BATCH MICROREACTOR STUDIES OF BASE CATALYZED LIGNIN DEPOLYMERIZATION IN ALCOHOL SOLVENTS

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The depolymerization of organosolv-derived lignins by bases in methanol or ethanol solvent was studied in rapidly heated batch microreactors. The conversion of lignin to ether solubles by KOH in methanol or ethanol was rapid at 290 °C, reaching the maximum value within 10-15 minutes. An excess of base relative to lignin monomer units was required for maximum conversion. Strong bases (KOH, NaOH, CsOH) convert more of the lignin to ether soluble material than do weaker bases (LiOH, $Ca(OH)_2$, and Na_2CO_3). 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.

INTRODUCTION

Drawing on previous experiences with coal liquefaction,[1] Shabtai and coworkers have recently developed a two-stage process for conversion of lignin to reformulated gasoline compositions.[2] The first stage of this process involves low-temperature (250-290 °C) base-catalyzed depolymerization (BCD) using supercritical methanol or ethanol as a reaction medium, whereas the second stage involves hydroprocessing of the depolymerized lignin intermediate. Using batch microautoclave reactors we have studied the lignin depolymerization reaction and here we report results for the time dependence of lignin depolymerization and the effect of base type and concentration. In previous model compound studies we observed the conversion of ethanol to acetic acid under reaction conditions.[3] As this reaction has the potential to neutralize the base catalyst, we have also conducted controlled studies of the conversion of methanol and ethanol to formic and acetic acid under the lignin depolymerization conditions.

EXPERIMENTAL

The Alcell lignin samples used in this study were obtained from Repap Technologies Inc. (Valley Forge, PA) by the National Renewable Energy Laboratory and supplied to Sandia National Laboratories where they were used in the as-received condition. Alcell lignin is derived from mixed hardwoods by an ethanol organosolv pulping method.

Baseline Depolymerization Studies:
The reaction studies were conducted in microreactors consisting of capped ¾" Swagelok bulkhead unions (internal volume approximately 14 cm^3). In each baseline run, 0.434 g of as-received Alcell 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 heated in a fluidized sand bath to 290 °C. The fluid in the reactor equilibrates at the bath temperature in 90 seconds. After the desired reaction time had elapsed (0-60 minutes), the reactors were removed from the bath and rapidly quenched in water. One to three duplicates were performed for each reaction time. As a control, blank runs with no heating were also carried out.

After the reactors were cooled, the liquid and solid products of the reaction were rinsed from the vessel with deionized water and acidified to a pH of 2 with concentrated HCl. 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 by following a similar procedure in experiments that eliminated the ether extraction step.

Effect of Base Type and Concentration: To evaluate the effect of base type and concentration, the reaction conditions were standardized at 290 °C, 60 minute reaction time, and ethanol solvent. Similar ion equivalents of the bases were added to the reactors to evaluate and compare

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the bases individually and in combination. NaOH was added to the reactor as an ethanolic solution. CsOH, LiOH, Ca(OH)$_2$, and Na$_2$CO$_3$ were weighed into the reactors as solids.

Neutralization of Base by Organic Acids: To evaluate the rate of conversion of alcohols to acids. 3 mL aliquots of a solution consisting of 10% (w/w) base in alcohol solvent were transferred to microreactors fashioned from capped ¼" Swagelok unions (internal volume approximately 8 cm^3). As before, the sealed reactors were heated in a fluidized sand bath to the desired reaction temperature (260-290 °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.

RESULTS AND DISCUSSION

Lignin Depolymerization:
Figure 1 illustrates the solubility results from the baseline lignin depolymerization studies. The maximum conversion to water and ether solubles occurs during the first 15 minutes of the reaction. Conducting the reactions in ethanol rather than methanol resulted in a smaller amount of insoluble products. 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.[1] The ethanol-derived products appeared to have an oily character, causing problems in determining the water insoluble fraction. 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. The conversion data compares well to the results of Shabtai and coworkers. Our data for Alcell lignin in 10% KOH/methanol shows average yields of insolubles ranging from 14 to 17% at reaction times of 15 to 60 minutes. The data of Shabtai and coworkers collected for experiments conducted in a 300 ml autoclave over reaction times of 15 to 90 minutes shows average yields of insolubles ranging from 6.5 to 9.0% of the original mass.[2,4]

Figure 2 illustrates the effect of different bases on lignin conversion. Note that the bases are compared at comparable concentrations rather than weight loadings. Clearly the stronger bases, NaOH, KOH, and CsOH are required to achieve significant depolymerization. Figure 3 illustrates the effect of base concentration on the lignin conversion for the three bases that exhibited significant conversion. Included on the figure is a line separating regions where the base concentration is either in stoichiometric excess or stoichiometric deficit. In other words, the line represents the amount of base where there is one equivalent of hydroxide ion for each lignin monomer. The calculation assumes an average molecular weight of 180 g/mol for a lignin monomer.[5] The figure plainly shows that a stoichiometric excess of base is required for maximum lignin conversion.

In previous model compound studies of the lignin depolymerization reaction, we have detected the formation of acetic acid from ethanol.[3] This suggests that the reason excess base is required is that the base catalyst is neutralized during the reaction by conversion of the solvent to organic acids. Figure 4 illustrates that this reaction proceeds relatively rapidly for KOH and ethanol 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 1, 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 4 are the first order fit to the data. Figure 5 is the resulting Arrhenius plot for the data in Figure 4 and for similar reactions carried out with methanol and NaOH. The lines in the Arrhenius plot are nearly parallel suggesting that a similar reaction pathway is followed for all the cases and giving an average activation energy of 50 kcal/mol. As can be seen in Figure 4, this 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. Additional work is required to determine the effects of these parameters on the lignin depolymerization reaction rate for comparison.

