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**HYDRODEOXYGENATION AND DEALKYLATION  
OF MODEL LIGNIN COMPOUNDS**

by

Dee A. Erickson

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**ABSTRACT**

Dealkylated phenols can be produced from lignin by depolymerization followed by deoxygenation and dealkylation. The dealkylated phenols can be converted to methyl phenyl ethers and used as a high octane blending stock for gasoline. To break apart lignin molecules it is necessary to use a catalyst which contains hydrogenation, hydrogenolysis, and dealkylation functions.

Most of the research on the hydrotreating of feedstocks from alternative fuel sources has focused on catalysts commonly used for the processing of petroleum. Since most petroleum sources contain significant amounts of sulfur, these catalysts have a high tolerance to sulfur. Lignin-derived feedstocks, however, contain very little sulfur. To use these catalysts for the processing of lignins, sulfur must be added to the feed to maintain the active sulfide surface. For this study, assorted modified alumina supports have been prepared and impregnated with molybdenum and various noble metals. The molybdenum catalysts were sulfided before use. Products from the different catalysts were compared. The noble metal catalysts were found to be more active than the sulfided catalysts. Noble metals are poisoned by sulfur, but this does not present a problem for

the processing of lignins.

The development of a catalyst suitable for lignin processing will be summarized. Assorted modified alumina supports were prepared and impregnated with molybdenum and various noble metals for this study. Physical properties of the catalysts were obtained using nitrogen adsorption with the Braunauer, Emmet, and Teller method (BET) to determine the surface area of a catalyst. X-ray Diffraction (XRD) was used to determine the crystallinity. The catalysts were then tested in a bench scale packed tube reactor using two model compounds that have chemical properties similar to fragmented lignin: 4-propylphenol (4-PP) and 4-propylguaiacol (4-PG). The liquid and gas products were analyzed using gas chromatography (GC) to determine the catalytic reactions which had occurred. Gas chromatography/Mass spectroscopy (GC/MS) was used to identify extraneous peaks and confirm the compound identifications from the GC analysis.

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## INTRODUCTION

### 1.1 Background

Biomass has long been considered as a substitute for petroleum as a potential raw material from which liquid fuel could be produced. The most commonly used fuel not derived from petroleum is ethanol. Currently, most of the ethanol made in the United States is produced from corn. Since corn is valuable as a food source it is a rather expensive raw material. Currently, excess supplies of corn and subsidies from the federal government make the production of ethanol from corn economically feasible. This situation is likely to change, however, and it will be necessary to find a less expensive raw material for future production. One candidate for an alternative source of ethanol is lignocellulosic materials, or woody biomass. This category includes crop residues (such as corn stocks) and wood. These materials are inexpensive since they have no value as food.

Woody biomass contains three major fractions which must be isolated, then processed separately (see Figure 1.1). The largest fraction is crystalline cellulose. The second fraction is hemicellulose. Together these fractions comprise seventy-five percent of most woody biomass.

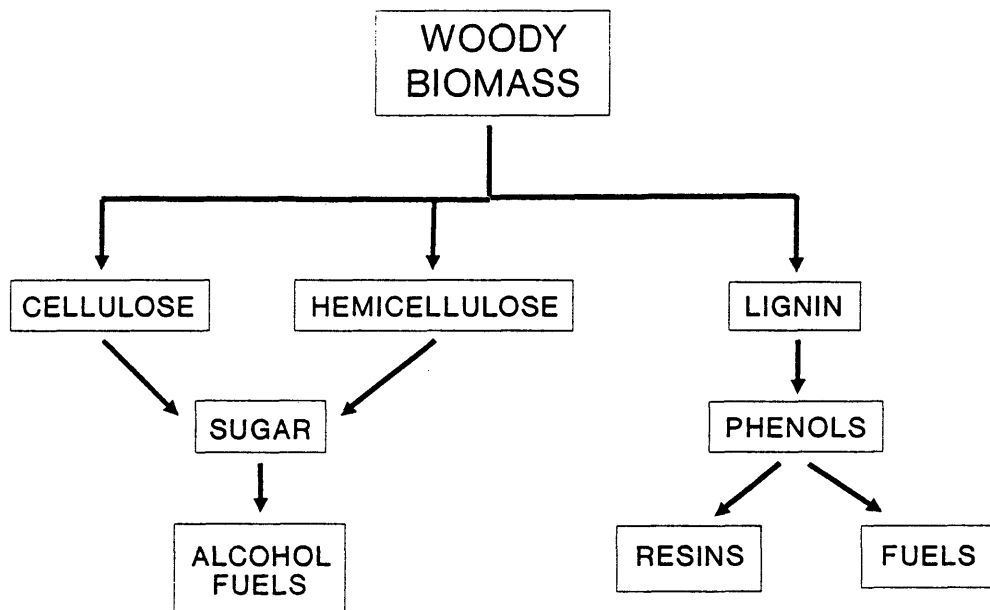


Figure 1.1 Components of Woody Biomass

Using different processes, both of these components can be hydrolyzed to sugar, then converted to ethanol through a fermentation process. The remaining fraction, lignin, cannot be fermented to alcohol because of its polymeric-like structure. Depolymerization of the lignin, followed by dealkylation and partial deoxygenation will yield a mixture containing primarily phenols. Phenols are valuable as a chemical feedstock for the production of polymeric resin. Phenols can also be converted to a valuable liquid fuel by catalytic reaction with methanol to produce methylphenylethers. This high-octane oxygenated liquid can be added to gasoline to help it burn cleaner by increasing the oxygen content and raising the octane number of the fuel.

### 1.2 Statement of the Problem

The purpose of this project is to develop a catalyst which will facilitate the conversion of lignin to a liquid fuel suitable for blending with gasoline. Ideally, the lignin will be converted in one step to a mixture containing primarily monomeric phenols. To yield a mixture of single-ring aromatic phenolic compounds, the lignin must undergo depolymerization to separate the aromatic units and hydrodeoxygenation (HDO) to remove oxygen in excess of one

per aromatic ring. It will also be necessary to dealkylate the resulting mixture to produce lower molecular-weight compounds which fall within the gasoline boiling range. To promote this conversion a catalyst must contain hydrogenation, hydrogenolysis, and dealkylation functions.

Following depolymerization and partial deoxygenation of lignin, a mixture of low molecular weight phenols and hydrocarbons will result. This is desired since saturated hydrocarbons are less valuable for gasoline blending than the corresponding aromatic hydrocarbons, and less hydrogen is consumed when hydrogenation is minimized. However, complete oxygen removal is undesirable. Oxygenated fuels burn cleaner and are therefore better suited for gasoline blending. The current objective for lignin HDO is the removal of all the oxygen in excess of one atom per ring, leaving low molecular-weight phenols. Subsequently, the phenols can be converted to methyl aryl ethers (MAE) in a separate catalytic step.

The catalyst used is similar to those used in the processing of petroleum. Most petroleum sources contain significant amounts of sulfur, so petroleum catalysts require a high tolerance to sulfur. In fact, the feed must contain a specified level of sulfur in order for the catalyst to remain active. Lignin-derived feedstocks,

however, contain very little sulfur. To effectively use molybdenum-based catalysts for processing lignin, sulfur must be added to the lignin feedstock to maintain the  $\text{MoS}_2$  in an active state.

The specific objective of the research for this thesis is to model the lignin feed and to develop a catalyst which will produce the desired products. It is also necessary to determine the optimum operating conditions for the catalyst.

The specific research objectives for this research are the following:

1. Prepare large batches of phosphated alumina supports for testing in the laboratory using model compounds and for use in a batch autoclave reactor using actual lignin.
2. Develop and manufacture a catalyst that will dealkylate and deoxygenate lignin.
3. Determine the best operating conditions for hydrotreating lignin.

## LITERATURE SURVEY

### 2.1 Introduction

Most research involving the treatment of feedstocks from alternative sources has been focused on catalysts used for the processing of petroleum. Since a necessity of petroleum hydroprocessing is the removal of sulfur and nitrogen from the feed, the primary focus has involved optimization of hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). Hydrodeoxygenation (HDO) of crude oil has not received as much attention, since the oxygen content of petroleum crude oils is typically less than one-half percent of the total by weight (1). The oxygen content of synthetic fuels and extracts from coal and biomass is much higher (2). Feedstocks derived from woody biomass are highly oxygenated and can contain as much as 30 percent oxygen (3). Therefore, HDO is one of the most important aspects of lignin hydrotreating.

### 2.2 Hydrotreating Catalysts

Conventional catalysts for petroleum refining are molybdenum-based. Commonly used catalysts are nickel (or cobalt) with molybdenum on supports of alumina or silica(1-12 The  $\text{MoO}_3$  on the surface of the catalyst support is

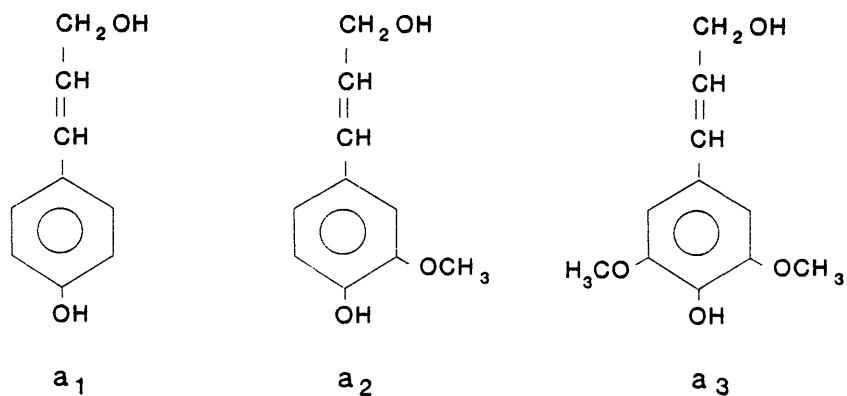
converted to  $\text{MoS}_2$  during a sulfiding step prior to use. Sulfur must be present in the system to replace the surface sulfur atoms lost as  $\text{H}_2\text{S}$  during hydrotreating in order for the catalyst to maintain its high activity level (4). In petroleum crude oil, the amount of sulfur normally present is sufficient to maintain the active surface coverage. In lignin, however, there is very little sulfur present. Lignin is composed of the types of aromatic building blocks shown in Figure 2.1(a) and has very little sulfur present. If traditional hydrotreating catalysts were used for processing lignin, it would be necessary to add sulfur to the system. Another problem with using sulfided catalysts is that there is a possibility that the products would be contaminated with sulfur (3). However, the low sulfur content of lignin makes it an ideal candidate for catalytic conversion using noble metal catalysts. Catalyst impregnated with noble metals such as platinum and palladium, are known to be very active. Because these metals are so sensitive to sulfur, they have not been extensively studied for use in hydroprocessing of petroleum.

### 2.3 Model Lignin Compounds

Attempts have been made to determine the types of molecules that make up lignin (See Figure 2.1(a)). Lignin

typically contains aromatic rings linked together with both oxygen and hydrocarbon bridges. The spectra of pyrolyzed lignin contain compounds such as alkyl-substituted phenols, cresols, guaiacols, catechols, and dimethoxy phenols (see Figure 2.1(b)) (5). These compounds represent the more stable components present in lignin, and should serve as good model compounds.

Characterization studies of lignin have indicated the presence of more than one oxygen per aromatic ring. Some representative lignin type structures are shown in Figure 2.1(a) (6). Some researchers (7,8) have reported hydrodeoxygenation of compounds which contain several oxygen-containing substituents on each aromatic ring, such as guaiacol and substituted guaiacols. The research goal of most HDO studies is the complete removal of all oxygen present. Although the research objectives of this study are slightly different, the results obtained by previous researchers are valuable.

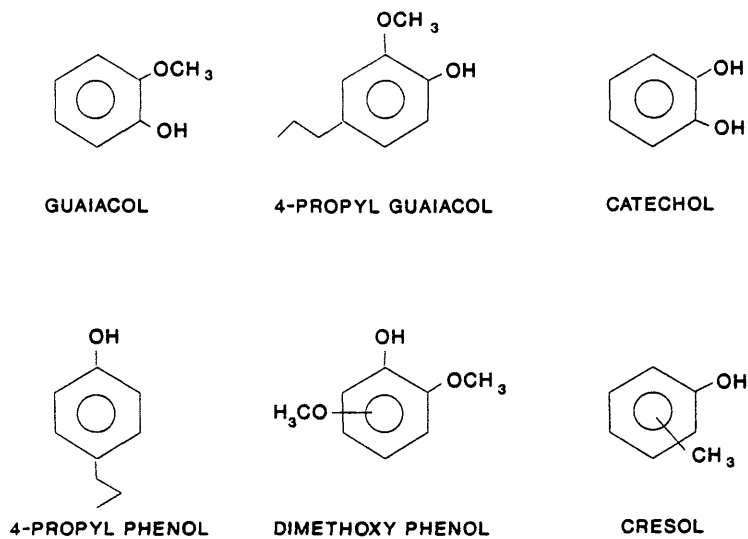


(a) Cinnamyl Alcohols, the building units of lignins.

$a_1$ . p-coumaryl alcohol

$a_2$ . coniferyl alcohol

$a_3$ . sinapyl alcohol



(b) Lignin model compounds

Figure 2.1 Lignin Structures

There are many problems involved in testing catalysts using an actual hydrotreating feed. The complexity of the feed results in numerous competing surface reactions which can obscure important details about the role of each catalyst function. Interpretation of the results of an experiment using a complex feed is very difficult and often misleading. Since lignin is a very complex mixture of compounds, fundamental studies on this mixture are not practical. The proper selection of compounds which contain the functional groups to be studied in the conversion process can overcome most of these problems. Using model compounds, it is possible to propose a reaction mechanisms based on the product distribution obtained. Some of the compounds which have been used as model lignin compounds for HDO are guaiacol, 4-propylguaiacol, cresols, and phenols (7,9,10). Since the starting products are well-defined, it is feasible to determine the types of reactions which must have occurred to yield the products. It also is relatively easy to assess the impact of reaction variables such as temperature, pressure, and catalyst on the product selectivity and yield. A weakness in model compound studies is that extrapolation of the findings to lignin, which is a high molecular weight feed, may be difficult. This is apparent by examining studies of actual lignin where

competing reactions such as coking and condensation have occurred (11).

A catalyst must contain several active components to promote the transformation of lignin into a useful liquid chemical or fuel product. A hydrogenolysis function is necessary to promote the removal of oxygen (HDO). The catalytically active metal or metal sulfide normally provides the hydrogenation and hydrogenolysis activity. An acid function on the catalyst is required for the promotion of depolymerization or dealkylation (12,13). Acidity is normally provided on the support of the catalyst.

## 2.4 Hydrodeoxygenation Catalysts

2.4.1 Molybdenum-based Catalysts An extensive research effort of catalytic hydrodeoxygenation (HDO) literature was conducted in 1983 by Furimsky (1). He presents a compilation of reaction mechanisms for HDO of furans and benzofurans, the compounds most commonly used for deoxygenation studies. Hydrodeoxygenation of phenols are also discussed, since phenolic products appear as intermediates in the reaction.

Phenols are among a group of oxygen-containing compounds which require both hydrogenation and

hydrogenolysis functions in the catalyst to achieve complete hydrodeoxygenation (1). This is related to the increased stability of the carbon-oxygen bond in phenol. This stability arises from the interaction between the lone pair of electrons on oxygen and the aromatic ring. The most common path for hydrodeoxygenation involves the hydrogenation of the ring prior to hydrogenolysis of the bond between the carbon and oxygen (14,15,5). Once the ring is saturated, the weak C-O bond is readily cleaved. This is an important consideration in the design of catalysts which will facilitate partial deoxygenation of lignin. Selecting appropriate reaction conditions and catalysts can limit ring hydrogenation, thus preventing complete deoxygenation of the reactant.

A study was undertaken by Weigold in 1982 to determine the activity of a Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst for the conversion of various phenols (16). A large difference in the hydrodeoxygenation reactivities was found, depending on the nature and position of the substituent. The most active compound tested was m-cresol. This was thought to be due to the lack of steric hindrance and the favorability of the spacing between the methyl and hydroxyl group. The least active compound tested was 2-ethyl phenol. The low activity was attributed to the difficulty of this compound to bond to

the catalyst surface due to steric hindrance. Aubert and coworkers also noticed a lowered reaction rate of ortho-substituted phenols compared to the unsubstituted phenols (17). However, since the rates of para-substituted phenols were also reduced, it was thought to be due to electronic effects, rather than steric hindrance.

A study was conducted by Elliot in 1983 to examine the catalytic activity of various catalysts for the conversion of phenol (3). For this study, an autoclave batch reactor was used. The initial conditions used for the experiments were temperatures of 300-400°C and pressures of 900-1750 psig. The most active HDO catalyst was found to be sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> at 400°C and 2000 psig initial conditions in the reactor. The major product was benzene. Substituted phenols were also tested in this study to determine how substituents on the phenolic ring affect the reaction rate and pathway of the reaction. For these experiments a non-sulfided (reduced) Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst was used. The experiments were performed at 400°C for one hour, with an initial hydrogen partial pressure of 2000 psig. Using 4-ethyl phenol, the major products were, in decreasing order, ethylphenols, phenol, and ethylbenzene. The large quantity of ethylphenol isomers formed (21 wt%) indicates that migration of alkyl substituents is the predominant reaction,

followed by dealkylation and a small amount of deoxygenation. Guaiacol was also tested under these condition. In the catalytic reaction of guaiacol, extensive polymerization occurs, and deoxygenation is not a major reaction.

Hurff and Klein also studied the reactions of guaiacol in a batch autoclave reactor in 1983 (5). Initial conditions used for this study were 430°C and 500 psig. They used a sulfided Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. The reaction of guaiacol yielded catechol, phenol, benzene, and cyclohexane as major products. The selectivity to phenol was good (40 percent), but the activity of the catalyst was low.

Several researchers have proposed the existence of two active sites on Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst. One site is active for C-O hydrogenolysis. The other is responsible for dehydrogenation (10). Site 1 involves sigma-bonding adsorption through the oxygen atom. Site 2 involves pi-bonding through the benzene ring. At higher pressures (>100 psig), the important pathway for HDO of phenol is hydrogenation of the aromatic ring, followed by rapid deoxygenation of the resulting cyclohexanol (17,18).

