are a polymer of phenylpropane-based monomers joined by ether and carbon-to-carbon linkages. In native (unprocessed) lignins, generally two thirds or more of the total linkages are ether bonds, while the remaining are carbon-carbon bonds [1]. Several common linkages between the phenylpropane monomers are shown in Figure 1 below.



**Figure 1.** Chemical bonds commonly found in lignin – the monomer units have been simplified for clarity.

All lignocellulosic biomass contains significant quantities of lignin (roughly 15-30%). Unlike cellulose and hemicellulose, the other principal constituents of biomass, lignin can not be converted to fermentable sugars. Thus, any fermentation-based ethanol production process (from biomass) will produce a large quantity of lignin by-product. Most of the lignin entering a biomass-to-ethanol process will be present in the solid residue remaining after the dilute acid pretreatment and simultaneous saccharification and fermentation (SSF) steps. This high molecular weight lignin is soluble in aqueous basic solutions, and can be readily recovered from the protein, unconverted carbohydrate, and other non-lignin materials present in the residue by solubilization.

Capturing the value of the lignin residue will significantly enhance the economic competitiveness of biomass-to-ethanol conversion. The simplest approach to lignin utilization is to burn the residue for process heat, as is currently done in the pulp and paper industry (this also helps recover valuable pulping chemicals for recycle). However, given the molecular structure of lignin, it is potentially more productive to convert the lignin into valuable high-octane fuel additives (gasoline blending agents) such as aromatic hydrocarbons and/or ethers. Sandia National Laboratories was a participant in a cooperative effort with the National Renewable Energy Laboratory and the University of Utah to develop and scale-up a process for this conversion.

The process in question, originally proposed and researched by Shabtai and coworkers [2], is a two stage process related to processes developed for coal liquefaction [3]. The first stage involves base-catalyzed depolymerization (BCD) using supercritical methanol or ethanol (250-290 °C) as a reaction medium. The use of supercritical alcohol, rather

than aqueous pulping solutions, builds on previous successes in converting low rank coals [3-12]. During depolymerization, ether linkages are broken (see below), resulting in smaller and lower molecular weight lignin products. Because smaller molecular weight compounds tend to have greater solubility, the extent of depolymerization can be characterized by the amount of water and ether insoluble material remaining after the reaction. The second stage involves hydroprocessing the depolymerized lignin intermediate.

Sandia's primary role in the effort was to utilize rapidly heated batch microreactors to perform kinetic studies, examine the reaction chemistry, and to develop alternate catalyst systems for the BCD process. This report summarizes the work, some of which has been previously reported [13,14], performed at Sandia during FY97 and FY98 with alcohol based systems. More recent work with aqueous based systems will be presented in a second report.

## **2. Experimental**

**2.1 Baseline Lignin Studies:** The technical lignin samples used in this study were obtained from the manufacturers by the National Renewable Energy Laboratory and supplied to Sandia National Laboratories where they were used in the as-received condition. The Alcell lignin sample from Repap Technologies Inc. (Valley Forge, PA) was derived from mixed hardwoods by an ethanol organosolv pulping method. The Indulin AT lignin sample from Westvaco (Charleston Heights, SC) was a softwood Kraft lignin. This sample had been treated by Westvaco to reduce the nitrogen, ash, and to some extent the sulfur content of the lignin relative to their typical commercial product. Analysis of these lignins [15] shows that they are indistinguishable from lignins used in the two-dimensional round robin lignin analysis conducted in 1991 for the International Energy Agency, Bioenergy Agreement, Biomass Conversion Annex VII.

The lignin depolymerization studies were conducted in microreactors consisting of capped ¾" Swagelok bulkhead unions (internal volume approximately 14 cm<sup>3</sup>). In each baseline run, 0.434 g of as-received Alcell or Indulin lignin was weighed into the reactor, and then 4.4 ml of a 10% (w/w) solution of KOH in research grade methanol or ethanol was added. The reactor was then securely sealed and rapidly heated in a fluidized sand bath to 290 °C. This is above the critical temperature for both methanol and ethanol. Tests in which thermocouples were swaged into a union containing the reaction mixture indicated that approximately 90 seconds is required for the fluid in the reactor to equilibrate at the bath temperature. After the desired reaction time had elapsed, the reactors were removed from the bath and rapidly quenched in water (about 30 seconds are required to remove and quench a reactor). Reactions were carried out in duplicate for times ranging from 0-60 minutes, with 0 indicating the reactor was allowed to come to temperature for 90 seconds, and then removed from the bath. The 30 second removal and quench time are not included in the reported reaction times. As a control, blank runs with no heating were also carried out. In many cases, duplicate reaction tests were repeated, resulting in as many as four data points for each time period.

