Catalytic hydrogenolysis of sorbitol to polyhydric alcohols
by Robert N Currie

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

Abstract:
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The greatest problem to date is maintaining catalyst activity for an industrially feasible operating period. This deactivation is reportedly associated with the acidic conditions during the reaction. The reported research provided data and correlations on catalyst life while maintaining a high degree of conversion. This was done by testing and optimizing the use of different types and concentrations of co-catalyst. The product stream pH could also be controlled by the type and , concentrations of cocatalyst in the feed. The co-catalyst that yielded the highest conversion of sorbitol was sodium hydroxide, at the determent of decreased glycerol concentration in the product stream. Barium hydroxide was the optimum co-catalyst with respect to overall sorbitol conversion to glycerol. A corresponding decrease in product pH with conversion was observed in this research for continuous hydrogenolysis of sorbitol. The catalyst life for this continuous system was extended to 460 hours while maintaining a high to moderate conversion.

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Robert N. Currie

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

The production of polyhydric alcohols from a renewable resource, such as from hydrogenolysis of sorbitol is greatly needed in an era of increasing dependence on petroleum. Significant work has already been conducted on the hydrogenolysis of sorbitol in batch type processes. However, to make hydrogenolysis of sorbitol a feasible alternative to other methods of producing polyhydric alcohols more work is needed in the area of continuous processes.

The greatest problem to date is maintaining catalyst activity for an industrially feasible operating period. This deactivation is reportedly associated with the acidic conditions during the reaction. The reported research provided data and correlations on catalyst life while maintaining a high degree of conversion. This was done by testing and optimizing the use of different types and concentrations of co-catalyst. The product stream pH could also be controlled by the type and concentrations of co-catalyst in the feed. The co-catalyst that yielded the highest conversion of sorbitol was sodium hydroxide, at the determent of decreased glycerol concentration in the product stream. Barium hydroxide was the optimum co-catalyst with respect to overall sorbitol conversion to glycerol. A corresponding decrease in product pH with conversion was observed in this research for continuous hydrogenolysis of sorbitol. The catalyst life for this continuous system was extended to 460 hours while maintaining a high to moderate conversion.

CHAPTER 1

INTRODUCTION

The production of polyhydric alcohols from a starch feedstock has been of significant interest since the early 1930s. During World War II glycerol was in high demand for the production of trinitroglycerin (TNT). The primary feedstock or producing glycerol, animal fat, could not fulfill the increase in demand caused by the war. Alternate methods of glycerol production were developed including the hydrogenolysis of saccharides. During World War II, a German plant was built by I.G. Farbenindustrie, A.- G.,Werke, Hoechst for the production of a glycerol substitute, "glycerogen", which was of suitable quality for cosmetics or as a humectant [1]. This "glycerogen" contained significant amounts of ethylene glycol and propylene glycol, making "glycerogen" unsuitable for use in the manufacturing of TNT or pharmaceuticals. Today these by-products, as well as the glycerol have developed into new markets and are in high demand. Currently polyhydric alcohols are economically produced from petroleum fractions. However, the conversion of non-petroleum and renewable resources to polyhydric alcohols is desirable in an era of increasing dependence on petroleum [2]. One such reaction is the hydrogenolysis of sorbitol to polyhydric alcohols shown in Figure 1. However, significant side reactions also occur under the hydrocracking conditions. The two principle ones are shown in Figures 2 and 3.

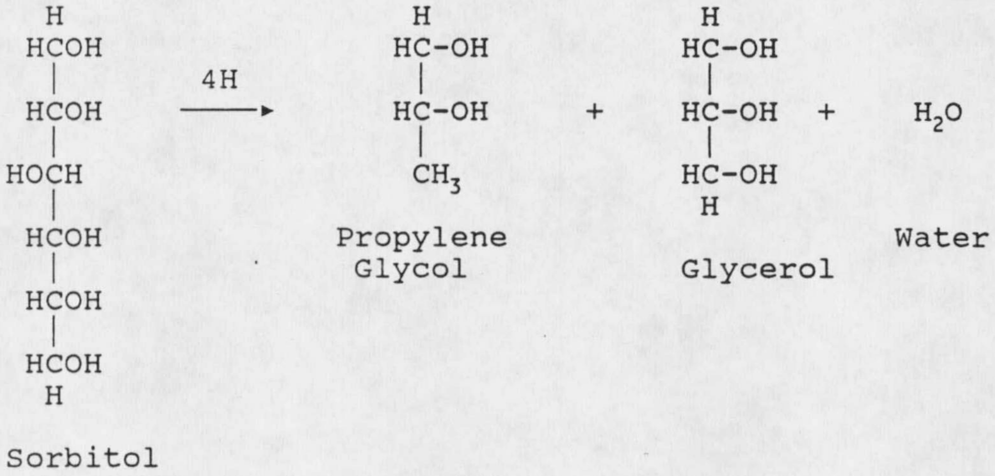


Figure 1 Hydrogenolysis of sorbitol.