2.4.2 Noble Metal Catalysts Some researchers also investigated non-traditional hydrotreating catalysts. Elliot tested a palladium catalyst to determine its activity

for the conversion of phenol (3). It had excellent hydrogenation activity, but did not promote the removal of oxygen. Fishel and co-workers tested Pt/Al<sub>2</sub>O<sub>3</sub> to determine its activity for conversion of dibenzofuran (19). It was found to have ring-opening activity at conditions less severe than those used with traditional molybdenum-based catalysts.

### 2.5 Cracking Catalysts

Steric hindrance could be a problem in the hydrotreatment of lignin. High molecular-weight lignin must first be depolymerized to yield single ring structures. The smaller molecules can then access the active sites on the catalyst surface which promote deoxygenation. Dealkylation, or cracking, normally occurs on acid sites present on the catalyst support.

The dealkylation activity of a hydrotreating catalyst increases with acidity. This occurs because the cracking ability of the catalyst is allowed to proceed at a lower temperature, reducing coke formation (12). Catalytic cracking involves the formation of a carbonium ion on the surface of the catalyst. This can happen in two ways. The first involves the addition of a proton to an olefinic or aromatic compound. The second involves the abstraction of a

hydride ion from a saturated hydrocarbon (20). Once the carbonium ion is formed, a variety of ionic surface reactions are possible. These include cracking, isomerization, disproportionation, and coke formation.

Researchers typically study the reactions of a simple compound which can be catalytically cracked to yield relatively few products. The most common model compound used to study catalytic cracking is cumene (isopropylbenzene). The benzene ring remains intact in catalytic cracking of alkyl aromatics, while the alkyl side chains are split off to yield the corresponding olefin (20).

The acidity of a catalyst support affects the activity of the catalyst in several ways. It was found that increasing the acidity of a support decreases the hydrogenation of benzene (21). Since the production of aromatics is preferred, an acidic support can be used to minimize hydrogenation.

The dealkylation of cumene to form benzene and propylene is often used as a test reaction for catalyst support acidity. A study by Huang and Richardson showed that as the acid sites of a catalyst were neutralized by sodium, the dealkylation of cumene decreased (22).

Another study relating the acidity of a catalyst and its effect on the dealkylation activity was performed in

1986 by Boorman and coworkers (12). The increase in acidity was provided by the addition of hydrofluoric acid to the catalyst support. The acidity was found to have a profound effect on cumene conversion. The conversion increased from 2.2% using the basic Co-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst to 53.3% using the same catalyst doped with hydrofluoric (HF) acid. This was attributed to the fact that dealkylation occurs on acid sites on the catalyst. These findings indicate that dealkylation and hydrogenation activity are both affected by catalyst support acidity.

There are several acidic catalyst supports that will promote dealkylation and depolymerization of lignin. Silica-Alumina catalysts are very acidic at certain Si:Al ratios (20). Zeolite catalysts are also known for their high acidity (23). Alternatively, it is also possible to modify the surface of a relatively non-acidic support to change its acidity. The addition of HF to a catalyst support greatly increases its acidity (24). Addition of phosphorus, both to a prepared alumina support and to the hydrogel during the preparation of the support increases the acidity of the support. When the support is prepared from a stoichiometric hydrogel containing a P:Al ratio of less than 1.0, the final support contains the same atomic ratio as that present in the hydrogel (25). This relatively new

acidic catalyst support is composed of amorphous phosphated alumina (P:Al). Not only are P:Al supports more acidic than alumina, but the addition of phosphorus to an alumina hydrogel during the preparation of the support increases the median pore size (12,26). Large catalyst support pore sizes are important for the hydrotreatment of large molecules such as lignin. Pores which are too small for the molecules to enter cannot be accessed and do not contribute to the catalytic activity.

There has been widespread disagreement about the effect phosphorus has in a hydrotreating catalyst. Incorporation of phosphorus into an alumina support increases the total acidity of the support, as measured using ammonia temperature-programmed desorption (TPD) (12). Ratcliff and co-workers found that the addition of phosphorus to an alumina hydrogel results in increased dealkylation of 4-propylguaiacol (9,27). This was attributed to increased acidity of the resulting aluminophosphate catalyst support. Another study using TPD showed a decrease in the number of strong acid sites, while the total acidity of the catalyst increases (28). A decrease in overall acidity with increasing phosphorus content was observed by Gishti et al, based on results from acid-catalyzed test reactions of model compounds (29). Some of the differences can be attributed

to variations in the preparation of the catalysts. The catalysts used in two of the studies (13,26) were made using a coprecipitation method originally proposed by Kehl (30). The catalyst produced is an amorphous phosphate-aluminum-oxygen support. For the other studies (28,29), commercial alumina catalyst supports were modified with phosphorus. The phosphorus and the catalytically active metals were impregnated onto the commercial alumina support. The catalyst prepared for these studies most likely had phosphorus concentrated on the surface of the catalyst, not distributed uniformly throughout the bulk.

In summary, a catalyst which contains both hydrogenolysis and dealkylation activity may make it possible to produce low molecular weight, single-ring phenolic compounds from lignin. Using the proper combination of an active bi-functional catalyst and the optimum temperature and pressure, it should be possible to obtain the desired product distribution during the hydrotreatment of lignin. The conditions at which optimal yields of low molecular weight phenols will be obtained are those which will prevent the hydrogenation of the aromatic rings. There are three important reasons to prevent saturation of the aromatic rings. The first is to avoid excess consumption of hydrogen during hydrotreating. The

second reason is that aromatic products are more valuable as fuel blending stocks. The last reason is to prevent complete removal of oxygen in the lignin feed.

## EXPERIMENTAL

### 3.1 Catalyst Support Preparation

Large batches of coprecipitated phosphated alumina catalyst support were made for testing. The procedure used for the preparation of the supports is similar to that used previously by M. Maholland (13), except the batches are four times as large. The amount of phosphoric acid used in the following procedure is varied to change the phosphorus to aluminum atomic ratio. To make a support with a P:Al ratio of 0.5 [P:Al(0.5)], the following procedure was used:

1. PREPARATION OF ACID SOLUTION: A quantity of 800 grams of aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ ) was dissolved in 8 liters of deionized water. 122.9 grams of concentrated phosphoric acid ( $\text{H}_3\text{PO}_4$ ) was added to the solution.
2. PREPARATION OF BASIC SOLUTION: 800 mL of  $\text{NH}_4\text{OH}$  was dissolved in 800 mL deionized water.
3. A 2 liter separatory funnel was filled with the acid solution. The basic solution was transferred into a 1 L buret.
4. A volume of 4 L of deionized water was added to a 5 gallon nalgene container. The pH was adjusted to 9.0 with  $\text{NH}_4\text{OH}$ .

5. The acid solution was added to the nalgene receptacle at a rate of approximately 400 mL/minute and the basic solution at the rate necessary to maintain the pH of the solution at 9.0. The mixture was continuously agitated with a heavy duty mixer.
6. The funnel and buret were refilled as necessary until the supply of one of the solutions was depleted. The solution was stirred for an additional hour.
7. The hydrogel between three buchner funnels connected to water aspirators. The hydrogel was allowed to filter until most of the water had been removed. Before the surface of the hydrogel cake appeared dry, 500 mL of deionized water (pH = 9.0) was added to the funnel to wash the hydrogel. Six 500 mL washes were added to each funnel.
8. The funnels were left connected to the aspirator for at least a half hour after the last wash has been added to the last funnel.
9. The hydrogel cakes were transferred to glass dishes and baked at 65°C overnight. The oven used had air flowing through to prevent water condensation.
10. In the morning the temperature was turned up to 120°C. The catalyst was allowed to bake at 120°C for 24 hours.

The catalyst was stored in crucibles and transferred to a muffle furnace. The temperature was raised to 500°C over five hours. The catalyst was calcined at 500°C for 18 hours. The catalyst was then removed from the furnace and allowed to cool to room temperature. The catalyst was transferred to a glass jar and stored in a desiccator which contained no desiccant.

11. The catalyst support was crushed using a mortar and pestle and screened to a size of 20/40 mesh.

### 3.2 Catalyst Impregnation

The supports prepared in the laboratory were impregnated with various catalytically active metals. Supported metal catalysts were used for several reasons. The primary motivation was an economic one. Many of the catalytically active materials used are quite expensive. Using a supported catalysts, a large surface area can be obtained with a small amount of the active material. Another reason is that many materials used as catalyst supports exhibit catalytic activity of their own. The following procedure is used to impregnate P:Al(0.8) support with 0.3% Pt for this project:

1. A platinum solution was prepared in a volumetric flask by dissolving 0.0577 gram  $\text{PtCl}_4$  in D.I. water. The solution was diluted to 10.0 mL.
2. 5.0 grams of 20/40 mesh catalyst support was transferred to a 3-neck flask.
3. One neck of the flask was connected to an aspirator and another to the tip of a 10 mL buret. The third neck was closed off using a stopper.
4. 4.5 mL of the platinum solution was added to the buret after the stopcock was closed.
5. The aspirator was turned on to evacuate the flask. The flask was allowed to evacuate for 5-10 minutes.
6. The solution was added to the flask by opening the stopcock of the buret. As soon as the buret was emptied, the stopcock was closed.
7. The round-bottom flask was agitated by hand vigorously for several minutes to evenly distribute the solution among the catalyst particles.
8. The flask was disconnected from the aspirator and the buret. The wet catalyst was transferred into a crucible. Dry at  $120^\circ\text{C}$  for 24 hours.

9. The dried impregnated catalyst was moved to a muffle furnace at room temperature. The temperature was raised to 500°C over several hours. The catalyst was calcined at 500°C for 24 hours.

### 3.3 Catalyst Characterization

The catalysts prepared in the laboratory at the Colorado School of Mines were analyzed to determine total surface area, crystallinity, and water absorptivity.

3.3.1 Surface Area The total surface areas of the catalysts were determined using the Brunauer, Emmett, and Teller (B.E.T) method. Measurements were made on a Micromeritics Accusorb surface area analyzer using nitrogen as the adsorbate.

3.3.2 Crystallinity The crystallinity of several of the catalysts prepared was determined using a Rigaku powder diffractometer. A current of 100 mA and a potential of 40 kV was used. The x-ray source was a copper K $\alpha$  target.

3.3.3 Water Absorptivity The water absorptivity was measured to determine the volume of water to be used in the preparation of the salt solution to be used in the subsequent impregnation step.

The absorptivity was obtained using a copper nitrate solution ( $\text{Cu}(\text{NO}_3)_2$ ). The blue solution was used to visually determine the volume of solution required for each gram of support to evenly coat each particle. This volume of water was used to prepare the solutions containing the molybdenum or platinum salts. The weighed sample of catalyst support was placed in a 250 mL three-neck flask. One neck was connected to a water aspirator. A one hole rubber stopper was inserted in the center neck. The tip of a 25 mL volumetric pipet to which a teflon stopcock had been added (to control the flow) was inserted through the hole in the stopper. The remaining neck was not needed and was fitted with a rubber stopper. The impregnating solution was added to the 25 mL pipet. The flask was evacuated for 5 minutes using a water aspirator.

The stopcock was opened to add a volume of impregnating solution to the support. The flask was agitated vigorously while adding the solution. The stopcock was closed when all the particles appeared wet, but before the pore spaces within the catalyst support were saturated. Saturation was

assumed when the particles stick to the side of the flask and to each other. The volume of solution added to the catalyst was recorded, along with the weight of support used. Water absorptivity of the catalyst supports was considered to be the amount of water just necessary to wet all the support particles. The volume of solution necessary to wet the support particles without any saturation is divided by the weight of the catalyst support to obtain the water absorptivity.

#### 3.4 Catalyst Testing

The primary model compound used for this study is 4-propylphenol(4-PP). This model allows both the deoxygenation and dealkylation functions of the catalyst to be monitored. The ideal catalyst will completely dealkylate and partially deoxygenate 4-propylphenol to yield primarily phenol, with benzene as a minor product. 4-propylguaiacol (4-PG) was also tested. Using 4-PG as a model, the ideal catalyst will remove the propyl side chain and one of the oxygen groups to yield phenol.

The schematic for the reactor system used for testing the activity of the catalysts is shown in Figure 3.1. The catalyst bed was packed into a vapor phase reactor made of a 1/2" O.D. 316 stainless steel tube. The reactor tube was

heated in a Lindberg tube furnace.

## CATALYTIC REACTOR PLUG-FLOW

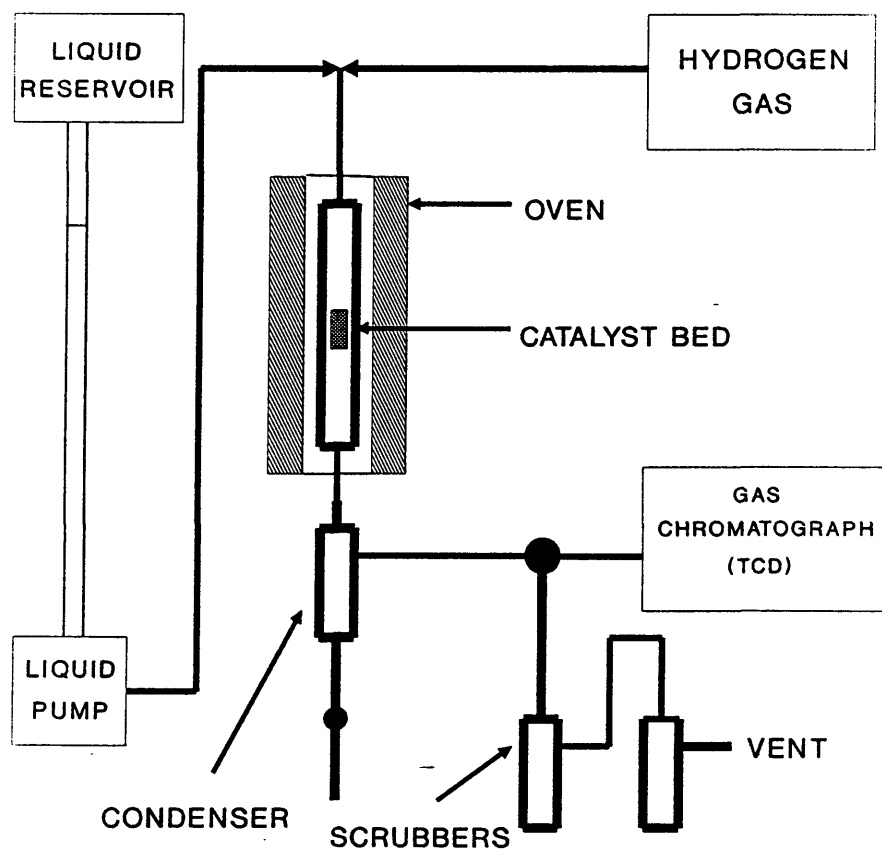


Figure 3.1 Reactor Schematic

The liquid feed was stored in a buret surrounded by an ice water jacket to minimize evaporation during the run. The feed was pumped into the reactor tube with a Milton Roy MiniPump high pressure liquid pump. The products from the reaction were condensed in a 250 ml steel collection vessel surrounded by coiled copper tubing through which ice water was pumped. The liquid products were collected during the run in a septum-capped vial and analyzed using a HP 5840A gas chromatograph with a thermal conductivity detector. The column used for the analysis was 3 m 1/8" stainless steel tubing packed with Supelco 10% SP-1000 on 80/100 mesh Supelcoport. Compound identities were confirmed using an HP 5890 GC/MS.

3.4.1 Catalyst Sulfiding The molybdenum-based catalysts were presulfided using a methyl sulfide/heptane solution and hydrogen gas. This procedure is a modification of the usual sulfiding procedure described in the literature (2). To avoid the hazards of using hydrogen sulfide gas, the sulfur-containing liquid was used. At the conditions used, the methyl sulfide reacted to form hydrogen sulfide in situ. This method should have been comparable to using 10% H<sub>2</sub>S/H<sub>2</sub> gas. The catalyst was first heated to 175°C in hydrogen at 100 psig and maintained at 175°C with a hydrogen

flow rate of 15 cm<sup>3</sup>/min for one hour. A liquid pump set to deliver 10 ml/hr of 3.4 vol% methyl sulfide in heptane was started. The outlet gas flow was adjusted to maintain the pressure at approximately 125 psig after the liquid flow was started. The temperature was then raised to 200°C and held for one hour. Then the temperature was raised to 400°C and held for two hours. The reactor was then cooled to 100°C, sealed up and left in the sulfur atmosphere under pressure until the experimental run was made.

3.4.2 Reaction Conditions A standard condition of 350°C, 500 psig, and space velocity of 1 g-feed/hr/g-catalyst was used for each catalyst in order to compare their performance. The effect of temperature and pressure variations on the catalytic reactions was studied in several of the experiments. The feed mixture was composed of 10 wt% 4-propylphenol (4-PP) or 4-propylguaiacol (4-PG) in heptane or hexane. The feed for the runs using sulfided catalysts also contained 3 wt% methyl sulfide to maintain the catalyst in the active sulfide form. Samples were collected periodically and analyzed to determine when steady state was attained.

3.4.3 Catalyst Testing Procedure The following procedure was used to test the catalysts for this study:

1. A 5/8" round circle was cut from stainless steel wire screen material. This screen was inserted into the reactor tube using a 3/8" O.D. wooden dowel. The screen was positioned approximately 4 cm below the center of the experimentally determined isothermal zone of the reactor in order to assure that the catalyst is at the center of the isothermal region.
2. A small amount of glass wool was gently placed on top of the screen. Approximately 1 g  $\alpha$ -alumina was added to the reactor. A quantity of 0.2 g catalyst was weighed out and transferred to a small jar. A 0.2 gram portion of  $\alpha$ -alumina was added to the catalyst. The mixture was agitated, then the diluted catalyst was added to the reactor.
3. Roughly 3 grams of  $\alpha$ -alumina was added to the top of the catalyst bed and covered with glass wool.
4. The reactor tube was inserted into the system. A 1/16" thermocouple was inserted into the reactor tube from the top and gently forced into the

catalyst bed. The on/off valve downstream from the reactor was closed. Helium was added until the pressure in the system reached 600 psig. The helium valve was then closed tightly. The system was allowed to remain pressurized for several hours or overnight.