After the reactors were cooled, they were carefully opened, relieving the pressure resulting from the formation of gaseous products. In the few cases where pressure was not released upon opening, the contents were discarded and the experiment was repeated since this was considered to be indicative of a leak during the reaction. The liquid and solid products of the reaction were rinsed from the vessel with deionized water and acidified to a pH of 2 (verified by pH paper) with concentrated HCl causing a precipitate to form. The recovered products were then covered and refrigerated overnight to allow the precipitate to grow and settle. The solid products were then recovered with a preweighed Whatman 541 filter. The solids were rinsed/extracted with deionized water followed by diethyl ether until the filtrate ran clear. The filter paper and remaining solids were allowed to air dry, and were then transferred to a 45 °C vacuum oven. After drying overnight, the filter papers and remaining solids were removed from the oven, allowed to air equilibrate for at least one hour and weighed. The results are expressed as the mass of unconverted lignin as a percentage of the original mass. The amount of converted material that was ether soluble, but not water soluble, was obtained by difference using a similar procedure in experiments that eliminated the ether extraction step.

**2.2 Simulated Distillation:** A simulated distillation type analysis was performed on the water insoluble products (ether solubles + “unconverted material”) from a number of runs to assess the degree of depolymerization occurring during the depolymerization step. The samples were analyzed in a fashion similar to ASTM D2887 using an HP 5890 gas chromatograph and AC Analytical Controls’ D2887 simulated distillation software.

**2.3 Effect of Base Type and Concentration:** As a follow on to the baseline lignin depolymerization experiments, similar studies were conducted with a number of different bases and combinations of bases including CsOH, NaOH, LiOH, Ca(OH)<sub>2</sub>, and Na<sub>2</sub>CO<sub>3</sub>. The reaction conditions were standardized at 290 °C, 60 minute reaction time, Alcell lignin, and ethanol solvent. Similar ion equivalents of the bases were added to the reactors to evaluate and compare the bases individually and in combination. NaOH was added to the reactor as an ethanolic solution. The remaining bases were weighed into the reactors as solids.

**2.4 Model Compound Studies:** Model compound studies were conducted in capped ¼” Swagelok unions (internal volume approximately 8 cm<sup>3</sup>). In general, solutions of 10% model compound (w/w) were prepared by adding the model compound to 10% (w/w) KOH/ethanol solutions. Three milliliters of the resulting solution were transferred to the reactors that were then sealed. The reaction procedure then followed that of the lignin studies. The model compounds chosen for study included phenol, anisole, phenetole, guaiacol, phenyl ether, benzyl phenyl ether, 2,3-dihydrobenzofuran, biphenyl, diphenylmethane, bibenzyl, and trans-stilbene, all of which contain C-C or C-O linkages similar to those found in native or technical lignins. Control experiments using only ethanol and KOH were also carried out.

In cases where the model compound was insoluble in the KOH/ethanol solution at the 10% level, the compound was added in an amount near the solubility limit. For biphenyl and bibenzyl, 5% solutions were prepared. For guaiacol and trans-stilbene, saturated

solutions were prepared by adding an amount of the compound to a KOH/ethanol solution in excess of the solubility limit. After an extended mixing time, the resulting solution was filtered through a 0.45  $\mu\text{m}$  syringe filters.

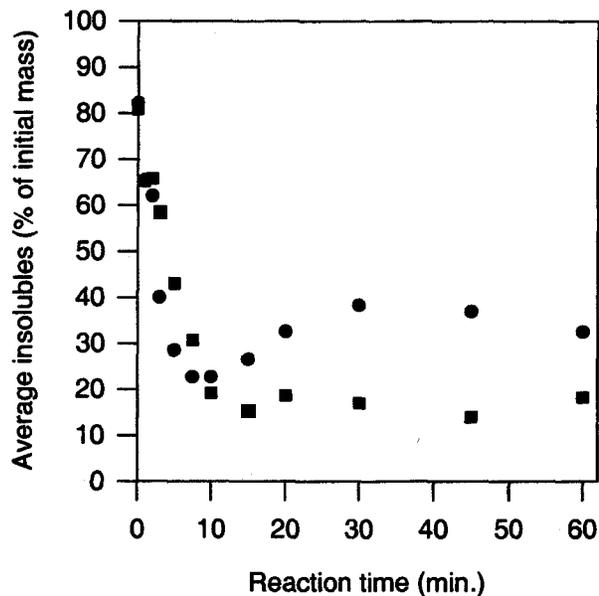
Unlike the lignin studies, the products from the model compound studies were acidified with excess formic acid so no precipitate formed, and then diluted with ethanol. Analysis was conducted with an HP 5890 gas chromatograph using a narrowbore 30 meter DB-Wax column (0.5  $\mu\text{m}$  phase) and an FID detector. External standards in ethanol were used for quantification of the model compounds. Product identification was carried out by using the same column in an HP 5890 gas chromatograph with a series 5972 mass selective detector.