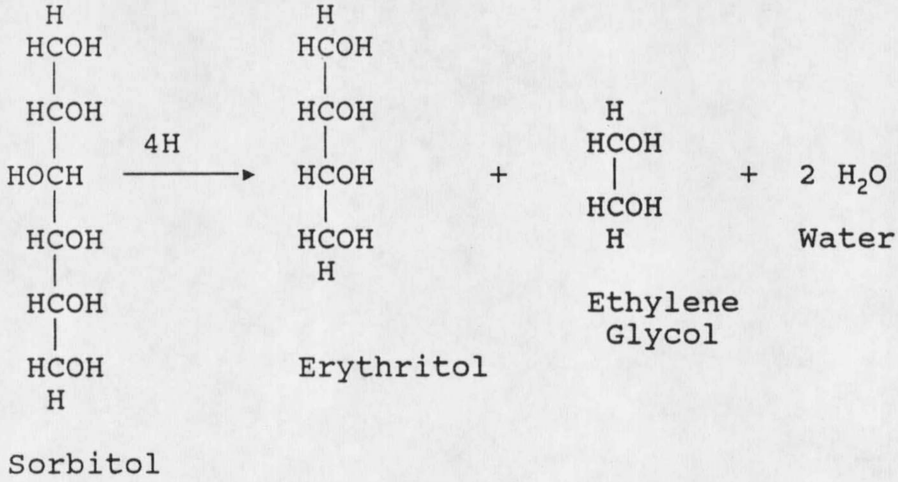


Figure 2 Formation of by-products.

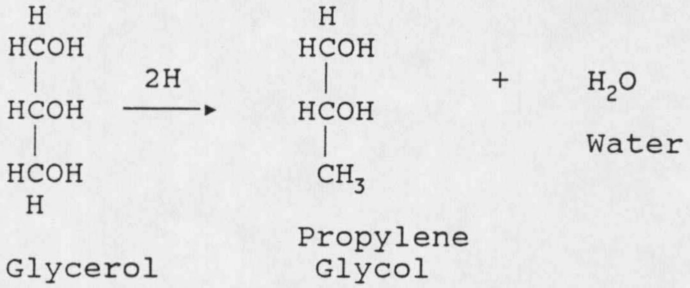


Figure 3 Glycerol conversion to propylene glycol.

Presently many industries have large quantities of sugars which could feasibly be converted to polyhydric alcohols. Sorbitol, a sweetener used in toothpaste, confections, and other foods is also used in the manufacturing of ascorbic acid, and as an industrial surfactant. Currently the market value of sorbitol is low enough to make its conversion to polyhydric alcohols economically viable. Since World War II, demand for glycerol has developed into other areas besides its historical use in the manufacturing of TNT. Today it is used extensively in pharmaceutical products, toiletries, and as a humectant in the tobacco and leather industries. Glycerol is also used as a feedstock for a growing list of polymers and resins. Ethylene glycol is used primarily as an anti-freeze and a solvent. Propylene glycol has uses as a nontoxic antifreeze, a solvent, and as an emulsifying agent in foods.

A chronological listing of the significant studies in the area of sorbitol hydrogenolysis starts with patents received by I.G. Farbenindustrie, A.-G. These patents claim the production of glycerol and propylene glycol by hydrogenolysis of sugars, starches, cellulose, or other materials with hydrogen in the pressure range of 70-100 atm, and a temperature in excess of 150 °C [3]. Lautenschlager et al., received a patent in 1932 for the hydrogenolysis of sugar in an aqueous media [4]. Larchar in 1934 claimed a process for the hydrogenolysis of sorbitol and dextrose with a nickel-chromium catalyst at a pressure of 160 atm and a temperature of 200 °C [5]. From 1934-1938 in three publications, Yosikawa reported using an iron-nickel catalyst in a pressure range of 40-150 atm, with a temperature range of 250-300 °C, for the hydrogenolysis of sugars to polyhydric alcohols [6,7,8].

The first large scale process was developed by I.G. Farbenindustrie, A.-G., which was followed by Lenth and DuPuis, who built a pilot plant to research this reaction and determine its economical feasibility [9]. In a batch type process, at 240 °C, and 1500 psi, sorbitol dissolved in a methanol-water solution was hydrocracked with a copper-aluminum oxide catalyst. The average yield was about 60 wt% of the sugar fed to the reactor. Their conclusion, based on a batch process without the use of co-catalysts, was that the hydrogenolysis of sugars was not economically feasible.