5. The pressure in the system was checked to make sure the system had not leaked. If the pressure was not maintained in the reactor, the system was leak-tested and repaired. After all leaks were corrected, the experiment was resumed. The reactor was depressurized by opening the on/off valve and the needle valve downstream from the reactor.
6. After the helium was released, the system was pressurized to 500 psig with hydrogen. The hydrogen mass flow meter and the needle valve at the reactor outlet were set to maintain a hydrogen flow of approximately 50 mL/min.
7. The temperature of the catalyst bed was raised to 450°C over one hour. The catalyst was allowed to reduce at 450°C for two hours. The heating tapes on the inlet gas and the outlet gas lines to the GC were turned on to prevent condensation.

8. The temperature of the catalyst bed was then reduced to 350°C. The hydrogen flow was lowered to 20 mL/min.
9. The feed mixture was added to the jacketed buret. A submersible water pump was immersed in an insulated container filled with ice and water. The pump was turned on to circulate cooling water around the jacketed feed buret and the condenser.
10. After the conditions had stabilized at 350°C, 500 psig, and gas flow of approximately 20 mL/min., the liquid feed pump was turned on to deliver a liquid flow of 3.5 mL/Hr.
11. The buret level was monitored and recorded to determine the actual liquid flow rate. The gas flow rate was adjusted periodically to maintain the desired pressure in the reactor.
12. Liquid samples were collected at half-hour intervals. Samples were saved after the system reached a steady state, usually several hours after the liquid flow was started.
13. The reaction was allowed to continue at the desired conditions until steady state, as evidenced by the analysis of the products by gas chromatography, was attained.

14. After the experiment was finished, power to the liquid pump, the submersible water pump, and the heating tapes was shut off.
15. The needle valve downstream from the reactor was opened to depressurize the reactor. When the pressure reached approximately 50 psig, a slow flow of helium (approximately 10 mL/min.) was turned on to flush the system. Leave the helium flowing through the system overnight.
16. The reactor tube was removed the following day. The catalyst bed was pushed out from the bottom and the particles were examined for signs of discoloration and coking.

## RESULTS AND DISCUSSION

### 4.1 Catalyst Characterization

4.1.1 Total Surface Areas The total B.E.T. surface areas measured for the catalyst supports are shown in Table I. The current results column refers to the data obtained for the catalysts used for this study. The column labelled previous results are results obtained earlier by Maholland (13). The surface area decreases as the amount of phosphorus incorporated into the catalyst support increases. These results for the large batches, shown in Table I, are virtually identical to those of smaller batches made by Maholland (13) and Robb (31) in the laboratory previously. This indicates that the catalyst supports can be duplicated without difficulty.

Table I. Surface Areas of Bulk Catalysts

P:Al Ratio	Previous Results (m <sup>2</sup> /gram)	Current Results (m <sup>2</sup> /gram)
0.5	166.8	164.7
0.8	134.0	133.7

4.1.2 Crystallinity The x-ray diffraction patterns for several of the catalysts tested are shown in Figure 4.1. Figures 4.1-a and 4.1-b are diffraction patterns for the samples characterized which contain no phosphorus (P:Al 0.0). The diffraction pattern for the support only (Figure 4.1-a) contains major diffraction lines at approximately 37.0, 45.2, and 66.2 degrees  $2\theta$ . These diffraction lines correspond to the diffraction pattern for gamma-alumina, which is typically formed under the conditions used in this preparation. The experimental results are shown in Table II, along with reference data for a gamma alumina standard. The addition of molybdenum to the support produces the diffraction pattern shown in Figure 4.1-b. In addition to the diffraction lines for gamma-alumina, a line at 23 degrees  $2\theta$  is apparent. This probably corresponds to  $\text{MoO}_3$  and suggests that some small crystallites of  $\text{MoO}_3$  are present on the surface of the support. The experimental data for this peak is shown in Table III, along with reference data for molybdenum oxide. The low intensity of the line indicates that much of the molybdenum oxide is highly dispersed and/or is present in a non-crystalline form.

## EFFECTS OF PHOSPHATE

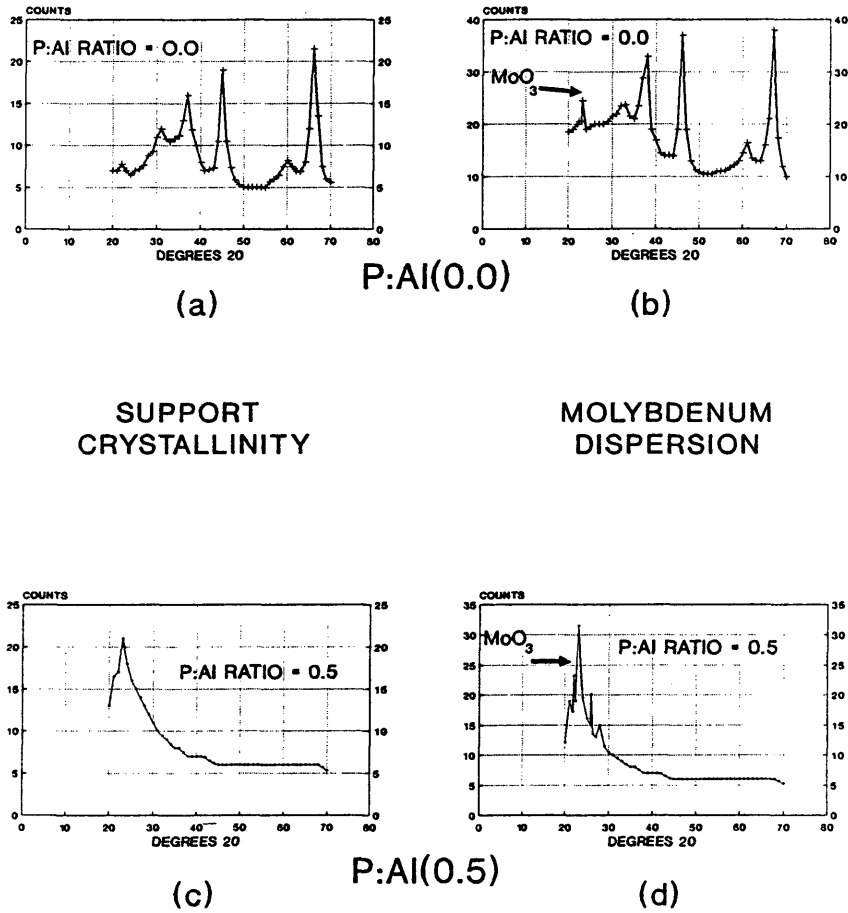


Figure 4.1 X-ray Diffraction Patterns

Table II. Catalyst Support Diffraction Lines

Major Diffraction Lines for Supports ( $2\theta$ )

gamma Alumina	P:Al(0.0) Support
37.6	37.0
45.8	45.2
66.8	66.2

AlPO <sub>4</sub> Aluminophosphate	P:Al(0.5) Support
21.8	23.2
28.2	
35.7	

Table III. Molybdenum Diffraction Lines

MoO <sub>3</sub>	Mo/ P:Al(0.0)	Mo/ P:Al(0.5)
22.7	23.2	23.2
24.7		
26.3		26.5

Figures 4.1-c and 4.1-d are diffraction patterns for the samples which contain phosphorus. Both contain phosphate at a phosphorus to aluminum (P:Al) atomic ratio of 0.5. The diffraction pattern for the support only (Figure 4.1-c) contains one wide diffraction line at approximately 23 degrees  $2\theta$ . The diffraction pattern for the support impregnated with molybdenum (Figure 4.1-d) is similar, with the addition of a significant diffraction line at approximately 26.5 degrees  $2\theta$ . This data is listed in Table III. Data for crystalline aluminophosphate,  $\text{AlPO}_4$ , is also listed for comparison. The diffraction line at 26.5 degrees  $2\theta$  agrees well with the  $\text{MoO}_3$  reference data, but the other two diffraction lines in the  $\text{MoO}_3$  reference are not evident. Their detection may be obscured by the strong support diffraction line at 23.2.

It is apparent that the addition of phosphate to the support has completely destroyed the crystallinity of the alumina, since the gamma-alumina diffraction lines have vanished. The broad line at 23 degrees  $2\theta$  probably corresponds to aluminum phosphate with a very low order of crystallinity. The addition of the diffraction line at 23.2 degrees  $2\theta$  is probably due to the formation of crystallites of molybdenum oxide.

Comparing figures 4.1-b and d, it is evident that the molybdenum oxide diffraction line is larger in the catalyst which contains phosphate and suggests that the molybdenum is more poorly dispersed in the phosphate catalyst. This is in agreement with the earlier work of Maholland (13).

4.1.3 Water Absorptivity The "water absorptivity" value used for the impregnation of the active metals onto the catalyst supports was found to be the same as the "water absorptivity" value determined previously for these catalyst supports by Maholland (13). For the P:Al(0.5) catalyst, a value of 1.0 ml/g was used and the P:Al(0.8) was found to have an absorptivity of 0.9 ml/g. The water absorptivity decreases with increased phosphorus content in the support, presumably due to the reduction in surface area.

#### 4.2 Catalyst Testing

The experimental conditions for each catalyst run are shown in Table IV.

Table IV. Run Conditions

DATE	RUN #	CATALYST	TEMP (oC)	PRESSURE (psig)	SAMPLE TYPE	FEED	TIME (Hrs)
05/20/88	1	Mo-CR-4-PAL 0.5	350	500	LIQUIDS	4-PP	6
05/24/88	2	Mo-CR-3-PAL 0.0	350	500	LIQUIDS	4-PP	7
10/05/88	3	Pt/BaO-Al <sub>2</sub> O <sub>3</sub>	350	500	LIQUIDS	4-PP	7
10/10/88	4	Pt-Re/BaO-Al <sub>2</sub> O <sub>3</sub>	350	500	LIQUIDS	4-PP	7
10/20/88	5	Pt/P:Al(0.8)	350-450	500	LIQUIDS	4-PP	12
12/19/88	6	Pt/P:Al(0.8)	350	500-200	LIQUIDS	4-PP	12
01/03/89	7	P:Al(0.8)	350-450	500	LIQUIDS	4-PP	8
01/10/89	8	Pt/P:Al(0.8)	350-450	200	LIQUIDS	4-PP	12
01/12/89	9	Pt/P:Al(0.8)	350-200	500	LIQUIDS	4-PP	13
04/10/89	10	Pt/P:Al(0.8)	350-450	200	GASES	4-PP	11
04/13/89	11	P:Al(0.8)	350-450	200	GASES	4-PP	11
04/18/89	12	Pt/P:Al(0.8)	350-450	200	L&G	4-PG	17

The primary reactions which 4-propylphenol was found to undergo under the conditions used for these experiments are shown in Figure 4.2 (see data listed in Appendix A). The type of reaction and the catalyst function responsible for it is shown for each step. In Figure 4.2, platinum is used to represent the metal component. For the molybdenum-based catalysts, the sites represented in the figure as platinum would be provided by molybdenum sulfide.

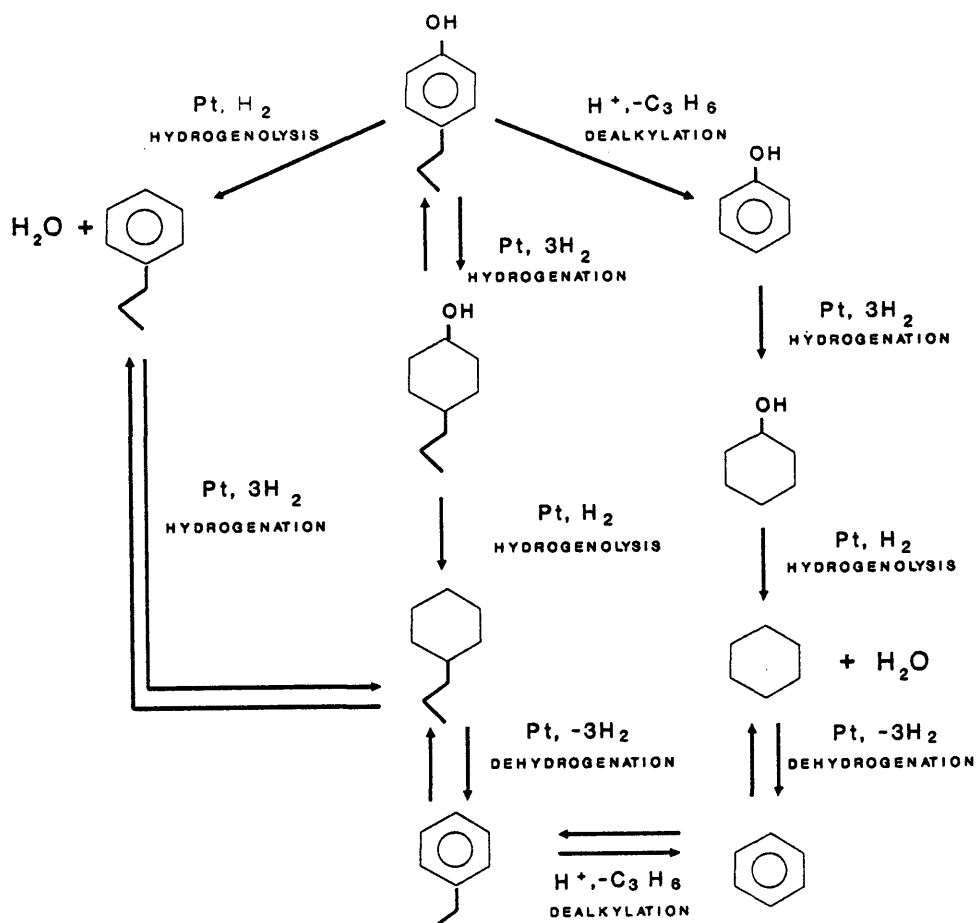


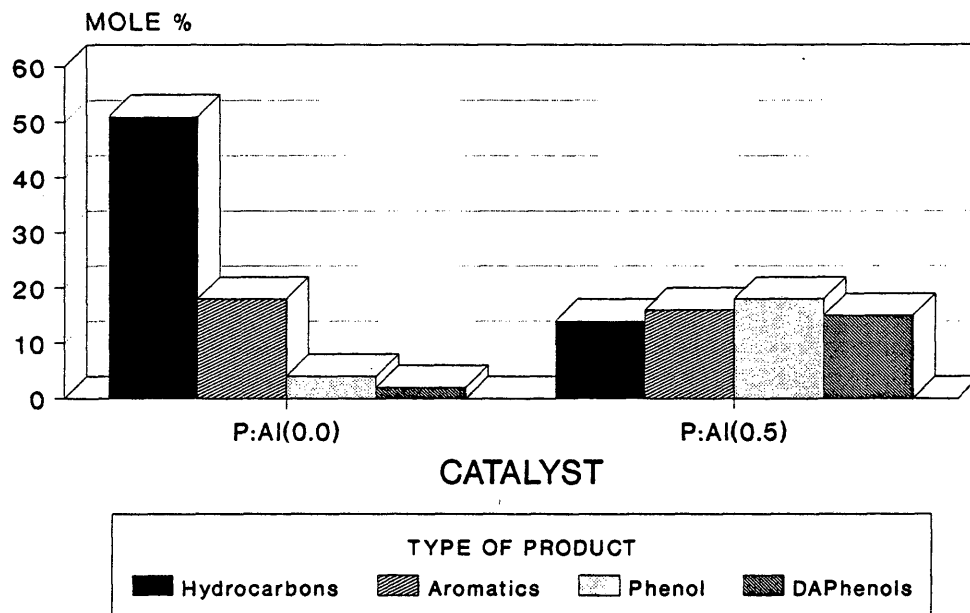
Figure 4.2 Catalytic reactions for 4-Propylphenol

4.2.1 Molybdenum Catalysts Various catalysts were tested to determine which type of catalytic functions they performed. For runs 1 and 2, molybdenum oxide was impregnated on two different supports previously prepared in the laboratory. One support had a phosphorus to aluminum atomic ratio of 0.5. The abbreviation used for this catalyst is Mo/P:Al(0.5). The other support contained no phosphorus [Mo/P:Al(0.0)]. Using these catalysts, with the same active metal sulfide, it is possible to determine what role the support plays in the catalytic transformations of 4-propylphenol.

These molybdenum catalysts were sulfided in situ, then tested using 4-propylphenol (4-PP) as a model compound. The reaction conditions were 350°C and 500 psig. The liquid products were collected and then analyzed using a gas chromatograph equipped with a thermal conductivity detector.

The products obtained were identified and quantitated to determine the role of the support in the conversion of 4-propylphenol. The product compositions are given in Table B-I in Appendix B and presented graphically in Figure 4.3.

### Product Types for Sulfided Molybdenum Catalysts



(P=500 psig, T=350 °C)

Figure 4.3 Product Types Using Molybdenum Catalyst

The conversion, defined as one minus the mole fraction of the unreacted starting material in the liquid product, is approximately the same for both catalysts, (69% for P:Al 0.5, 76% for P:Al 0.0) but the product distribution is considerably different. The predominant product type using the P:Al (0.0) catalyst run was saturated hydrocarbons, followed by a smaller quantity of aromatic hydrocarbons. A small amount of phenol was produced, along with even smaller quantities of transalkylated dialkylphenols. The P:Al (0.5) catalyst produced a fairly even distribution of products in the four groups.

The results for the sulfided molybdenum catalysts indicate that the addition of phosphate to the alumina has little effect on the total conversion of 4-propylphenol to reaction products, but has a marked effect on the product selectivity. The addition of phosphorus increases the support acidity which in turn increases the desired dealkylation reaction, see Figure 4.2. A similar result was obtained in earlier work using benzofuran as the model compound (13).