**2.5 Neutralization of Base by Organic Acids:** To evaluate the conversion rate of alcohol solvents to organic acids, 3 mL aliquots of a solution consisting of 10% (w/w) base in alcohol were transferred to microreactors fashioned from capped  $\frac{3}{4}$ " Swagelok unions (internal volume approximately 8  $\text{cm}^3$ ). As before, the sealed reactors were heated in a fluidized sand bath to the desired reaction temperature (260-290  $^{\circ}\text{C}$ ), and after the desired reaction time had elapsed, the reactors were removed from the bath and quenched in water. The contents of the reactor were then quantitatively sampled, diluted with deionized water and titrated with HCl to determine the free hydroxide content. In cases where solid precipitates formed in the reactor, the entire contents were dissolved in DI water and titrated. Titrations were performed with a Mettler DL70ES autotitrator.

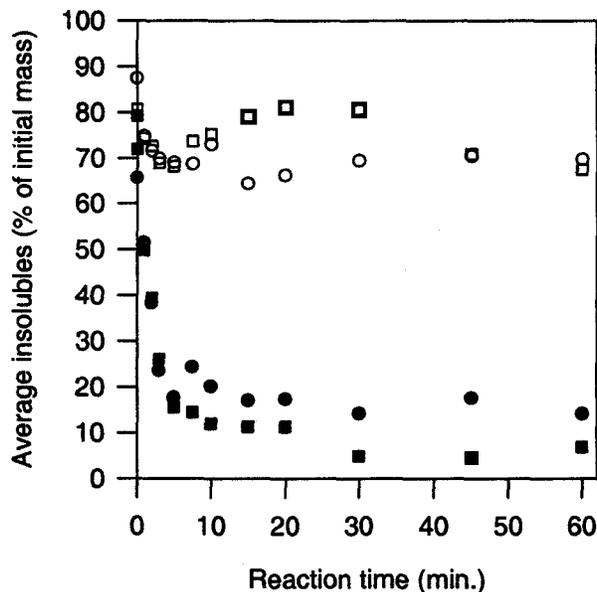
### **3. Results and Discussion**

**3.1 Baseline Lignin Studies:** Figures 2 and 3 summarize the solubility results from the baseline lignin depolymerization studies. The maximum conversion to water and ether solubles of both Kraft and organosolv lignins occurs during the first 15 minutes of the reaction. Additional reaction time appears to be detrimental in some cases, e.g. the conversion of Indulin AT in methanol. For both methanolic and ethanolic cases, the Alcell lignin showed greater maximum conversion to soluble products than did Indulin AT. This is despite potentially greater losses in recovering the Indulin lignin from the reaction vessel as it tended to adhere to the sides of the vessel.

Conducting the reactions in ethanol solutions resulted in a smaller amount of insoluble products compared to methanol solutions for both lignins. This is in contrast to results reported for coal, where the methanol/KOH combination resulted in a greater conversion to THF solubles than did ethanol/KOH [3]. A difference in texture for the precipitated products for the different solvents was also noted for both lignins; the ethanol-derived products appeared to have an oily character. This characteristic was most pronounced for the Alcell lignin, and caused problems in determining the water insoluble fraction of this lignin. In this case it was impossible to be certain when a sample was fully dry due to the apparent presence of volatile organics. This uncertainty may account for the increase in water insolubles for this material occurring after 10 minutes (Figure 3).



**Figure 2.** Water and ether insoluble material remaining after reaction of Indulin AT lignin in methanolic (●) and ethanolic (■) KOH solutions at 290 °C. In control experiments with no heating, insolubles were 96% and 91% for methanolic and ethanolic cases respectively.

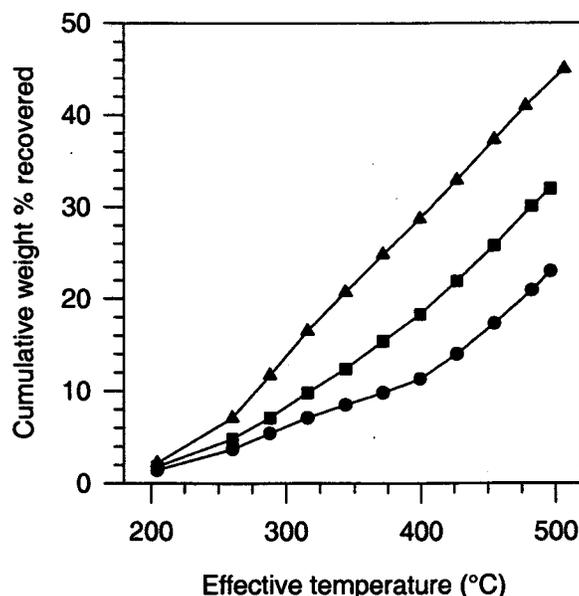


**Figure 3.** Insoluble material remaining after reaction of Alcell lignin in methanolic (● water and ether insoluble, ○ water insoluble) and ethanolic (■ water and ether insoluble, □ water insoluble) KOH solutions at 290 °C. In control experiments with no heating, insolubles were 92% and 79% of the original lignin mass for methanolic and ethanolic cases respectively.