ACKNOWLEDGEMENTS

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[3] Miller, J. E., Evans, L., Littlewolf, A., Trudell, D. E. submitted to Fuel.

[4] J. Shabtai, University of Utah, personal communication, February 1997.

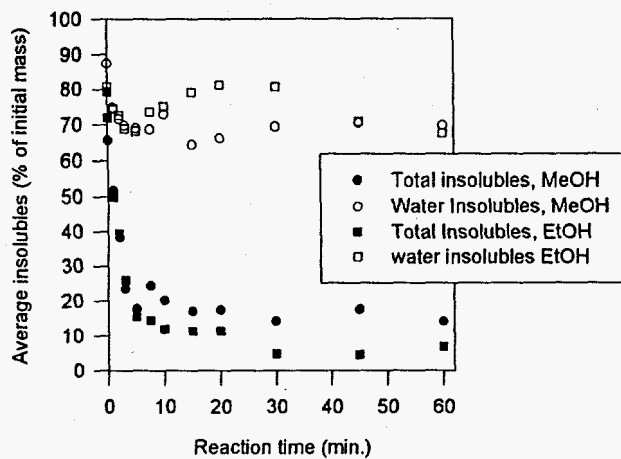[5] D. Johnson, National Renewable Energy Laboratory, unpublished analysis of Alcell lignin.

Figure 1. Conversion of Alcell lignin to water and ether solubles by KOH in methanol and ethanol.
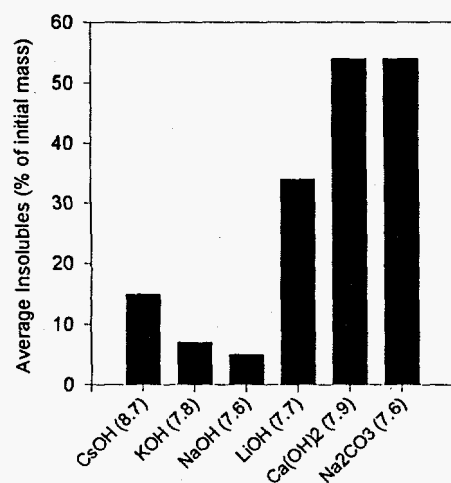

Figure 2. Conversion of Alcell lignin by different bases in ethanol solvent at 290 °C. Numbers in parentheses represent the milliequivalents of base in the reactor.
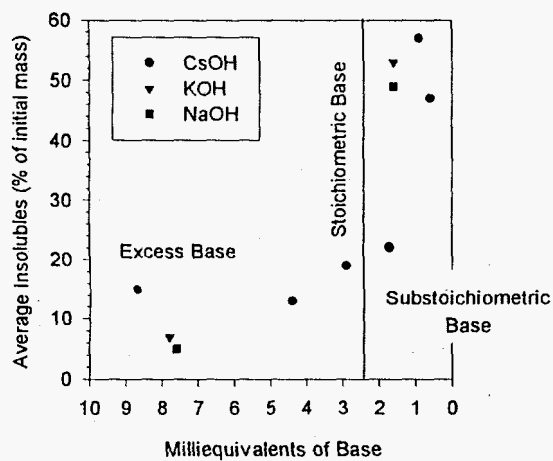

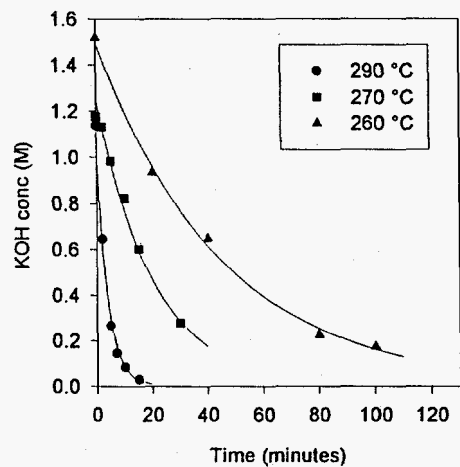**Figure 3.** Effect of base concentration on conversion of Alcell lignin in ethanol at 290 °C.

Figure 4. Rate of ethanol conversion to acetic acid in the presence of KOH as measured by the neutralization of KOH.
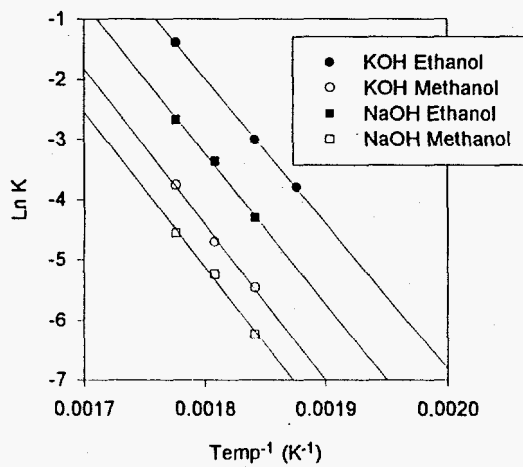

Figure 5. Arrhenius plots for the conversion of ethanol and methanol to organic acids by NaOH and KOH.