The Mo/P:Al(0.0) catalyst demonstrates good activity for deoxygenation, but poor dealkylation activity. Dealkylation normally occurs on acid sites. The low dealkylation activity exhibited by the catalyst confirms the

lack of acidity determined previously by Maholland using temperature programmed desorption (TPD) (13). The principle product formed using this catalyst was propylcyclohexane. The high concentration of saturated hydrocarbons indicates that an active hydrogenation function is present.

The amount of propylbenzene produced relative to propylcyclohexane using the P:Al (0.0) catalyst at 350°C, 500 psig is 51.8%. Using the P:Al (0.5) catalyst, the amount of propylbenzene produced relative to propylcyclohexane at 350°C, 500 psig is 14.2%. From Appendix D, the equilibrium distribution of these products is 3% propylbenzene, 97% propylcyclohexane. The excess propylbenzene observed in using both catalysts indicates that at these conditions, equilibrium has not yet been attained. It also indicates that the equilibrium between these two products is being approached from propylbenzene, since this compound is observed in excess relative to propylcyclohexane. In order to form propylbenzene from 4-propylphenol, the oxygen must be removed from the aromatic ring directly, without a saturated intermediate. This direct hydrodeoxygenation must result from a strong hydrogenolysis function.

The Mo/P:Al(0.5) catalyst has good dealkylation activity, as evidenced by the amount of phenol produced.

Since dealkylation occurs on acid sites, the increased acidity confirms Maholland's TPD results which showed P:Al(0.5) to be considerably more acidic than P:Al(0.0) (13).

The addition of phosphate reduces the hydrogenation function of the molybdenum catalyst, as indicated by the drastic decrease in saturated products. Richardson (23) reported an inverse relationship between support acidity and hydrogenation. Since the more acidic catalyst minimized hydrogenation, the results obtained agree with those of Richardson. These results indicate that in order to produce phenolics, an acidic support is necessary to prevent complete deoxygenation. Also, saturation of the ring consumes valuable hydrogen, while converting valuable aromatic compounds to saturated ones, which are less valuable for gasoline blending.

The reduction in activity of the hydrogenation function resulted in the formation of a large concentration of transalkylated products. These are undesirable by-products of dealkylation, since the goal is to remove the alkyl side chains and remove them from the reactor in the gas phase. When transalkylation occurs, the alkyl groups are not being removed and the average molecular weight is not lowered. Using this catalyst, the number of moles of dialkylphenols

produced was nearly as high as the number of moles of phenol. Most of the propyl groups removed from one molecule of 4-propylphenol are probably reattached to another. Dealkylation occurs through a mechanism in which a surface proton attacks a reactant molecule to form an adsorbed sigma complex. The propyl group is removed and attaches to the surface. The propyl group can then lose a hydride to the surface to form propene. If a good hydrogenation function is present, propene is saturated to form propane, which is removed from the reactor with the gas stream. In this experiment, the alkyl groups linger on the surface and bond to another adsorbed reactant molecule to form dipropylphenol.

4.2.2 Noble Metal Catalysts Platinum catalysts were studied because they exhibit much better hydrogenation and hydrogenolysis activity than  $\text{MoS}_2$ . The purpose of using an active hydrogenation site on a catalyst was not to promote saturation of the ring, but to determine if it reduced or eliminated the transalkylation reaction. Experiments were designed to determine if the selective hydrogenation of propene over saturation of the aromatic ring could be achieved. For experimental runs 3 and 4, two catalysts were prepared using a barium modified alumina support, Pt/BaO-

$\text{Al}_2\text{O}_3$  and Pt-Re/BaO- $\text{Al}_2\text{O}_3$ . The addition of barium oxide effectively eliminated the surface acidity. The oxide ion interacts with the alumina, eliminating acid sites. Therefore, the dealkylation and deoxygenation (hydrogenolysis) activity of the platinum or platinum-rhenium combination can be observed separately from the activity an acidic support provides. The product distributions for these runs are also shown in Table B-I in the appendix.

In both runs 3 and 4, the predominant product formed is propylcyclohexane (PCH), followed by propylbenzene (PB). For the platinum catalyst, the relative quantities formed were 8.5% propylbenzene, 91.5% propylcyclohexane. Using the Pt-Re catalyst, the distribution was 7.6% propylbenzene, 92.4% propylcyclohexane. From Appendix D, the equilibrium distribution of these products is 3% propylbenzene, 97% propylcyclohexane. The same trend was seen using the molybdenum catalysts. The excess propylbenzene observed in both experiments indicates that at these conditions, equilibrium may not yet have been attained. It also indicates that the equilibrium between these two products is being approached from propylbenzene, since this compound is observed in excess relative to propylcyclohexane. The oxygen must be removed from the aromatic ring directly,

without a saturated intermediate. This indicates that the platinum catalysts also contain a strong hydrogenolysis function.

Both the platinum and platinum-rhenium catalysts on barium oxide modified supports had high deoxygenation activity. The lack of phenol produced indicates that platinum metal, alone or in combination with rhenium, does not catalyze dealkylation. It appears that the small amount of dealkylation which did occur resulted in the transalkylation of the propyl group. The addition of rhenium to the catalyst did not change the product selectivity significantly, but it did increase the activity of the catalyst.

The product distribution obtained in these experiments does not meet the desired criteria for the conversion of 4-propylphenol to primarily phenolics and aromatic hydrocarbons. However, by simply increasing the temperature, the equilibrium distribution can be shifted in favor of aromatics, which are considerably more valuable as a gasoline additive. In Appendix D it is shown that, at equilibrium, an increase of 100°C, to 450°C changes the product distribution dramatically. The relative distribution between propylbenzene and propylcyclohexane at 450°C is 90% propylbenzene, 10% propylcyclohexane.

The experiments using sulfided Mo catalysts showed that the acidic P:Al support promotes dealkylation. For the remaining experiments, the strong hydrogenation and hydrogenolysis functions of platinum were combined with the dealkylation activity of an acidic P:Al support. In experimental run 5, the pressure was held constant at 500 psig, while the temperature was varied between 350 and 450°C. The following temperature cycle was used:

350°C - 3.5 Hours  
400°C - 2.0 Hours  
450°C - 3.0 Hours  
350°C - 2.5 Hours  
11.0 Hours

The data for this experiment is displayed in Table B-II in the appendix. At the same conditions, this catalyst is much more active than the molybdenum-based catalysts tested previously. At the initial conditions, which are the same as those used for the previous experiments, propylcyclohexane and propylbenzene were the major products. There was also a significant quantity of cyclohexane produced. This indicates that deoxygenation is the predominant reaction occurring. In Table V, the amount of propylbenzene produced relative to propylcyclohexane for the conditions studied is shown.

Table V. Relative Quantity of Propylbenzene

Temperature (degrees C)	350	400	450	350
	Percent Propylbenzene			
Observed	24.2	51.4	74.9	31.5
Equilibrium	3.0	38.8	89.6	3.0

The equilibrium amount calculated (in Appendix D) is also shown for comparison. This data indicates that, at the lower temperatures (350 and 400°C), HDO occurs by direct cleavage of the aromatic carbon-oxygen bond, without prior saturation of the ring since there is an excess of propylbenzene, relative to propylcyclohexane. This is in agreement with the results obtained using Pt/BaO-Al<sub>2</sub>O<sub>3</sub>. The situation changes at 450°C. Under these conditions, the amount of propylbenzene relative to propylcyclohexane is smaller than expected at equilibrium, based on the thermodynamic calculations in Appendix D. This probably indicates that the primary path for HDO at 500 psig, 450°C involves saturation of the aromatic ring prior to the removal of oxygen. The reason for the change in the predominant reaction pathway between 400 and 450°C is not clear.

A significant quantity of cyclohexane was also produced in experimental run 5. The quantity of benzene relative to cyclohexane is also shown in Table VI. At the lower temperatures, there is more benzene than there would be at equilibrium. This could only occur if the predominant reaction producing these products involves production first of benzene, some of which then is converted to cyclohexane. At 450°C, the distribution is that expected at equilibrium. In this case it is not possible to determine the direction from which direction equilibrium was approached.

Table VI. Relative Quantity of Benzene

Temperature (degrees C)	350	400	450	350
	Percent Benzene			
Observed	12.5	34.7	61.6	22.8
Equilibrium	0.4	9.2	61.3	0.4

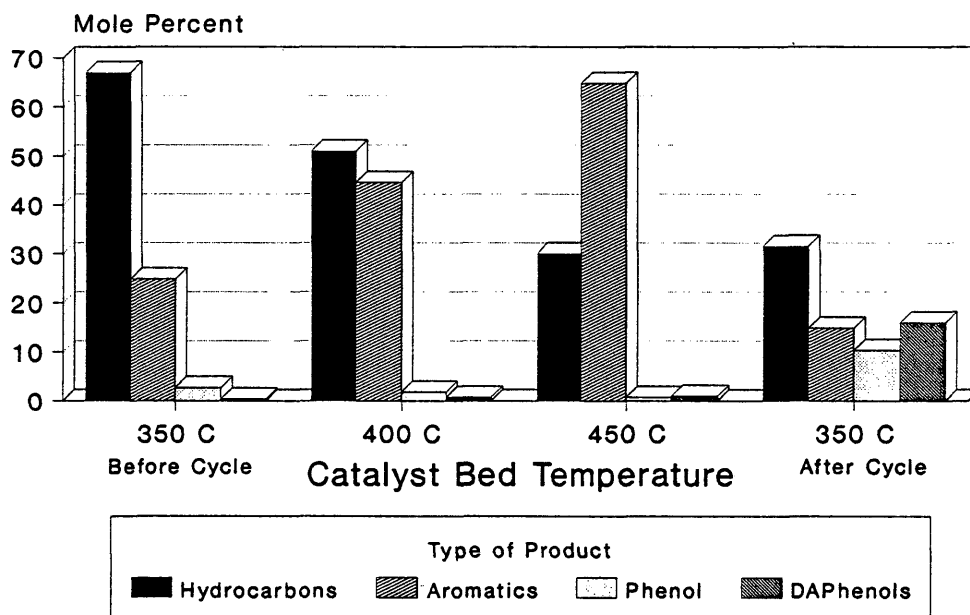
The presence of benzene and cyclohexane in the products indicates that this catalyst promotes dealkylation. Dealkylation was not a significant reaction in run 4. The only difference between the catalyst used for this experiment and the one used previously is the composition of the catalyst support. The catalyst used in this experiment had a phosphorus to aluminum atomic ratio (P:Al) of 0.8, and the catalyst used for the previous experiment contained no phosphorus (P:Al 0.0). Also, the acid sites on the catalyst support used for run 4 were neutralized using barium oxide. Therefore, the dealkylation activity exhibited in run 5 and not present in run 4 is attributable to the acid sites on the P:Al(0.8) support.

The effect of temperature on the product distribution is shown in Figure 4.4. The production of saturated hydrocarbons (HC) decreases as the temperature is increased,

while the amount of aromatic products increases, which follows the trend one would expect from thermodynamic calculations (see Appendix D). The predominantly aromatic product mix produced could be valuable as a blending stock for gasoline.

The effect of temperature on the various catalyst functions (reaction type) is shown in Figure 4.5. The large deoxygenation activity suggests that the hydrogenolysis activity of this catalyst is very high. At all the conditions tested in this experiment, deoxygenation of the feed was nearly complete. The dealkylation reaction is favored at the higher temperatures, while transalkylation remains small. Upon returning to the original conditions, it was obvious that the catalyst had suffered a significant loss in activity, probably due to coking. When the catalyst was removed from the reactor, the color of the catalyst particles ranged from tan to black, indicating that coking had occurred.

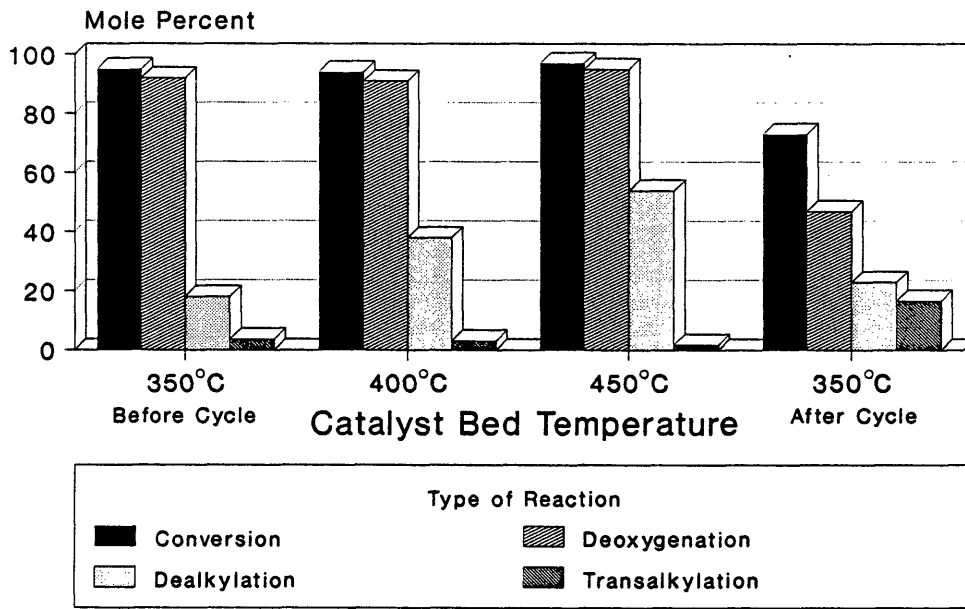
### Effect of Temperature on Product Distribution [Pt/P:Al(0.8)]



Pressure • 500psig

Figure 4.4 Product Type as a Function of Temperature

### Effect of Temperature on Reaction Type [Pt/P:Al(0.8)]



Pressure = 500psig

Figure 4.5 Reaction Type as a Function of Temperature

Since aromatic products have a higher octane number than their saturated counterparts, they are more valuable as blending components. Therefore, it is desirable to minimize saturation of the aromatic phenolic ring. Experimental run 6 was performed to determine the effect changes in total pressure may have on the product distribution using the Pt/P:Al(0.8) catalyst. For this experiment the temperature was maintained at 350°C while the pressure was reduced from 500 psig to 200 psig.

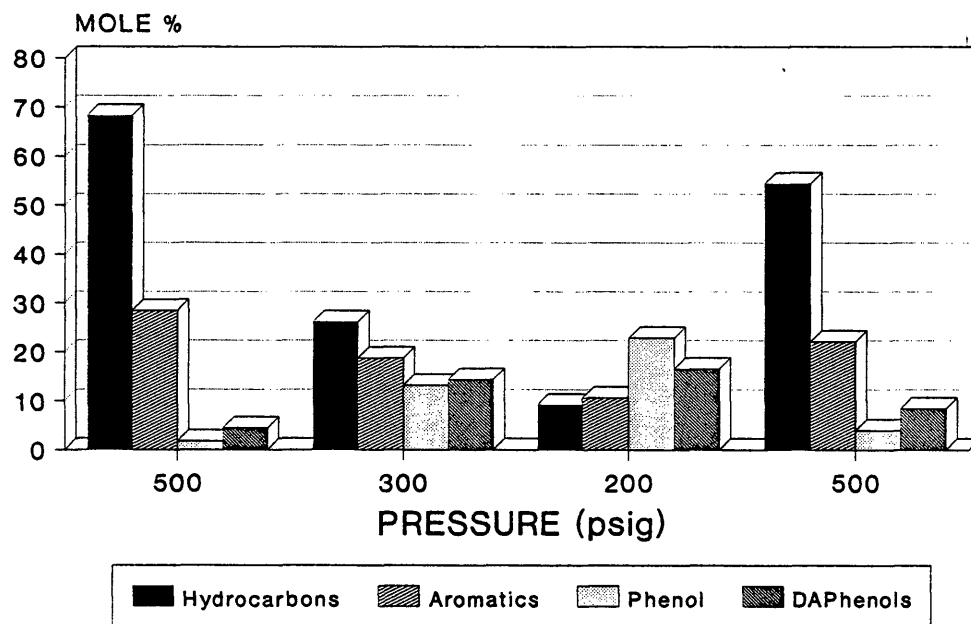
The pressure was lowered in this experiment to reduce ring saturation. The purpose of the experiment was to increase the production of phenol. That can best be accomplished by preventing the saturation of the aromatic ring during the reaction, since oxygenated substituents are easily removed from a saturated ring. In addition, dealkylation occurs more readily from an aromatic ring than a saturated one and should be favored by a decrease in hydrogenation activity. These results are shown in Table B-III in Appendix B. The amount of phenol produced increased substantially as the pressure in the reactor was lowered to 200 psig. The conversion decreases, as does the amount of saturated hydrocarbons produced.

The type of products formed are shown in Figure 4.6. The primary product formed at the initial conditions is saturated hydrocarbons. The production of both saturated hydrocarbons (SHC) and aromatic hydrocarbons (AHC) decreased as the pressure decreased. However, the relative distribution of products changes. The ratio of aromatic to saturated hydrocarbons (AHC/SHC) increases from approximately 0.4 at 500 psig to approximately 1.3 at 200 psig. The predominant product at 200 psig is phenol.

A relatively large amount of transalkylated products are also produced at these low pressure conditions. The relative occurrence of the various reaction types is shown in Figure 4.7. The activity of the catalyst declined with the decrease in pressure. The reduction in the amount of deoxygenation is the most significant change in the reaction type as the pressure was lowered. The products obtained in this experimental run indicate that it may be possible to dealkylate and partially deoxygenate lignin to form phenol using this catalyst at these conditions.

The reduction in the total pressure resulted in a significant decrease in saturation of the aromatic ring, in agreement with the change predicted, based on the thermodynamic data in Appendix D.