The baseline microreactor data for Alcell lignin in 10% KOH/methanol (Figure 3) gave average yields of insolubles ranging from 14 to 17% at reaction times of 15 to 60 minutes. In similar studies conducted by Shabtai and coworkers in a 300 ml autoclave

over reaction times of 15 to 90 minutes, the Alcell lignin yielded average insolubles ranging from 6.5 to 9.0% of the original mass [2,16]. The most obvious difference between these studies that may account for the larger yield of unconverted lignin in the microreactors is the absence of prolonged heatup and cooldown periods. There are also differences in product recovery and workup necessitated by the small quantities employed in the microreactors. The soxhlet extraction procedure made practicable by the larger quantities used in the autoclave experiments is likely more efficient than the techniques employed in this study. Another possible contributing factor is the absence of active stirring in the microreactors.

**3.2 Simulated Distillation:** A D2887 simulated distillation type analysis was performed on samples of water insoluble fractions from the treatment of Alcell lignin with KOH/ethanol solutions. The as-received lignin was compared to samples taken during the first 15 minutes of processing and to samples taken after extended reaction periods to assess the degree of depolymerization occurring during the process. A potential weakness of the applying the simulated distillation approach to lignin is that the technique was designed for petroleum fractions and utilizes petroleum and normal alkane standards, rather than the oxygenated type species comprising lignin.



**Figure 4.** Simulated distillation analysis of as-received Alcell lignin (●) and the water insoluble fractions treated with KOH/Ethanol solutions at 290 °C for 10 minutes (■) and 2 hours (▲).

In order to assess the utility of the simulated distillation technique for a lignin derived material, a number of known compounds were chosen to model lignin monomers and dimers. The model compounds included anisole, phenetole, 2,3-dihydrobenzofuran, guaiacol, phenyl ether, bibenzyl, benzyl phenyl ether, and trans-stilbene. These compounds were analyzed individually and in combination by the simulated distillation technique. The resulting boiling points compared well to the known values, and in every case the simulated distillation value was lower than the actual value. The greatest

discrepancy was for bibenzyl (268 °C simulated vs. 284 °C actual) and the least was for phenetole (167 °C simulated vs. 170 °C actual). Also, the recovery of the model compound mixtures was > 95% indicating similar FID responses for the model compounds and the standard oils. Thus it was concluded that the simulated distillation technique could be reasonably applied to the lignin derived material.

The results of the simulated distillation analysis are shown in Figure 4. The water insoluble fractions of samples reacted for 10 minutes and 2 hours are both clearly more volatile than the as-received lignin. In addition, comparing the 10 min and 2 hour samples shows that although the maximum conversion to solubles occurs in 10 minutes or less (Figures 2 and 3), reactions continue to occur. This is consistent with changes seen in the water insolubles curve over the 10 to 60 minute time frame for the ethanolic solvent case in Figure 3. An important result for the simulated distillation was that even for the two hour reaction case, the total hydrocarbon recovery was less than 50%. This suggests that the reaction products still contain a large degree of oligomeric material.

**3.3 Effect of Base Type and Concentration:** The results for the depolymerization of Alcell lignin in ethanol with alternate bases and combinations of bases are presented in Table 1. Results for experiments evaluating the effect of base concentration are also presented. The experiments for different bases were conducted at similar molar base equivalents to facilitate comparisons.

**Table 1:** Effect of different bases, concentrations, and combinations of bases on the conversion of Alcell lignin to soluble products in ethanol at 290 °C for 1 hour.

Experiment	Milliequivalents of Base in Reactor						% Insolubles
	CsOH	KOH	NaOH	LiOH	Ca(OH) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	
Baseline	--	7.8	--	--	--	--	7
1	--	1.6	--	--	--	--	53
2	--	--	--	--	7.9	--	54
3	--	1.5	--	--	6.4	--	43
4	8.7	--	--	--	--	--	15
5	4.4	--	--	--	--	--	13
6	2.9	--	--	--	--	--	19
7	1.7	--	--	--	--	--	22
8	0.9	--	--	--	--	--	57
9	0.6	--	--	--	--	--	47
10	0.6	--	--	--	6.4	--	69 <sup>a</sup>
11	--	--	7.6	--	--	--	5
12	--	--	1.6	--	--	--	49
13	--	--	1.5	--	6.1	--	24
14	--	--	--	--	--	7.6	54
15	--	--	1.5	--	--	6.1	52
16	--	--	--	7.7	--	--	34
17	--	--	--	1.6	--	--	54
18	--	--	--	1.6	6.2	--	94

a. Products were a hard solid material that was very difficult to recover from reactor.