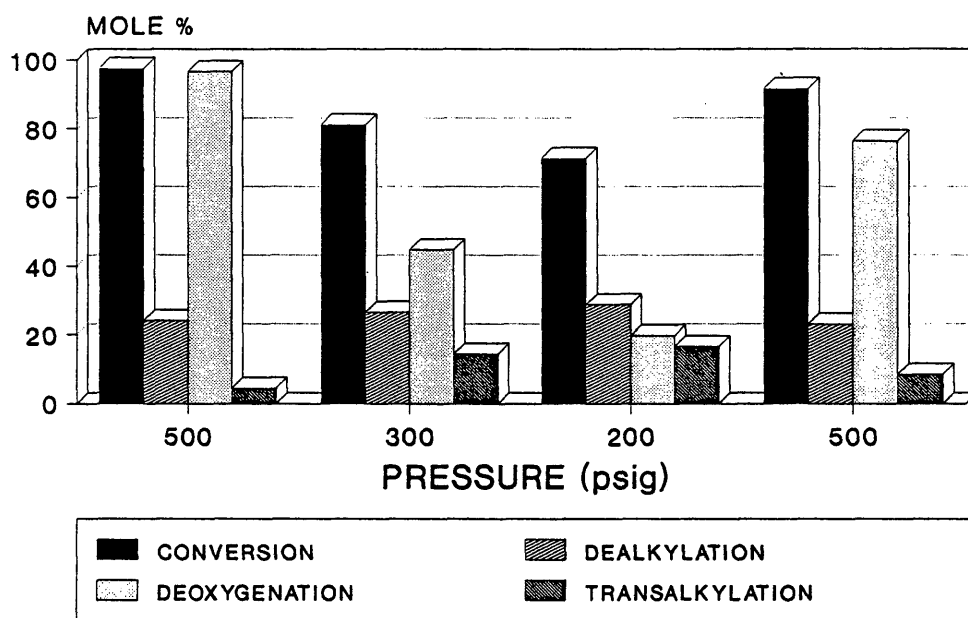
Product Distribution for  
Pt/P:Al(0.8) as a Function of Pressure



TEMP • 350°C

Figure 4.6 Product Type as a Function of Pressure

### Reaction Type as a Function of Pressure for Pt/PAI (0.8)



TEMP = 350°C

Figure 4.7 Reaction Type as a Function of Pressure

As the amount of ring hydrogenation decreases, the hydrodeoxygenation (hydrogenolysis) of oxygen from phenolic compounds also decreases. The reduction in the amount of deoxygenation is the most significant change in the reaction type as the pressure was lowered. This is what one would expect from the relatively weaker carbon-oxygen bond strength in cyclohexanol compared to that in phenol.

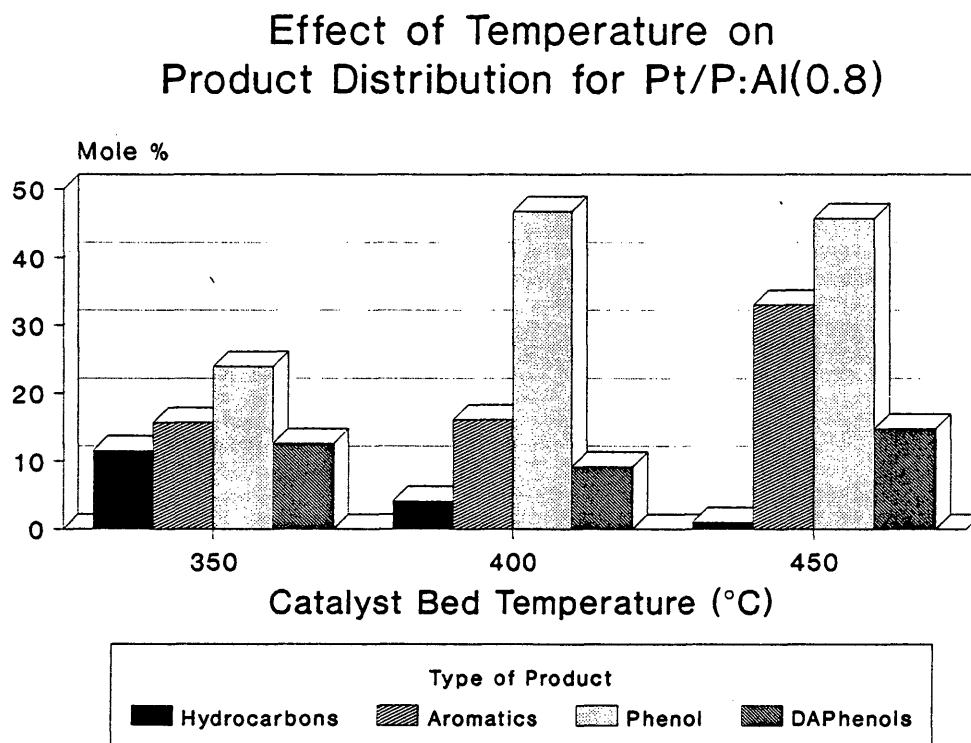
In Appendix D it is shown that at equilibrium, deoxygenation of both phenol and cyclohexanol is highly favorable under these reaction conditions. For more complex compounds which contain oxygen in excess of one oxygen atom per ring, the hydrodeoxygenation activity does not necessarily decrease with pressure. Both oxygens can interact with the ring pi-system, strengthening the C-O bond, but each to a lesser degree than when just one oxygen group is present. Therefore the removal of the first (of two) oxygen group requires less energy than the removal of the final group. Therefore, it may be possible to remove all the oxygen in lignin in excess of one per ring, leaving phenol as the primary product by choosing the proper reaction conditions.

The optimal pressure for this reaction is lower than 500 psig, but the activity at 200 psig and 350°C is low. Hydrogenation of the propene does not occur as readily at

200 psig as it does at higher pressures, as evidenced by the amount of transalkylation which occurred. To achieve higher conversion of the feed and to increase hydrogenation an attempt was made to optimize reaction conditions. In experimental run 8, the pressure was maintained at 200 psig, while the temperature was varied from 350°C - 450°C. Table B-IV contains the data for this run. Again, the amount of aromatic products increases with temperature. The total amount of transalkylation remained fairly constant, although the distribution changed. The amount of 2,6-dipropylphenol was small at low temperatures, but significant (14%) at 450°C. The trend was reversed for the other dipropylphenols; their concentrations decreased with increasing temperature. This variation is probably due to the mode of adsorption on the surface of the catalyst. It has been speculated that two types of bonds can form between phenols and catalyst surfaces, sigma bonds and pi bonds. When the 4-propylphenol is adsorbed through the oxygen atom (sigma bond), only the 2- and 6- positions on the ring are accessible to the catalyst surface. When the 4-propylphenol adsorbs "flat" on the catalyst surface through the aromatic ring, all positions are accessible to adjacent acid sites on the catalyst surface. All four isomers of dipropylphenol are formed at 350°C. This data could indicate that at the lower

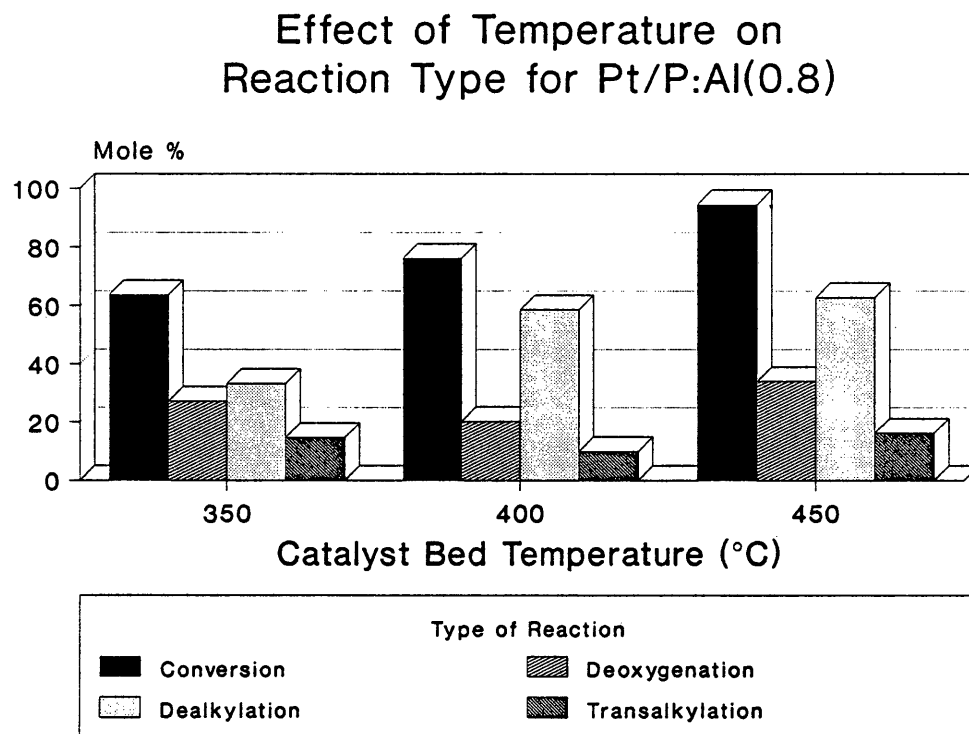
temperature, the dominant mode of adsorption of 4-propylphenol is pi-adsorption. In this configuration all the positions on the catalyst are accessible, and substitution will occur around the ring. However, the 2- and 6- locations are somewhat sterically hindered compared to other positions on the ring. At 450°C, 2,6-dipropylphenol is the only isomer formed in significant quantity. This might identify sigma bonding as the dominant mode, since 2- and 6-are the only two positions which have access to the catalyst surface when the phenol bonds through the oxygen atom. The trend was reversed for the other dipropylphenols. Their concentrations decreased with increasing temperature.

The types of products formed in run 7 are shown in Figure 4.8. As at the higher pressure, the amount of saturated hydrocarbons decreases while the concentration of aromatic hydrocarbons increases with increasing temperature. The production of phenol was highest at 400°C. The effect of temperature on the reaction type at 200 psig is shown in Figure 4.9. Since deoxygenation and transalkylation reactions are both minimized at 400°C, this appears to be the best temperature for the desired reactions. Of those tested, the best reaction condition to achieve the desired product mix is determined to be 200 psi, 400°C.



Pressure • 200 psig

**Figure 4.8 Product Type as a Function of Temperature**



Pressure = 200 psi

Figure 4.9 Reaction Type as a Function of Temperature

Experimental run 9 was conducted to determine which reactions occur at temperatures below 350°C. As shown in Table B-V, the activity decreases substantially as the temperature approaches 200°C, with propylcyclohexane the only major product formed. These results indicate that the conversion of lignin will not give a desirable product distribution at lower temperatures.

Experimental run 7 was performed to determine what catalytic activity the support [P:Al(0.8)] itself has for the conversion of 4-propylphenol. These results, shown in Table B-VI indicate that dealkylation is the only significant reaction which is catalyzed by the support. No significant amount of saturated hydrocarbons were detected, which indicates that the strong hydrogenation function for ring saturation is present on the Pt, not on the support. The data for this run also shows a temperature dependence for the preferred mode of adsorption of 4-propylphenol. At 350°C all the dipropylphenol isomers appear in the product stream. At 450°C, however, only the 2,6- isomer is present. This could indicate the dominance of pi-bonding at low temperatures, and sigma-bonding at higher temperatures.

The high conversion attained in this experiment was not seen by Maholland (13), who tested the same catalyst support using dibenzofuran as the model compound. It has not yet

been determined whether the difference in conversion is due to the difference in the model compound used, or if it due to differences in laboratory procedure.

The catalyst exhibited evidence of coking when it was removed from the reactor after this experiment. Most of the catalyst particles in the diluted catalyst bed were dark grey or black. The alpha alumina above and below the catalyst bed was light tan colored, except directly above the catalyst layer, where it was brown.

4.2.3 Gas Analysis Two additional experimental catalyst screening runs (numbers 10 and 11) were made to analyze the gases produced. The catalysts used were Pt/P:Al(0.8) catalyst and P:Al(0.8) support. Both experiments were started at the standard condition (350°C, 500 psig). The pressure was then dropped to 200 psig. The temperature was varied between 350°C and 450°C. The following cycle was used:

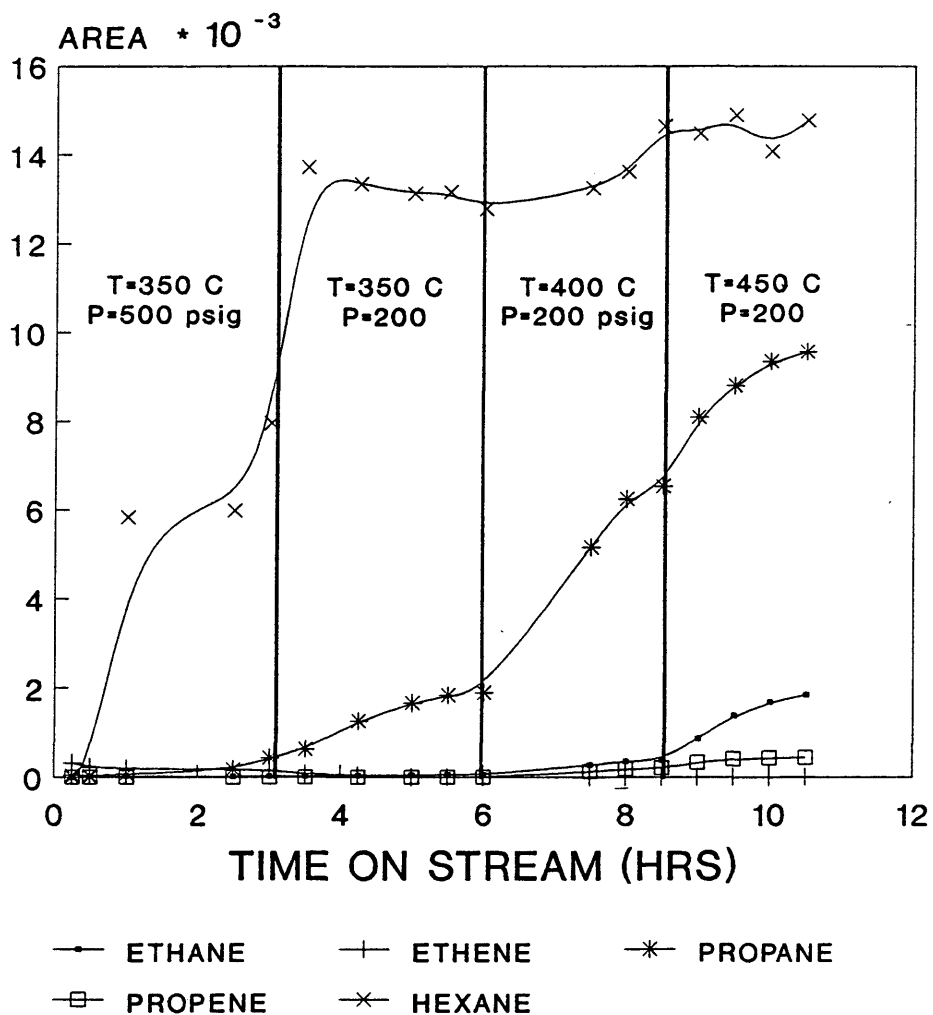
<u>TEMP</u>	<u>PRESSURE</u>
350°C	500 psig
350°C	200 psig
400°C	200 psig
450°C	200 psig

The results for the platinum catalyst used in experimental run 10 are shown in Figure 4.10. The data is also tabulated in Table C-I in Appendix C. The predominant gas detected is hexane, which is the diluent used in the feed and is not of interest in the gas analysis. The only gas produced in significant quantity using the platinum catalyst was propane.

At the initial conditions little gas was detected. The pressure was then reduced to 200 psig. With each temperature elevation the amount of propane present in the gas stream increased. At the final conditions of 450°C, 200 psig, detectable quantities of ethane and propylene were also present.

The results for the experiment in which the support without platinum [P:Al(0.8)] was used as the catalyst (run # 11) are shown in Figure 4.11. The results are also tabulated in Table C-II in the appendix. In this experiment, using the same conditions, no significant quantity of any gas was formed until the temperature reached 450°C. At this temperature the major gas product was propylene. Other products formed, in order of decreasing quantities were ethane, ethylene, and propane. For this experiment the quantity of unsaturated products exceeded the quantity of saturated products formed.

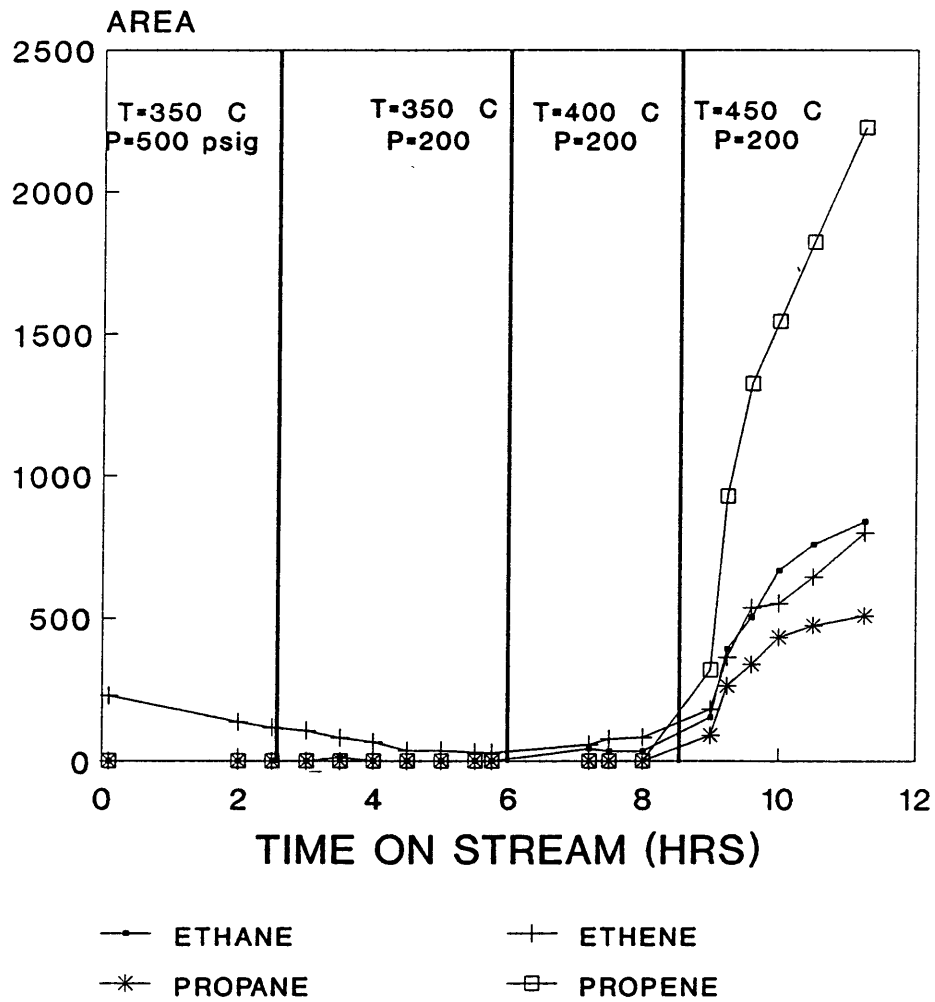
### Gases Produced Using Pt/P:Al(0.8) Catalyst



4-Propylphenol Feed

Figure 4.10 Platinum Catalyst Gas Products

## Gases Produced Using P:Al(0.8) Support



4-Propylphenol Feed

Figure 4.11 Catalyst Support Gas Products

However, the total amount of gas products was considerably smaller than for the platinum containing catalyst.

The platinum on the catalyst used for experimental run 10 made a considerable impact on the product distribution, when compared to the results for experimental run 11, using the unimpregnated support. The ratio of propane to propene was several orders of magnitude higher using the platinum catalyst compared to the support itself. This confirms the assertion made previously, based on analysis of the liquid products that the platinum provides the hydrogenation function required to saturate the alkyl groups removed from the ring. It is necessary to saturate the alkyl groups to prevent coking, or carbonaceous buildup on the catalyst, and also to prevent the transalkylation of feed molecules to form undesirable high molecular weight products.

4.2.4 4-Propylguaiacol Experiment In order to assess the deoxygenation function of the Pt/P:Al(0.8) catalyst using a compound which contains more than one oxygenated substituent, 4-propylguaiacol was tested. This compound is more representative of lignin, since it contains two oxygen substituent per aromatic ring. The liquid samples collected during the 4-propylguaiacol experimental run were analyzed using GC/MS. The data is tabulated in Table B-VIII in the appendix. The results, shown in Figure 4.12 appear to follow the same trends observed previously using 4-propylphenol as the model feed compound. The production of phenol, the desired product, increased with rising temperature. At conditions of 200 psig and 450°C, the concentration of phenol was quite high relative to the other products. The predominant product group at these conditions was cresols. The methyl substituent on the cresols most likely comes from the methoxy group on a 4-propylguaiacol molecule. There was also a significantly large concentration of substituted phenols (C<sub>3</sub> and larger) with high molecular weights. These are undesirable products because, when methylated, they will have boiling points above the gasoline upper limit.

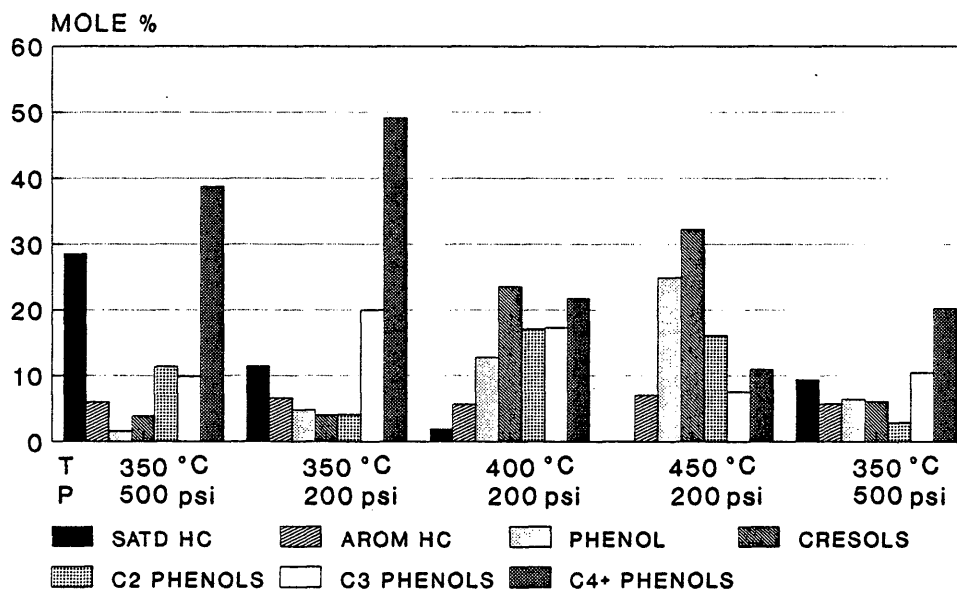
The high concentration of phenol and substituted phenols and the lack of catechols in the products lends

credibility to the theory that only one oxygenated substituent on an aromatic ring is sufficiently stable to remain attached over an active catalyst.

The entire catalyst bed, including the diluent  $\alpha$ -alumina above and below were very dark gray in color after experimental run 12 using 4-PG as the feedstock. This indicates that extensive hydrocarbon deposition (coking) occurred. Coking did not occur to this extent using 4-propylphenol as the feedstock. This may be related to the observation made by Hurff and Klein (2) that the pyrolysis product spectra of compounds which contain two ortho oxygen substituents contain coke, while the spectra of pyrolyzed singly oxygenated phenols do not.

It is expected that lignin, which contains aromatic rings with several oxygen substituents, will also have a tendency to polymerize and leave coke deposits of the catalyst. However, coking normally occurs at higher temperatures. If the desired product mix can be achieved at 400°C, which is likely based on the results obtained in this run, it would be advantageous to maintain the reactor conditions at this temperature.

### Effects of Temperature and Pressure on 4-Propylguaiacol Products



Pressure = 200 psi

Figure 4.12 4-Propylguaiacol Liquid Products

4.2.5 Reproducibility of Experimental Data The results of the four different experimental runs performed using the same catalyst at the same initial condition are shown in Figure B-VII in Appendix B. The average for each component in the four runs is calculated, along with the standard deviation. Run 5 was the first experiment using the platinum catalyst. The results of this run are somewhat different from the results of the other three experiments. This could be attributed to the fact that the reaction conditions were not maintained as consistently as they were in the later experiments. Even when the results for run five are included, the relative standard deviation for the major products are within fifteen percent. The last three experiments show better consistency, which indicates that the results reported for this research are probably accurate to within this margin of error.

### CONCLUSIONS

The experiments performed using platinum on acidic supports indicate that noble metal catalysts may contain the catalytic functions required to hydrotreat lignin. The platinum catalysts tested are more active than the molybdenum-based sulfided catalysts. In addition, the noble metal catalysts are active in the reduced form and do not require presulfidization. If the hydrogenolysis activity can be moderated to reduce the deoxygenation function, it may be possible to use a platinum catalyst to convert lignin into a valuable high-octane liquid fuel suitable for gasoline blending.

**RECOMMENDATIONS FOR FURTHER STUDY**

1. Experiment further to determine the best way to impregnate platinum on to the surface of aluminophosphate catalysts. It may be possible to attain a more evenly dispersed supported metal by using an acidic metal salt solution.
2. Test other metals to see what activity they exhibit for HDO and dealkylation of model lignin compounds. Others which may work are nickel and palladium. These metals, however, are more sensitive to sulfur. Since lignin can contain a small amount of sulfur (<0.5%), tests should be done to check how rapidly the active metal is deactivated in the presence of sulfur.
3. Vary the reaction conditions (temperature and pressure) to determine the optimal conditions for the desired reactions to occur.
4. Conduct model lignin compound studies to determine the long-term activity of the catalyst. Also, a long term study would allow deactivation potential of the

catalyst to be determined.

5. Fundamental studies which help understand the chemistry on the surface would be useful in choosing the best catalyst and reaction conditions.
6. Re-run experimental run 9 to confirm the high dealkylation activity exhibited by the catalyst support.

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**APPENDIX A. SYSTEM CALIBRATION DATA**

### RELATIVE RESPONSE FACTORS

Relative response factors for the HP 5840 TCD detector used for this study were determined using two-component mixtures. Response factors were determined for the starting materials and those compounds catalytically produced during the experiments, when these were available commercially in pure form. Benzene was assigned a thermal response of 100 so that a direct comparison could be made between the experimentally determined values and those found in the literature (32,33). The relative response factors obtained are shown in Table A-I.

Table A-I. TCD Relative Response Factors

COMPOUND	M.W.	EXPERIMENTAL:		LITERATURE:	
		THERMAL RESPONSE	WEIGHT FACTOR	THERMAL RESPONSE	WEIGHT FACTOR
Hexane	86	123	0.70	123	0.7
Heptane	100	142	0.70	143	0.7
Cyclohexane	84	115	0.73	114	0.735
Methylcyclohexane	98	120	0.82	120	0.82
Ethylcyclohexane	112	137	0.82	145	0.775
Benzene	78	100	0.78	100	0.78
Propylcyclohexane	126	156	0.81	158	0.8
Toluene	92	121	0.76	116	0.794
Undecane	156	217	0.72	198	0.79
Ethylbenzene	106	141	0.75	129	0.818
Propylbenzene	120	164	0.73	145	0.826
2,6-Diethylphenol	150	225	0.67		
Phenol	94	161	0.58		
2-Propylphenol	136	196	0.69		
4-Propylphenol	136	216	0.63		

**G.C. RETENTION TIMES**

Retention times for the compounds produced during the experiments were experimentally determined using comparisons to standards (GC) and using a computer library search routine to compare unknowns to reference mass spectra (GC/MS). Table A-II shows the G.C. retention times for various compounds using a three meter, 1/8 inch stainless steel column packed with Supelco column packing SP-1000 at the following conditions:

TEMP 1 - 100°C	INJ TEMP - 235°C
TIME 1 - 3 MINUTES	TCD TEMP - 250°C
RATE - 30°C/MINUTE	CHT SPD - 0.5
TEMP 2 - 220°C	ATTN - 4
TIME 2 - 30-60 MINUTES	FLOW - 20 cm <sup>3</sup> /min

Table A-II. Liquid Retention Times

COMPONENT	R.T. (min.)
CYCLOHEXANE	2.78
METHYLCYCLOHEXANE	3.53
ETHYLCYCLOHEXANE	5.21
BENZENE	5.86
PROPYLCYCLOHEXANE	6.29
TOLUENE	6.91
ETHYLBENZENE	7.71
PROPYLBENZENE	8.36
DIPROPYLBENZENE	10.14
PHENOL	17.03
2,6-DIPROPYLPHENOL	19.34
2-PROPYLPHENOL	20.56
4-PROPYLPHENOL	26.09
DIPROPYLPHENOL	29.84
DIPROPYLPHENOL	31.77
DIPROPYLPHENOL	40.47

Retention times for the gases produced during the experiments were determined by comparison to standards. The gases were analyzed using a three meter, 1/8 inch stainless steel column packed with Durapack Phenyl Isocyanate/Porasil C, 80/100 mesh manufactured by Waters Associates. The retention times for the gases are shown in Table A-III. The following G.C. conditions were used:

TEMP 1 - 60 °C	INJ TEMP - 235 °C
TIME 1 - 15 MINUTES	TCD TEMP - 250 °C
RATE - 0 °C/MINUTE	CHT SPD - 0.5
TEMP 2 - 60 °C	ATTN - 2
TIME 2 - 0 MINUTES	FLOW - 20 cm <sup>3</sup> /min

Table A-III. Gas Retention Times

Compound:	R.T. (min.)
Ethane	1.3
Ethylene	1.6
Propane	1.9
Propene	3.8
Butene	8.9
Pentene	20.5
Hexene	48.0

### CALIBRATION CURVES

To calibrate the Milton Roy minipump used to pump the liquid feed into the reactor, the liquid flow rate was measured for various pump settings and plotted. The best fit linear regression line was determined. The calibration curve for the liquid pump is shown in Figure A-1. The data shown was taken at pressures of approximately 500 psig. However, since the liquid is not compressible, the curve is valid for other pressures. Data was later taken to confirm this.

# LIQUID PUMP CALIBRATION CURVE

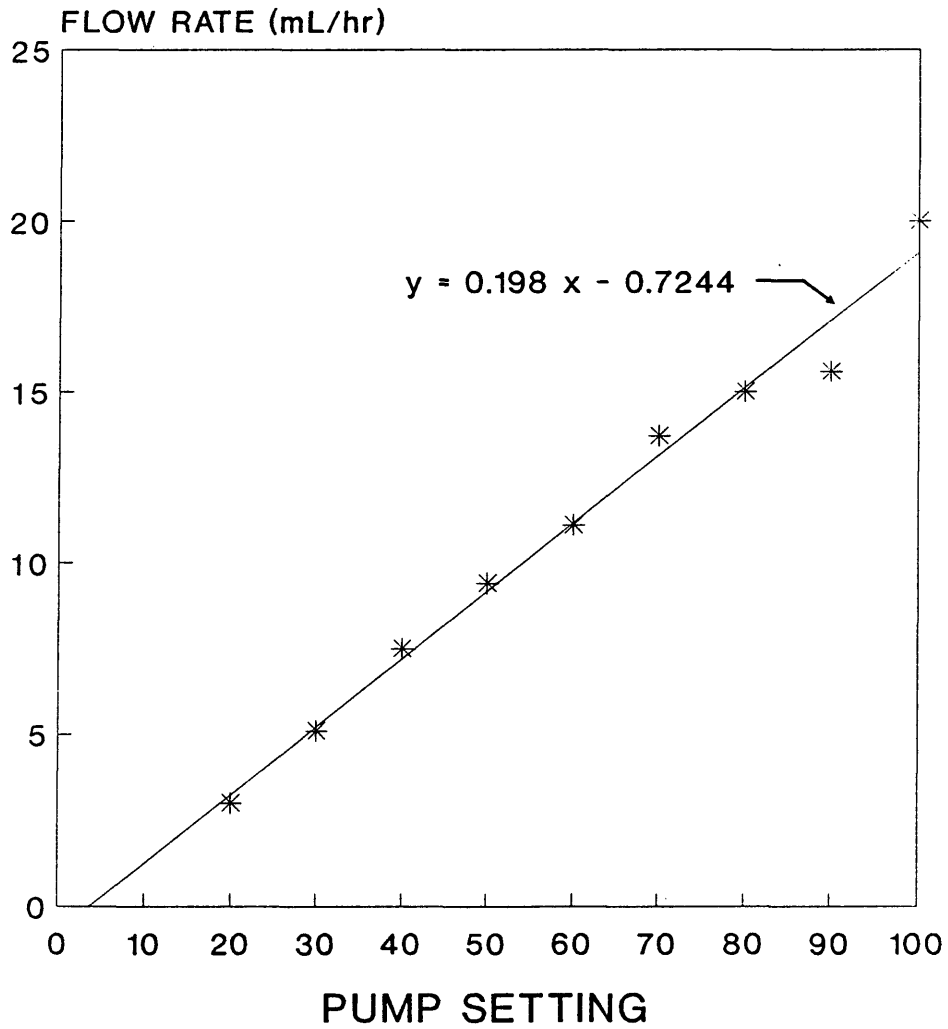


Figure A-1. Liquid Pump Calibration Curve

The hydrogen gas flow controller was calibrated to determine the relationship between the controller setting and the hydrogen flow rate. The calibration curves are shown in Figure A-2. The two curves obtained represent different hydrogen cylinder regulator (inlet) pressures. The flow rate was independent of the pressure inside the reactor (outlet pressure), but as shown in Figure A-2, the inlet pressure of the cylinder regulator had a significant impact on the hydrogen flow rate. As the inlet pressure increases, the flow rate increases at the same setting.