The first conclusion that can be drawn from Table 1 is that the strongest bases, CsOH, KOH, and NaOH, are the most effective at depolymerizing lignin when compared on a molar basis. A second important point that can be drawn from the table is that the highest conversions result when an excess of strong base is used in the reaction. For example, in the baseline case, roughly equivalent weights of KOH and lignin were in the reactor. Performing a comparison assuming a simple monomer unit, C<sub>9</sub>H<sub>10</sub>O (molecular weight of 134 g/mol), leads to the conclusion that there was 2.4 moles of base present in the reactor for every hypothetical monomer unit. Detailed analysis of the starting lignins has shown that the actual average molecular weight of a monomer unit is approximately 180 g/mol [15]. Thus, there may have actually been more than a 3-fold excess of base relative to lignin monomers during these experiments. Unfortunately, lowering the base concentration below the stoichiometric amount (2.4 meq, assuming an average MW of 180 g/mol) results in a large decrease in conversion to solubles. The effect appears to be least pronounced for CsOH. These results suggest that stoichiometric rather than base catalyzed reactions are dominating the overall process.

A final and very important conclusion that can be drawn from Table 1 is that combining alkali metal bases with Ca(OH)<sub>2</sub> can give synergistic effects. Experiments 12, 13, and 2 illustrate a strong positive effect of combining excess amounts of Ca(OH)<sub>2</sub> with a substoichiometric amount of NaOH. Insolubles were decreased from about 50% for the individual materials to less than 25% for the combined materials. There also appears to be a slight positive effect of Ca(OH)<sub>2</sub> on KOH (experiments 2 and 3). A similar effect has been noted for the interaction of KOH and Ca(OH)<sub>2</sub> on coal [17]. In contrast, Na<sub>2</sub>CO<sub>3</sub> had no synergistic effect with NaOH (experiments 12, 14, and 15). Furthermore, negative effects were observed upon the addition of Ca(OH)<sub>2</sub> to CsOH and LiOH (expts. 10 and 18). The reason for these differences is not known, but it is interesting to note that the negative effects were observed for cases where the strong bases had limited solubility in ethanol and were added to the reactor as solids. Thus the negative interaction may be related to a common ion effect on solubility.

**3.4 Model Compound Studies:** The results for the model compound screening studies are summarized in Table 2. Only the products that can be attributed to the model compounds are shown in the table; products derived solely from the ethanol solvent are not shown. As expected, the phenyl ether compounds were all converted to some degree under the reaction conditions. The model compounds not containing oxygen were stable under the reaction conditions. Trans-stilbene was an exception to this rule, as the double bond was hydrogenated, forming bibenzyl. Isomerization of the trans-stilbene to the cis form was also observed. Control experiments verified that the isomerization was not a result of the post-reaction formic acid addition.

For the noncyclic ethers, the preferred site for bond cleavage was the C-O bond most remote from an aromatic ring. This is evident in the conversion of anisole and phenetole to phenol, guaiacol to catechols, and the selectivity of benzyl phenyl ether to phenol and ethoxymethyl benzene. Further, phenyl ether, lacking a remote C-O bond, was less reactive than the other ethers. Guaiacol appeared to be the most reactive of these ethers,

but the result may have been skewed by the lack of solubility in the starting solution. The anticipated coproducts (methyl ethyl ether and diethyl ether) from anisole, guaiacol, and phenetole were not detected, probably due to evaporation loss of these volatile products when the reactors were opened.

The data suggest that numerous secondary reactions occur. Phenol was prone to reactions with the alcohol solvent or its products to form ethylated phenols. Thus, ethylated phenols were observed as minor and probably secondary products from anisole and phenetole. Similarly, ethylated catechols were observed in the conversion of guaiacol, although in this case the alkylated products were observed almost exclusively. The initial products from phenyl ether were evidently phenol and phenetole (formed through reaction with the ethanol). Phenetole then reacted further to produce additional phenol. In a similar fashion, benzyl phenyl ether initially reacted to primarily form phenol and ethoxymethyl benzene. Benzene propanol was also evidently formed to a very small degree. The benzyl alcohol product was probably produced through the secondary decomposition of the ethoxymethyl benzene. Alternately benzyl alcohol could have been produced through the cleavage of the aromatic C-O bond. However, phenetole would have been expected as a coproduct as in the phenyl ether case.