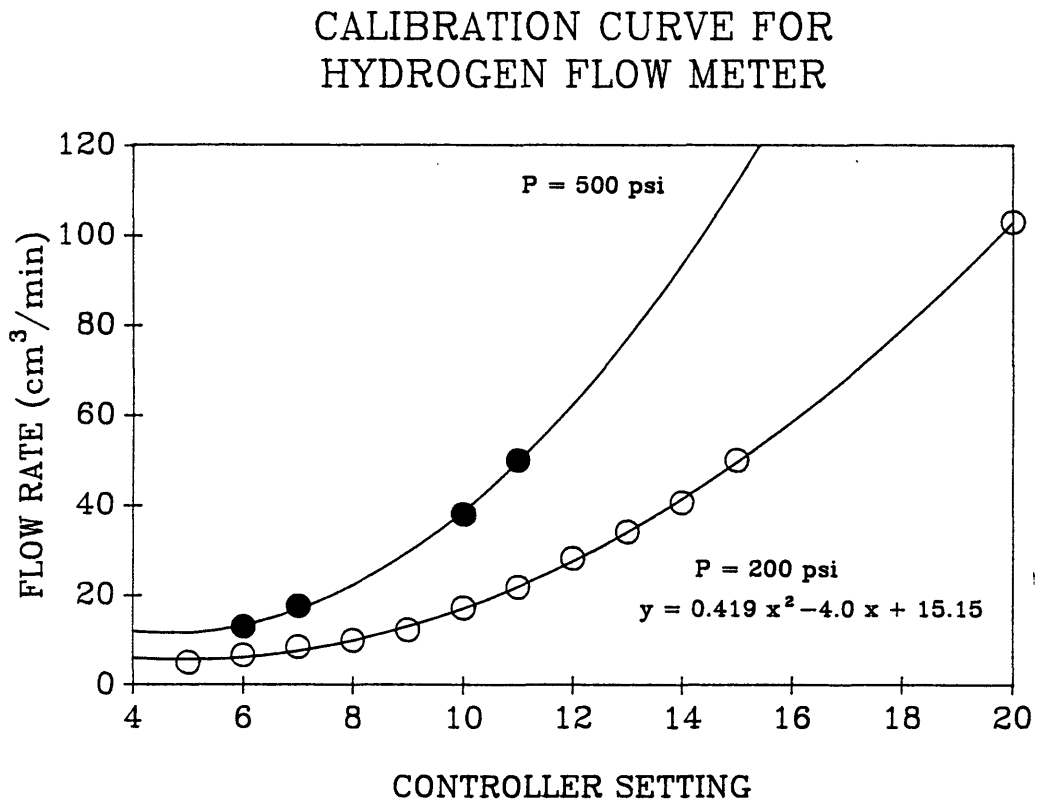


Figure A-2. Calibration Curve for Hydrogen Flow Meter

**APPENDIX B. GC DATA: LIQUID SAMPLES**

Table B-I. Liquid Product Composition (Mole Percent)

COMPONENT:	CATALYST TESTED			
	Pt/ BaO- Al <sub>2</sub> O <sub>3</sub>	Pt-Re/ BaO- Al <sub>2</sub> O <sub>3</sub>	Mo/P:Al (0.5) Sulfided	Mo/P:Al (0.0) Sulfided
CYCLOHEXANE	0.00	0.00	3.55	0.00
ETHYLCYCLOHEXANE	0.00	0.00	1.30	1.17
PROPYLCYCLOHEXANE	45.59	66.55	9.35	49.72
TOLUENE	0.00	0.00	2.20	8.21
PROPYLBENZENE	4.25	5.49	10.04	8.96
DIPROPYLBENZENE (?)	2.98	0.00	3.53	1.15
PHENOL	2.21	1.88	17.96	3.50
2,6-DIPROPYLPHENOL	0.00	0.00	1.20	0.00
2-PROPYLPHENOL	0.00	0.17	6.93	1.62
4-PROPYLPHENOL	35.65	18.66	30.58	23.75
DIPROPYLPHENOL	3.08	1.24	5.61	1.94
DIPROPYLPHENOL	0.00	0.00	4.94	0.00
DIPROPYLPHENOL	0.00	0.00	2.81	0.00
OPERATING CONDITIONS: Temperature (deg C): 350 Pressure (psig): 500 Space Velocity (g 4PP/hr gcat): 1 Catalyst Loading (g): 0.2 Feed Composition: 90% n-C7, 10% 4PP				

Table B-II. Liquid Product Composition Versus Temperature

TIME ON STREAM (HRS)		3	5.5	8.5	11
TEMPERATURE (°C)		350	400	450	350
COMPONENT	R.T.	MOLE PERCENT			
CYCLOHEXANE	2.78	13.31	23.72	20.43	9.90
METHYLCYCLOHEXANE	3.53	0.62	2.75	4.24	0.52
ETHYLCYCLOHEXANE	5.21	0.47	1.23	1.58	0.42
BENZENE	5.86	1.90	12.59	32.83	2.93
PROPYLCYCLOHEXANE	6.29	52.69	23.23	3.87	20.77
TOLUENE	6.91	1.51	3.26	12.62	0.78
ETHYLBENZENE	7.71	1.53	1.84	7.11	0.91
PROPYLBENZENE	8.36	16.85	24.56	11.53	9.65
DIPROPYLBENZENE(?)	10.14	3.20	2.38	0.72	0.67
PHENOL	17.03	2.65	1.67	0.65	10.34
2,6-DIPROPYLPHENOL	19.34	0.41	0.66	1.02	1.48
2-PROPYLPHENOL	20.56	2.42	2.11	1.30	7.83
4-PROPYLPHENOL	26.09	2.42	4.10	2.11	19.30
DIPROPYLPHENOL	29.84	0	0	0	4.66
DIPROPYLPHENOL	31.77	0	0	0	5.28
DIPROPYLPHENOL	40.47	0	0	0	4.56

OPERATING CONDITIONS:  
 Pressure (psig): 500  
 Space Velocity (g 4PP/hr gcat): 1.18  
 Catalyst: 0.2003 g of Pt/P:Al(0.8)  
 Feed Composition: 90.0% n-heptane, 10.0% 4-propylphenol

Table B-III. Liquid Product Composition Versus Pressure

TIME ON STREAM (hrs) PRESSURE (psig)	3.5 500	6.0 300	8.5 200	11 500
COMPONENT	MOLE PERCENT			
CYCLOHEXANE	12.62	5.75	2.03	10.59
METHYLCYCLOHEXANE	0	0	0	0
ETHYLCYCLOHEXANE	0	0	0	0
BENZENE	2.22	2.28	1.28	2.24
PROPYLCYCLOHEXANE	45.50	14.25	4.47	39.01
TOLUENE	0	0	0	0
ETHYLBENZENE	0	0	0	0
PROPYLBENZENE	21.05	11.96	6.37	16.77
DIPROPYLBENZENE	5.30	2.07	0.98	2.84
PHENOL	1.66	11.52	18.78	3.77
2,6-DIPROPYLPHENOL	0	2.41	2.58	0.85
2-PROPYLPHENOL	1.58	9.53	12.42	3.35
4-PROPYLPHENOL	3.17	22.03	31.38	10.78
DIPROPYLPHENOL	2.38	5.01	6.65	3.56
DIPROPYLPHENOL	2.93	6.47	7.57	4.67
DIPROPYLPHENOL	1.58	6.73	5.48	4.30
OPERATING CONDITIONS: Temperature (°C): 350 Space Velocity (g 4PP/hr gcat): 1.18 Catalyst: 0.2002 g of Pt/P:Al(0.8) Feed Composition: 90.0% n-heptane, 10.0% 4-propylphenol				

Table B-IV. Liquid Product Composition versus Temperature.

TIME ON STREAM	3.5	6.5	9	11	12.5
TEMPERATURE	350	350	400	450	350
PRESSURE	500	200	200	200	500
COMPONENT	MOLE PERCENT				
CYCLOHEXANE	19.10	5.15	2.77	1.02	6.79
METHYLCYCLOHEXANE	1.41	0	0	0	0
ETHYLCYCLOHEXANE	1.39	0	0	0	0
BENZENE	4.15	4.18	8.98	16.02	3.90
PROPYLCYCLOHEXANE	42.26	6.37	1.37	0	5.50
TOLUENE	0	0	0	5.62	0.71
ETHYLBENZENE	0	0.53	0	2.97	0
PROPYLBENZENE	24.89	8.90	6.38	6.98	4.08
DIPROPYLBENZENE(?)	6.80	2.07	0.74	1.41	0.87
PHENOL	0	23.96	46.78	45.73	18.34
2,6-DIPROPYLPHENOL	0	2.11	7.36	13.69	2.57
2-PROPYLPHENOL	0	11.07	9.67	3.17	11.20
4-PROPYLPHENOL	0	25.22	14.17	2.30	27.98
DIPROPYLPHENOL	0	3.69	0.53	0	6.24
DIPROPYLPHENOL	0	3.98	0.57	0.63	6.40
DIPROPYLPHENOL	0	2.76	0.70	0.47	5.42
OPERATING CONDITIONS:					
Space Velocity (g 4PP/hr gcat): 1.20					
Catalyst: 0.2002g Pt/P:Al(0.8)					
Feed Composition: 89.9% n-hexane, 10.1% 4-propylphenol					

Table B-V. Liquid Product Composition

TEMPERATURE (°C)	350	300	250	200	350
COMPONENT	MOLE PERCENT				
CYCLOHEXANE	19.4	13.6	3.6	1.2	14.23
METHYLCYCLOHEXANE	1.1	0	0	0	0.86
BENZENE	2.9	1.1	0	0	2.69
PROPYLCYCLOHEXANE	46.0	50.8	51.0	32.8	34.83
PROPYLBENZENE	23.7	17.6	8.0	2.6	17.98
DIPROPYLBENZENE(?)	6.8	3.2	0.3	0	4.63
PHENOL	0	1.4	4.8	2.4	2.99
2,6-DIPROPYLPHENOL	0	0.7	0.1	0	0.58
2-PROPYLPHENOL	0	2.6	1.5	0.6	1.72
4-PROPYLPHENOL	0	4.4	23.9	49.5	11.04
DIPROPYLPHENOL	0	2.5	6.1	3.3	3.13
DIPROPYLPHENOL	0	1.3	0.6	0	1.28
DIPROPYLPHENOL	0	0.8	0.3	0	1.07
OPERATING CONDITIONS:					
Pressure (psig): 500					
Space Velocity (g 4PP/hr gcat): 1.20					
Catalyst Loading: 0.2000g Pt/P:Al(0.8)					
Feed Composition: 89.9% n-C6, 10.1% 4PP					

Table B-VI. Activity of Blank Support  
(P:Al = 0.8)

TIME ON STREAM TEMPERATURE	3.5 350	7.5 450
COMPONENT	MOLE PERCENT	
PROPYLBENZENE	0	5.1
PHENOL	30.9	59.9
2,6-DIPROPYLPHENOL	2.1	18.8
2-PROPYLPHENOL	15.3	7.0
4-PROPYLPHENOL	34.2	9.1
DIPROPYLPHENOL	5.7	0
DIPROPYLPHENOL	6.5	0
DIPROPYLPHENOL	5.3	0
OPERATING CONDITIONS: Pressure (psig): 500 Space Velocity (g 4PP/hr gcat): 1.06 Catalyst: 0.2004g P:Al(0.8) Support Only Feed Composition: 90.0% n-Hex, 10.0% 4-PP		

Table B-VII. Results of Replicate Runs

COMPONENT:	RUN NUMBER:				AVERAGE:
	5	6	7	9	
	MOLE PERCENT				
CH	13.31	18.59	19.10	19.38	17.6 +/- 2.5
MCH	0.62	0	1.41	1.09	0.8 +/- 0.5
ECH	0.47	0	1.39	0	0.5 +/- 0.6
BENZENE	1.90	3.77	4.15	2.95	3.2 +/- 0.9
PCH	52.69	49.59	42.26	46.04	47.6 +/- 3.9
TOLUENE	1.51	0	0	0	0.4 +/- 0.7
EB	1.53	0	0	0	0.4 +/- 0.7
PB	16.85	20.52	24.89	23.73	21.5 +/- 3.1
DI-PB	3.20	4.16	6.80	6.81	5.2 +/- 1.6
PHENOL	2.65	1.73	0	0	1.1 +/- 1.1
2,6-DI-PP	0.41	0	0	0	0.1 +/- 0.2
2-PP	2.42	1.36	0	0	0.9 +/- 1.0
4-PP	2.42	2.49	0	0	1.2 +/- 1.2
DI-PP	0	1.52	0	0	0.4 +/- 0.7
DI-PP	0	1.87	0	0	0.5 +/- 0.8
DI-PP	0	1.01	0	0	0.3 +/- 0.4
CATALYST: Pt/P:Al 0.8 (DAE 10/17) REACTANT: 4-PROPYLPHENOL TEMPERATURE: 350 C PRESSURE: 500 psig					

Table B-VIII. 4-Propylguaiacol Liquid Data

T ( C )		350	350	400	450	350	
PRESSURE (psi)		500	200	200	200	500	
COMPONENT	MW	mole%	mole%	mole%	mole%	mole%	
CYCLOHEXANE	84.00	1.44	4.24	1.66	0.00	4.18	
BENZENE	78.00	0.01	0.91	1.91	2.44	1.98	
CYCLOHEXENE	82.00	0.00	0.00	0.00	0.08	0.33	
meCYCLOHEXANE	98.00	2.15	1.41	0.29	0.00	1.20	
TOLUENE	92.00	0.32	1.30	2.20	2.36	0.80	
et-CYCLOHEXANE	112.00	0.70	0.77	0.00	0.00	0.00	
et-BENZENE	106.00	0.00	0.00	0.10	0.32	0.00	
p-XYLENE	106.00	0.31	0.00	0.28	0.57	0.00	
pr-CYCLOHEXANE	126.00	6.46	5.09	0.00	0.00	3.71	
pr-BENZENE	120.00	1.89	4.38	1.18	1.23	2.96	
MESITYLENE	120.00	0.03	0.00	0.00	0.11	0.00	
4-^ET-TOLUENE	120.00	0.02	0.00	0.00	0.00	0.00	
PHENOL	94.00	1.56	4.75	12.78	24.89	6.44	
o-CRESOL	108.00	1.92	2.89	8.83	13.19	2.53	
p-CRESOL	108.00	1.95	1.14	14.72	19.06	3.58	
2,4-^XYLENOL	122.00	3.86	3.56	10.49	8.06	1.37	
4-et-PHENOL	122.00	0.18	0.45	5.38	5.32	1.36	
3-et-PHENOL	122.00	1.93	0.09	1.20	0.93	0.18	
2,3-XYLENOL	122.00	0.91	0.00	0.00	0.00	0.00	
2-isoPROPYLPHENOL	136.00	0.33	1.39	1.31	0.30	0.29	
2,6-diethylPHENOL	136.00	0.10	2.12	2.00	0.45	0.47	
2-propylPHENOL	136.00	1.75	3.22	2.97	1.84	0.82	
2,4,6-trime-PHENO	150.00	0.00	0.00	0.41	0.00	0.00	
4-propylPHENOL	136.00	1.40	15.34	12.59	4.86	9.33	
sec-butylPHENOL	150.00	0.80	0.68	0.93	0.31	0.30	
4-propylGUAIACOL	166.00	0.01	0.00	0.00	0.00	0.85	
4-et-CATECHOL	138.00	0.00	0.00	0.00	0.00	0.00	
naphthalene	128.00	0.00	0.00	0.00	0.57	0.00	
me-naphthalene	142.00	0.00	0.00	0.00	0.50	0.00	
sub-total	30.02	53.72	81.23	87.39	42.67		
UNCALIB PKS	136.00	69.98	46.28	18.77	12.61	57.33	
SUM TTL wt%	SUM TTL wt%		100.00	100.00	100.00	100.00	100.00

	350 500 CSM4G mole%	350 200 CSM7G mole%	400 200 CSM11G mole%	450 200 CSM14G mole%	350 500 CSM17G mole%
SATD HYDRO C	28.60	11.51	1.95	0.08	9.41
AROM HYDRO C	5.96	6.59	5.67	7.04	5.74
PHENOL	1.56	4.75	12.78	24.89	6.44
CRESOLS	3.87	4.04	23.56	32.25	6.11
C2 PHENOLS	11.39	4.10	17.08	16.05	2.91
C3 PHENOLS	9.87	19.94	17.27	7.56	10.45
C4 PHENOLS	17.62	23.25	16.70	4.87	5.16
C5 PHENOLS	12.31	18.52	4.12	6.04	8.00
C6 PHENOLS	5.00	7.31	0.88	0.00	7.06
C7 PHENOLS	3.80	0.00	0.00	0.00	0.00
CATECHOLS	0.00	0.00	0.00	0.00	37.87
NAPHTHALENES	0.00	0.00	0.00	1.07	0.00
UNCALIBRATED	69.98	46.28	18.77	12.61	57.33
CONVERSION	99.99	100.00	100.00	100.00	99.15
DEALKYTD PHENOLS	16.82	12.89	53.41	73.19	15.46
C3+ PHENOLS	48.61	69.02	38.97	18.47	30.67
SUM	99.99	100.00	100.00	99.85	99.15

## UNCALIBRATED PEAKUNCALIBRATED PEAKS -- TENTATIVE ASSIGNMENTS

SATURATED HYDROCARBONS						
C7	98.00	1.12	0.00	0.00	0.00	0.00
C8	112.00	2.80	0.00	0.00	0.15	0.00
C9	126.00	6.09	0.00	0.00	0.00	0.00
C10	140.00	7.66	0.00	0.00	0.00	0.00
C11	154.00	0.18	0.00	0.00	0.00	0.00
AROMATIC HYDROCARBONS						
C8	106.00	0.34	0.00	0.00	0.00	0.00
C10	134.00	2.70	0.00	0.00	0.00	0.00
C11	148.00	0.20	0.00	0.00	0.00	0.00
C12	162.00	0.15	0.00	0.00	0.00	0.00
PHENOLS						
C2	122.00	4.51	0.00	0.00	1.74	0.00
C3	136.00	6.40	0.00	0.00	0.57	0.00
C4	150.00	16.73	20.45	13.77	4.11	4.39
C5	164.00	12.31	18.52	4.12	6.04	8.00
C6	178.00	5.00	7.31	0.88	0.00	7.06
C7	192.00	3.80	0.00	0.00	0.00	0.00
CATECHOLS	152.00	0.00	0.00	0.00	0.00	37.87
SUMS		69.98	46.28	18.77	12.61	57.33
SATD HYDROC		17.85	0.00	0.00	0.15	0.00
AROM HYDROC		3.39	0.00	0.00	0.00	0.00

**APPENDIX C. GC DATA: GAS SAMPLES**

Table C-I. Gas Analysis for Platinum Catalyst Run

COMPOUND:	TOS	ETHANE	ETHENE	PROPANE	PROPENE	HEXANE
	(HRS)	PEAK AREA				
R.T.:		1.25	1.56	1.94	3.8	18
T= 350 C P= 500 psig	0.25	0	322	48	0	0
	0.5	19	233	37	0	0
	1	21	195	70	0	5829
	2.5	14	181	178	0	5981
T= 350 C P= 200 psig	3	27	155	440	0	7950
	3.5	21	79	632	0	13710
	4.25	40	42	1264	0	13340
	5	45	0	1660	0	13121
	5.5	57	0	1829	0	13150
	6	57	0	1893	0	12780
T= 400 C P= 200 psig	7.5	277	0	5161	122	13240
	8	355	0	6249	181	13610
	8.5	383	0	6536	203	14630
T= 450 C P= 200 psig	9	869	0	8086	332	14470
	9.5	1383	0	8794	408	14880
	10	1687	0	9354	432	14070
	10.5	1841	13	9570	446	14770
RUN: DAE10 CATALYST: Pt/P:Al(0.8)						

Table C-II. Gas Analysis for P:Al(0.8) Support Run

COMPOUND:	TOS	ETHANE	ETHENE	PROPANE	PROPENE	HEXANE
	(HRS)	PEAK AREA				
R.T.:		1.25	1.56	1.94	3.8	18
T= 350 C P= 500 psig	0.1	0	230	0	0	6440
	2	0	137	0	0	5695
	2.5	0	116	0	0	5836
T= 350 C P= 200 psig	3	0	105	0	0	5940
	3.5	13	81	0	0	6094
	4	0	66	0	0	15070
	4.5	0	36	0	0	15290
	5	0	36	0	0	15840
	5.5	0	30	0	0	13080
T= 400 C P= 200 psig	7.2	43	57	0	0	12190
	7.5	35	78	0	0	14970
	8	35	82	0	0	17550
T= 450 C P= 200 psig	9	152	180	89	319	12850
	9.25	393	364	264	929	11220
	9.6	504	537	339	1325	11550
	10	667	551	433	1543	11400
	10.5	759	645	474	1824	10460
	11.25	840	800	508	2227	11300
RUN: DAE11 CATALYST: P:Al(0.8)						

**APPENDIX D: THERMODYNAMIC DATA**

**ABBREVIATIONS USED IN APPENDIX D**

Benz	-	Benzene
CH	-	Cyclohexane
TOL	-	Toluene
MCH	-	Methylcyclohexane
ECH	-	Ethylcyclohexane
EB	-	Ethylbenzene
PCH	-	Propylcyclohexane
PB	-	Propylbenzene
CHol	-	Cyclohexanol
Phen	-	Phenol

## SAMPLE CALCULATIONS

Thermodynamic calculations were performed to determine the equilibrium distribution of various pairs of products. Thermodynamic data was obtained in the literature (34). A sample calculation is shown. All of the data was determined in a similar fashion.

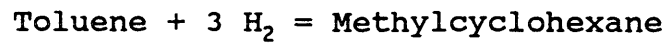


$$\Delta G_{\text{BENZ}} + \Delta G_{\text{WATER}} - \Delta G_{\text{PHEN}} = \Delta G_{\text{RXN}}$$

$$\ln K_p = -\Delta G/RT$$

$$K_p = \exp -(\Delta G/RT)$$

$$\begin{aligned} K_p &= \frac{P_{\text{H}_2\text{O}} * P_{\text{BENZ}}}{P_{\text{Phen}} * P_{\text{H}_2}} = \frac{(X_{\text{H}_2\text{O}} * P) (X_{\text{BENZ}} * P)}{(X_{\text{Phen}} * P) (P_{\text{H}_2})} \\ &= \frac{X_{\text{H}_2\text{O}} * X_{\text{BENZ}} * P}{X_{\text{Phen}} * P_{\text{H}_2}} \quad (P_{\text{H}_2} \text{ approx} = P) \\ &= \frac{X_{\text{H}_2\text{O}} * X_{\text{BENZ}}}{X_{\text{Phen}}} = \frac{(X_{\text{BENZ}})^2}{X_{\text{Phen}}} = \frac{X^2}{(1-X)} \end{aligned}$$



$$\frac{P_{\text{MCH}}}{P_{\text{TOL}} + P_{\text{MCH}}} = \frac{K_p * (P_{\text{H}})^3}{1 + (K_p * (P_{\text{H}})^3)}$$

$$\ln K_p = -\Delta G/RT$$

$$K_p = \exp -(\Delta G/RT)$$

600°K:

$$K_p = \exp -(5.21*10^3/(1.987*600))$$

$$K_p = \exp -(4.37)$$

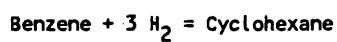
$$K_p = 0.0127$$

P = 200 psig = 13.6 atm:

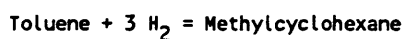
$$\frac{P_{\text{MCH}}}{P_{\text{TOL}} + P_{\text{MCH}}} = \frac{0.0127 * (13.6)^3}{1 + (0.0127 * (13.6)^3)}$$

$$= 0.969$$

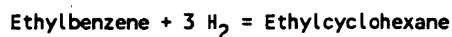
$$= 96.9\% \text{ MCH}$$



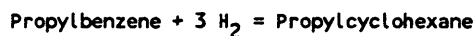
P (psig)	T (K)	$\Delta G_f$		$\Delta G_{RXN}$	Kp	%CH
		CH	Benz			
200	600	47.85	43.66	4190	2.976E-02	98.68
200	623	51.07	44.71	6361	5.865E-03	93.66
200	673	58.06	46.98	11081	2.519E-04	38.81
200	700	61.84	48.21	13630	5.548E-05	12.26
200	723	65.08	49.27	15808	1.664E-05	4.02
200	800	75.94	52.84	23100	4.885E-07	0.12
500	600	47.85	43.66	4190	2.976E-02	99.91
500	623	51.07	44.71	6361	5.865E-03	99.57
500	673	58.06	46.98	11081	2.519E-04	90.84
500	700	61.84	48.21	13630	5.548E-05	68.59
500	723	65.08	49.27	15808	1.664E-05	39.57
500	800	75.94	52.84	23100	4.885E-07	1.89



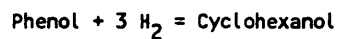
P (psig)	T (K)	$\Delta G_f$		$\Delta G_{RXN}$	Kp	%MCH
		MCH	TOL			
200	600	53.53	48.32	5210	1.265E-02	96.96
200	623	57.27	49.88	7388	2.559E-03	86.57
200	673	65.40	53.28	12123	1.156E-04	22.54
200	700	69.79	55.11	14680	2.608E-05	6.16
200	723	73.55	56.69	16863	7.985E-06	1.97
200	800	86.15	61.98	24170	2.492E-07	0.06
500	600	53.53	48.32	5210	1.265E-02	99.80
500	623	57.27	49.88	7388	2.559E-03	99.02
500	673	65.40	53.28	12123	1.156E-04	81.97
500	700	69.79	55.11	14680	2.608E-05	50.65
500	723	73.55	56.69	16863	7.985E-06	23.91
500	800	86.15	61.98	24170	2.492E-07	0.97



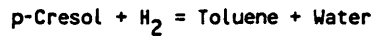
P (psig)	T (K)	$\Delta G_f$		$\Delta G_{RXN}$	Kp	%ECH
		ECH	EB			
200	600	63.7	57.63	6070	6.149E-03	93.93
200	623	68.0	59.76	8250	1.275E-03	76.25
200	673	77.4	64.40	12990	6.042E-05	13.21
200	700	82.5	66.91	15550	1.395E-05	3.39
200	723	86.8	69.07	17730	4.365E-06	1.09
200	800	101.3	76.29	25030	1.451E-07	0.04
500	600	63.7	57.63	6070	6.149E-03	99.59
500	623	68.0	59.76	8250	1.275E-03	98.05
500	673	77.4	64.40	12990	6.042E-05	70.39
500	700	82.5	66.91	15550	1.395E-05	35.45
500	723	86.8	69.07	17730	4.365E-06	14.66
500	800	101.3	76.29	25030	1.451E-07	0.57



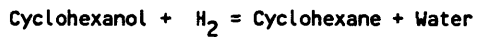
P (psig)	T (K)	$\Delta G_f$		$\Delta G_{RXN}$	Kp	%PCH
		PCH	PB			
200	600	73.07	66.49	6580	4.009E-03	90.99
200	623	77.97	69.20	8772	8.366E-04	67.82
200	673	88.62	75.08	13537	4.015E-05	9.18
200	700	94.37	78.26	16110	9.329E-06	2.30
200	723	99.29	80.99	18302	2.932E-06	0.73
200	800	115.78	90.14	25640	9.883E-08	0.02
500	600	73.07	66.49	6580	4.009E-03	99.37
500	623	77.97	69.20	8772	8.366E-04	97.05
500	673	88.62	75.08	13537	4.015E-05	61.24
500	700	94.37	78.26	16110	9.329E-06	26.85
500	723	99.29	80.99	18302	2.932E-06	10.35
500	800	115.78	90.14	25640	9.883E-08	0.39



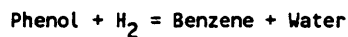
P (psig)	T (K)	$\Delta G_f$ CHol	Phenol	$\Delta G_{RXN}$	Kp	%CHol
200	600	17.16	8.62	8540	7.746E-04	66.11
200	623	20.75	9.94	10810	1.612E-04	28.88
200	673	28.56	12.81	15745	7.700E-06	1.90
200	700	32.77	14.36	18410	1.785E-06	0.45
200	723	36.38	15.69	20692	5.556E-07	0.14
200	800	48.47	20.14	28330	1.820E-08	0.00
500	600	17.16	8.62	8540	7.746E-04	96.82
500	623	20.75	9.94	10810	1.612E-04	86.39
500	673	28.56	12.81	15745	7.700E-06	23.26
500	700	32.77	14.36	18410	1.785E-06	6.56
500	723	36.38	15.69	20692	5.556E-07	2.14
500	800	48.47	20.14	28330	1.820E-08	0.07



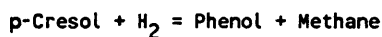
P(psig)	T(K)	$\Delta G_f$		Cresol	$\Delta G_{RXN}$	Kp	X(toluene)
		Tol	Water				
200	600	48.32	-51.16	17.05	-19890	1.760E+07	1.00E+00
200	623	49.88	-50.87	19.00	-19996	1.036E+07	1.00E+00
200	673	53.28	-50.25	23.25	-20226	3.704E+06	1.00E+00
200	700	55.11	-49.92	25.54	-20350	2.260E+06	1.00E+00
200	723	56.69	-49.63	27.51	-20447	1.518E+06	1.00E+00
200	800	61.98	-48.65	34.10	-20770	4.727E+05	1.00E+00
500	600	48.32	-51.16	17.05	-19890	1.760E+07	1.00E+00
500	623	49.88	-50.87	19.00	-19996	1.036E+07	1.00E+00
500	673	53.28	-50.25	23.25	-20226	3.704E+06	1.00E+00
500	700	55.11	-49.92	25.54	-20350	2.260E+06	1.00E+00
500	723	56.69	-49.63	27.51	-20447	1.518E+06	1.00E+00
500	800	61.98	-48.65	34.10	-20770	4.727E+05	1.00E+00



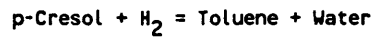
P(psig)	T(K)	CH	$\Delta G_f$		CHol	$\Delta G_{RXN}$	Kp	X(CH)
			Water					
200	600	47.85	-51.16	17.16	-20470	2.863E+07	1.00E+00	
200	623	51.07	-50.87	20.75	-20557	1.630E+07	1.00E+00	
200	673	58.06	-50.25	28.56	-20747	5.471E+06	1.00E+00	
200	700	61.84	-49.92	32.77	-20850	3.237E+06	1.00E+00	
200	723	65.08	-49.63	36.38	-20926	2.119E+06	1.00E+00	
200	800	75.94	-48.65	48.47	-21180	6.118E+05	1.00E+00	
500	600	48.32	-51.16	17.05	-19890	1.760E+07	1.00E+00	
500	623	49.88	-50.87	19.00	-19996	1.036E+07	1.00E+00	
500	673	53.28	-50.25	23.25	-20226	3.704E+06	1.00E+00	
500	700	55.11	-49.92	25.54	-20350	2.260E+06	1.00E+00	
500	723	56.69	-49.63	27.51	-20447	1.518E+06	1.00E+00	
500	800	61.98	-48.65	34.10	-20770	4.727E+05	1.00E+00	



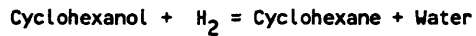
P(psig)	T(K)	$\Delta G_f$		Phenol	$\Delta G_{\text{rxn}}$	Kp	X(benz)
		Benz	Water				
200	600	43.66	-51.16	8.62	-16120	7.451E+05	1.00E+00
200	623	44.71	-50.87	9.94	-16109	4.481E+05	1.00E+00
200	673	46.98	-50.25	12.81	-16084	1.673E+05	1.00E+00
200	700	48.21	-49.92	14.36	-16070	1.042E+05	1.00E+00
200	723	49.27	-49.63	15.69	-16042	7.075E+04	1.00E+00
200	800	52.84	-48.65	20.14	-15950	2.279E+04	1.00E+00
-----							
500	600	43.66	-51.16	8.62	-16120	7.451E+05	1.00E+00
500	623	44.71	-50.87	9.94	-16109	4.481E+05	1.00E+00
500	673	46.98	-50.25	12.81	-16084	1.673E+05	1.00E+00
500	700	48.21	-49.92	14.36	-16070	1.042E+05	1.00E+00
500	723	49.27	-49.63	15.69	-16042	7.075E+04	1.00E+00
500	800	52.84	-48.65	20.14	-15950	2.279E+04	1.00E+00



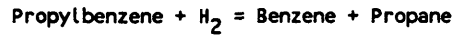
P(psig)	T(K)	$\Delta G_f$		Cresol	$\Delta G_{\text{rxn}}$	Kp	X(phen)
		Phenol	Methane				
200	600	8.62	-5.51	17.05	-13940	1.197E+05	1.00E+00
200	623	9.94	-4.95	19.00	-14009	8.219E+04	1.00E+00
200	673	12.81	-3.72	23.25	-14159	3.966E+04	1.00E+00
200	700	14.36	-3.06	25.54	-14240	2.794E+04	1.00E+00
200	723	15.69	-2.49	27.51	-14304	2.110E+04	1.00E+00
200	800	20.14	-0.56	34.10	-14520	9.268E+03	1.00E+00
-----							
500	600	8.62	-5.51	17.05	-13940	1.197E+05	1.00E+00
500	623	9.94	-4.95	19.00	-14009	8.219E+04	1.00E+00
500	673	12.81	-3.72	23.25	-14159	3.966E+04	1.00E+00
500	700	14.36	-3.06	25.54	-14240	2.794E+04	1.00E+00
500	723	15.69	-2.49	27.51	-14304	2.110E+04	1.00E+00
500	800	20.14	-0.56	34.10	-14520	9.268E+03	1.00E+00



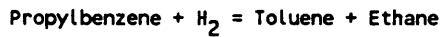
P(psig)	T(K)	$\Delta G_f$		Cresol	$\Delta G_{RXN}$	Kp	X(toluene)
		Tol	Water				
200	600	48.32	-51.16	17.05	-19890	1.760E+07	1.00E+00
200	623	49.88	-50.87	19.00	-19996	1.036E+07	1.00E+00
200	673	53.28	-50.25	23.25	-20226	3.704E+06	1.00E+00
200	700	55.11	-49.92	25.54	-20350	2.260E+06	1.00E+00
200	723	56.69	-49.63	27.51	-20447	1.518E+06	1.00E+00
200	800	61.98	-48.65	34.10	-20770	4.727E+05	1.00E+00
500	600	48.32	-51.16	17.05	-19890	1.760E+07	1.00E+00
500	623	49.88	-50.87	19.00	-19996	1.036E+07	1.00E+00
500	673	53.28	-50.25	23.25	-20226	3.704E+06	1.00E+00
500	700	55.11	-49.92	25.54	-20350	2.260E+06	1.00E+00
500	723	56.69	-49.63	27.51	-20447	1.518E+06	1.00E+00
500	800	61.98	-48.65	34.10	-20770	4.727E+05	1.00E+00



P(psig)	T(K)	$\Delta G_f$		CHol	$\Delta G_{RXN}$	Kp	X(CH)
		CH	Water				
200	600	47.85	-51.16	17.16	-20470	2.863E+07	1.00E+00
200	623	51.07	-50.87	20.75	-20557	1.630E+07	1.00E+00
200	673	58.06	-50.25	28.56	-20747	5.471E+06	1.00E+00
200	700	61.84	-49.92	32.77	-20850	3.237E+06	1.00E+00
200	723	65.08	-49.63	36.38	-20926	2.119E+06	1.00E+00
200	800	75.94	-48.65	48.47	-21180	6.118E+05	1.00E+00
500	600	48.32	-51.16	17.05	-19890	1.760E+07	1.00E+00
500	623	49.88	-50.87	19.00	-19996	1.036E+07	1.00E+00
500	673	53.28	-50.25	23.25	-20226	3.704E+06	1.00E+00
500	700	55.11	-49.92	25.54	-20350	2.260E+06	1.00E+00
500	723	56.69	-49.63	27.51	-20447	1.518E+06	1.00E+00
500	800	61.98	-48.65	34.10	-20770	4.727E+05	1.00E+00



P(psig)	T(K)	$\Delta G_f$		PB	$\Delta G_{RXN}$	Kp	X(benzene)
		Benz	Propane				
200	600	43.66	15.50	66.49	-7330	4.679E+02	9.98E-01
200	623	44.71	17.21	69.20	-7282	3.586E+02	9.97E-01
200	673	46.98	20.92	75.08	-7177	2.142E+02	9.95E-01
200	700	48.21	22.93	78.26	-7120	1.672E+02	9.94E-01
200	723	49.27	24.66	80.99	-7058	1.360E+02	9.93E-01
200	800	52.84	30.45	90.14	-6850	7.439E+01	9.87E-01
500	600	43.66	15.50	66.49	-7330	4.679E+02	9.98E-01
500	623	44.71	17.21	69.20	-7282	3.586E+02	9.97E-01
500	673	46.98	20.92	75.08	-7177	2.142E+02	9.95E-01
500	700	48.21	22.93	78.26	-7120	1.672E+02	9.94E-01
500	723	49.27	24.66	80.99	-7058	1.360E+02	9.93E-01
500	800	52.84	30.45	90.14	-6850	7.439E+01	9.87E-01



P(psig)	T(K)	$\Delta G_f$		PB	$\Delta G_{RXN}$	Kp	X(Toluene)
		Tol	Ethane				
200	600	48.32	5.96	66.49	-12210	2.805E+04	1.00E+00
200	623	49.88	7.10	69.20	-12219	1.936E+04	1.00E+00
200	673	53.28	9.57	75.08	-12239	9.438E+03	1.00E+00
200	700	55.11	10.90	78.26	-12250	6.682E+03	1.00E+00
200	723	56.69	12.05	80.99	-12250	5.050E+03	1.00E+00
200	800	61.98	15.91	90.14	-12250	2.222E+03	1.00E+00
500	600	48.32	5.96	66.49	-12210	2.805E+04	1.00E+00
500	623	49.88	7.10	69.20	-12219	1.936E+04	1.00E+00
500	673	53.28	9.57	75.08	-12239	9.438E+03	1.00E+00
500	700	55.11	10.90	78.26	-12250	6.682E+03	1.00E+00
500	723	56.69	12.05	80.99	-12250	5.050E+03	1.00E+00
500	800	61.98	15.91	90.14	-12250	2.222E+03	1.00E+00