**Table 2:** Conversion and products detected in model compound studies conducted in KOH/Ethanol at 290 °C for 1 hour.

Model Compound <sup>a</sup>	Conversion	Major and minor products
Phenol	20%	<b>2-ethyl phenol, 4-ethyl phenol</b>
Anisole	50%	<b>Phenol, 2-ethyl phenol, 4-ethyl phenol</b>
Phenetole	50%	<b>Phenol, 2-ethyl phenol, 4-ethyl phenol</b>
Guaiacol (1.8 %)	90%	<b>Ethylated catechols, catechol<sup>b</sup></b>
Phenyl ether	10%	<b>Phenol, Phenetole</b>
Benzyl Phenyl ether	30%	<b>Phenol, Ethoxymethyl benzene, Benzyl alcohol, Benzene propanol</b>
2,3-Dihydrobenzofuran	95%	<b>Phenol, 2-ethyl phenol, 4-ethyl phenol, di and triethyl phenols, other alkylated phenols</b>
Biphenyl (5 %)	unreactive	
Diphenyl methane	unreactive	
Bibenzyl (5 %)	unreactive	
Trans-stilbene (3.4 %)	30%	<b>Bibenzyl, cis-stilbene</b>

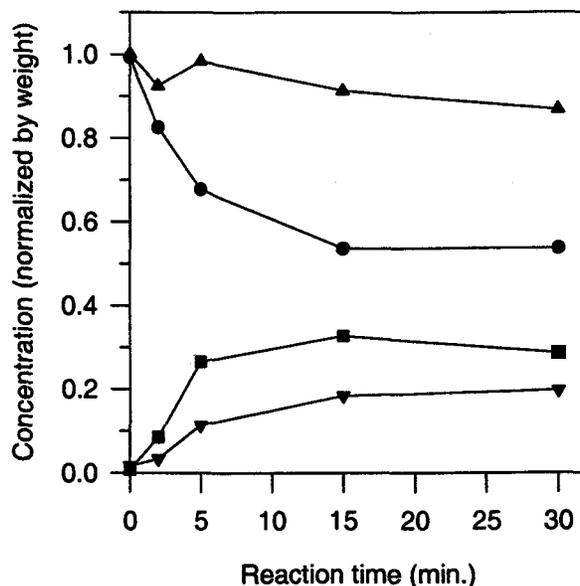
a. Not all compounds would go into solution at 10 weight %. In these cases the weight % model compound employed is shown in parentheses.

b. GC peaks were not well resolved. Mass spectra are consistent with a mixture of mono and diethyl catechols and catechol.

The cyclic ether 2,3-dihydrobenzofuran proved to be the most reactive compound tested, and gave a complex product distribution. Phenol and 2-ethyl and 4-ethyl phenol were major products. The presence of phenol suggests that at least one path of decomposition involved cleaving the C bonded to the aromatic ring. The ethylated phenols could then have resulted from secondary reactions of the phenol. Alternately, 2-ethyl phenol could have resulted from the cleavage of the ether bond. This however, would not account for

the presence of the 4-ethyl phenol, except through a rearrangement reaction. Secondary reactions between the solvent and phenolic products evidently led to a wide variety of polyethylated (primarily di and triethyl) phenols.

The model compound results are consistent with previous findings. Ross and Blessing tested anthracene and diphenyl ether in KOH/isopropanol solutions at 335 and 360 °C, respectively [12], and phenyl ether, biphenyl, bibenzyl, anthracene, and phenanthrene in KOH/methanol solutions at 400 °C [11]. In KOH/methanol, phenyl ether was converted to methylated phenols, anisole, and methylated anisole. No phenyl ether related products were identified in the KOH/isopropanol case. In both cases anthracene was extensively converted, primarily to dihydroanthracene. Biphenyl, bibenzyl, and phenanthrene were largely unconverted. Makabe and Ouchi tested the reactions of phenol, benzylphenyl ether, diphenylmethane, and anthracene in ethanol at 430-450 °C [18]. The predominant reactions observed were the splitting of ether linkages, the alkylation of aromatic rings, and the hydrogenation of aromatic rings.



**Figure 5.** Conversion of anisole (●) to phenol (■) in KOH/ethanol solutions at 290 °C. The anisole material balance (▲) accounts for change in molecular weight during the conversion. Reactions of the ethanol solvent to 1-butanol (▼) and other products were also observed.

In each model compound experiment performed in this study, a number of products were identified that could only have formed through reactions of the alcohol solvent. This was verified through control experiments in which no model compounds were added. The primary products detected were acetic acid and 1-butanol. Higher alcohols (hexanol) and acids (butanoic) were also detected. Esters, probably formed after the acidification step, were also evident, including a compound tentatively identified as 2-oxepanone. The formation of oxidation products from alcohols under similar conditions has been previously reported. Makabe and coworkers obtained sodium acetate (90% yield) and hydrogen gas from a NaOH/ethanol solution heated to 300 °C for 90 minutes [5]. Ethylene was also formed. Similarly, it was reported that isopropyl alcohol is converted

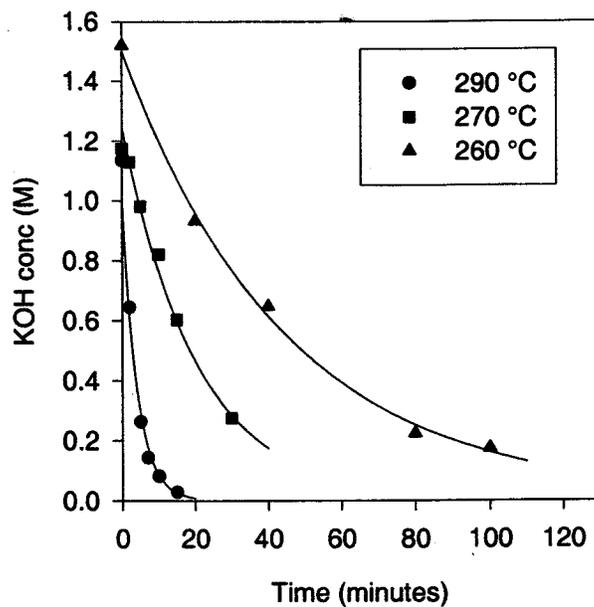
to acetone and hydrogen gas with KOH at 335 °C [12], and it has been suggested that methanol would undergo similar reactions [11,17]. These results suggest the higher order products in our system may have formed stepwise as follows: ethylene formation from ethanol, ethylene oligomerization, olefin hydrolysis (butanol, hexanol), alcohol oxidation (butanoic acid), esterification (upon acidification).

For comparison to the lignin reactions, the conversion of anisole was studied as a function of reaction time for three sets of duplicate runs. Representative data for a set of duplicate runs are presented in Figure 5. As in the baseline lignin studies, most of the conversion occurs during the first 15 minutes. Additional reaction time appears to result only in a small degree of secondary reactions. The material balance on anisole in the figure only accounts for the contributions of phenol (including the loss of CH<sub>2</sub>) and unconverted anisole. However, after 30 minutes of reaction time, over 85% of the initial anisole can be still be accounted for in this manner. The remaining material has at least partially been converted to ethylated phenols. The discontinuity in the material balance after 2 minutes was a feature that was exhibited in all three sets of duplicate runs that were carried out and may indicate the initial formation of intermediate products.

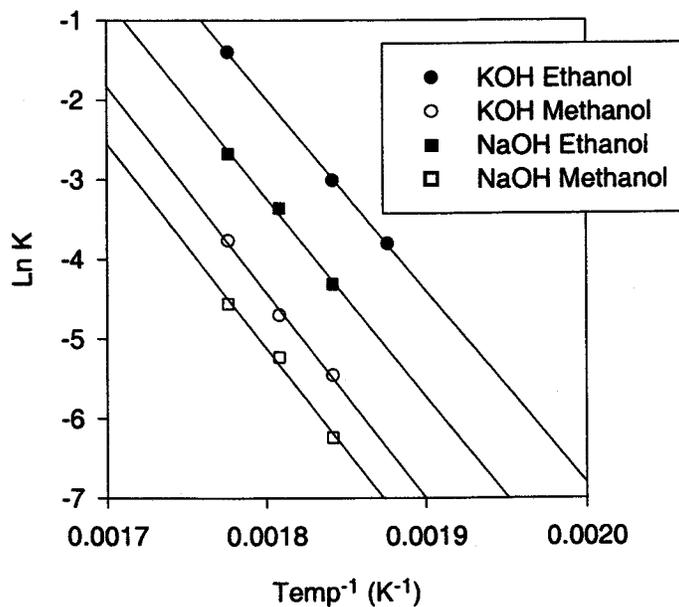
In order to at least partially characterize the reactions of ethanol, the appearance of 1-butanol was quantified and is shown in Figure 5. Reliable and reproducible quantification of acetic acid was not possible by GC due to poor resolution from formic acid. However, the GC data suggests that acetic acid was produced to a greater extent than the higher alcohols. Section 3.5 discusses control studies of acid formation where quantification was performed by acid-base titration.

**3.5 Neutralization of Base by Organic Acids:** Using titration, the formation of organic acids from methanol and ethanol in the presence of KOH and NaOH were studied as a function of time. Figure 6 illustrates that the conversion of ethanol to acetic acid proceeds relatively rapidly in the presence of KOH at 290 °C. Almost all the base is neutralized within the first 15 minutes of reaction. This, of course, would effectively end any base-catalyzed lignin conversion. Note that in Figure 2, lignin conversion has reaches its maximum at about 15 minutes reaction time. Assuming first order kinetics, reaction rate constants and Arrhenius parameters can be calculated for the reactions. The lines in Figure 6 are the first order fit to the data.

Figure 7 is the resulting Arrhenius plot for the data in Figure 6 and for similar reactions carried out with methanol and NaOH. Table 3 gives the Arrhenius parameters obtained from Figure 7. The activation energies (50 kcal/mol average) are similar suggesting that a similar reaction pathway is followed for all cases. As can be seen in Figure 6, the relatively large activation energy results in a significant temperature effect on the reaction rate. The combination of NaOH and methanol is the best case, giving the lowest conversion to acids. Thus by lowering the reaction temperature to 250 °C and by using NaOH and methanol rather than KOH and ethanol, the first order reaction rate constant for acid production (base neutralization) is lowered by a factor of more than 750 (Table 3). Additional work is required to determine the effects of these parameters on the lignin depolymerization reaction rate for comparison.



**Figure 6.** Conversion of ethanol to acetic acid in the presence of KOH as measured by the neutralization of KOH.



**Figure 7.** Arrhenius plots for the conversion of ethanol and methanol to organic acids by NaOH and KOH.

**Table 3.** Arrhenius parameters from Figure 6, and rate constants calculated using the parameters at 290, 270, and 250 °C.

System	A (min <sup>-1</sup> )	Ea (kcal/mol)	k <sub>290</sub> (min <sup>-1</sup> )	k <sub>270</sub> (min <sup>-1</sup> )	k <sub>250</sub> (min <sup>-1</sup> )
KOH/EtOH	e <sup>41.5</sup>	47.9	0.257	0.0531	0.00970
KOH/MeOH	e <sup>42.1</sup>	51.3	0.0220	0.00406	0.000657
NaOH/EtOH	e <sup>41.7</sup>	49.6	0.0722	0.0141	0.00243
NaOH/MeOH	e <sup>41.1</sup>	51.0	0.0109	0.00203	0.000333

#### 4. Summary and Conclusions

The batch microreactor studies demonstrate base catalyzed depolymerization reactions proceed in a reasonable time frame in alcohol solvents. Verification with lignins derived from ethanol production is required. The model compound studies verify that the primary reaction occurring during this depolymerization is the solvolysis of ether linkages. In ethanol solvent, phenols and ethyl ethers are the resulting products. These products are then subject to secondary reactions, i.e. ring alkylation and disruption of the new ether bond. The only evidence of C-C bond cleavage in the model compound studies was the production of phenol and 4-ethyl phenol from 2,3-dihydrobenzofuran. However, trans-stilbene was hydrogenated to bibenzyl and isomerized to cis-stilbene.

Kraft lignins are known to contain far fewer  $\alpha$ - and  $\beta$ -aryl alkyl ether linkages than native lignins. Rather, they contain linkages such as biphenyl, diphenyl methane, stilbene, diphenyl ethane, and diphenyl ether [19]. Analysis of the Alcell lignin used in this work has shown that it was also extensively modified during its isolation from wood [15]. Thus, considering that only etheric species were cracked in the model compound studies, one would expect a lignin derived from one of these pulping processes to yield oligomeric material upon being subjected to the treatment described herein. Lignins that have been less extensively modified may give significantly better results. If not, additional processing steps capable of cracking C-C bonds will probably be required to produce a light product appropriate for transportation fuel use.

Ethanol, a solvent that would be readily available from a fermentation process, rather than methanol, led to a more soluble product. The reason for the variation between solvents is not clear from this work, but could be related to alkylation of the aromatic rings by the solvents. In the model compound studies, every alkylated product identified was either a phenol or a catechol, indicating that the phenolic groups activate the aromatic ring for alkylation. Catechol appears to be more prone to alkylation than phenol, although additional experiments at similar concentrations of phenol and catechol are necessary to verify this trend. Consumption of ethanol via a ring alkylation process is economically undesirable. Hence, the alkylation reactions merit further study.

A key consideration in implementing a base driven depolymerization process is the cost and amount of base required to carry out the conversion. Obviously, the ideal process would use a minimum amount of an inexpensive, readily available, and easily recyclable

base. The best results in this study were obtained when a molar excess of a strong base (NaOH, KOH, CsOH), relative to lignin monomer units, was used. Lower concentrations resulted in decreased conversions, suggesting that stoichiometric reactions are dominating the process. High concentrations of inexpensive, weaker bases ( $\text{Ca}(\text{OH})_2$  and  $\text{Na}_2\text{CO}_3$ ) also resulted in poor conversions. Fortunately, a synergistic combination of a substoichiometric amount of NaOH and a larger amount of the less expensive  $\text{Ca}(\text{OH})_2$  can be used to achieve significant conversions.

The model compound work first showed that acetic acid was produced from the ethanol. Further studies with ethanol alone verified that acid formation is extensive and rapidly neutralizes the base at 290 °C, although the conversion is lower for methanol and at lower temperatures. In addition, the model compounds were converted to products with acidic character (i.e. phenols). Thus the reaction products may be expected to neutralize the base, stopping the forward reaction. This may explain the observed requirement for excess base to achieve maximum conversions. The synergistic effect of  $\text{Ca}(\text{OH})_2$  may result from it serving as a sacrificial base to be neutralized as the reaction progresses. That the effect is most pronounced when used in combination with NaOH may result from the fact that they are closer in base strengths than the other combinations studied. That is, the active component, NaOH, is less likely to be selectively neutralized first when compared to a stronger base.

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