Clark used 1 wt% $Ca(OH)_2$ as a promoter with a catalyst which consisted of 50 wt% nickel on Kieselguhr clay support [10]. An aqueous feed in the range of 40-99 wt% sorbitol was charged to a stirred reactor along with the catalyst slurry. The operating conditions were in the following ranges, temperature 215-245°C, pressure 2000-5600 psi, and reaction time up to 6.7 hours. Kinetic data published by Clark showed that hydrogenolysis of sorbitol was first order with respect to sorbitol, except at high hydrogen partial pressures. Clark reported Arrenhius plots and an activation energy of 18,000 cal/mole for the hydrogenolysis of sorbitol.

During the mid 1960s Van Ling et al., investigated hydrogenolysis of sucrose using $CuO-CeO_2-SiO_2$ as the catalyst with $Ca(OH)_2$ and NaOH as a promoter [11,12]. The use of $Ca(OH)_2$ yielded a maximum combination of hydrogenation selectivity (HS) and cleavage percentage (CP); with the hydroxyl ions increasing the CP and the calcium ions varying the HS. Van Ling used HS and CP calculations to determine the combination of reaction parameters that yielded the maximum conversion of sorbitol to glycerol. Cleavage percentage was defined by Van Ling as the ratio of the hydrogenolysis products (glycerol, propylene glycol, ethylene glycol, and tetritol) over the total of all the components in the reactor effluent. Hydrogenation selectivity was defined as the ratio of glycerol produced to the total amount of glycerol and propylene glycol formed during the reaction. This gave an indication of the amount of glycerol that was converted to propylene glycol.

Chang et al., conducted a more extensive kinetic study of sorbitol hydrogenolysis in 1985 [13]. Using similar reaction conditions as Clark, they determined that the rate of sorbitol hydrogenolysis is first order with respect to sorbitol. They further determined that the rate was -0.8 order with respect to hydrogen partial pressure, and second order with respect to catalyst amount. The activation energies of sorbitol hydrogenolysis was 21,000 cal/mole. The activation energy for sorbitol hydrogenolysis determined by Clark and Chang agree reasonably well.

Although extensive work has been conducted for the batch hydrogenolysis, a more economical means of producing polyhydric alcohols with a continuous process needs to be developed. Hellwig, was able to produce glycerol and glycols from sorbitol in a single stage upflow catalytic ebullated bed reactor [14]. Her operating conditions were similar to those used by Clark with the addition of a 1.2 liquid hourly space velocity (LHSV). The catalyst was comprised of nickel on an alumina support. No promoter was used in her research. The product distribution was reported to be 50 wt% glycerol, 20 wt% propylene glycol and the rest as other by-products. No mention was made of once through conversion of sorbitol, nor catalyst deactivation.

Van Ling et. al., used two continuous stirred tank reactors (CSTR) in series to convert sucrose to glycerol [15]. A $CuO-CeO_2-SiO_2$ catalyst and a $Ca(OH)_2$ co-catalyst were used with sucrose dissolved in a methanol-water solution. The operating conditions used were consistent with the ones described above with a LHSV of 1. The overall conversion was lower than a batch process and a significant amount of by-product formation was reported. Based on the low conversion and low market demand for the by-products, the continuous production of polyhydric alcohols was considered not economically feasible. No mention of run time nor catalyst deactivation was made.

The most comprehensive research to date for the continuous production of polyhydric alcohols from sorbitol was conducted by Hydrocarbon Research Incorporated (HRI) [16]. The reaction condition consisted of a temperature in the range of 200-260 °C and a hydrogen partial pressure of 1200-2000 psi. A LHSV in the range of 1.5 to 3.0 was used with 25 wt% sorbitol in water. 60 wt% high activity nickel on Kieselguhr clay support was used to pack the fixed bed reactor. $Ca(OH)_2$ ranging from 0.1 wt% to 1.0 wt% on a sorbitol basis was used as a promoter. Optimization of overall glycerol production was investigated by varying the temperature, feed concentration of sorbitol in aqueous or water-methanol solution, catalyst size, and hydrogen partial pressure.

Significant work was also conducted with regard to catalyst regeneration. Regeneration was shown to extend catalyst life by Chao, of HRI [17]. This procedure was conducted after every 16 hours of operation. This consisted of washing the catalyst with a 25 wt% water and 75 wt% methanol solution, then treating the catalyst with hydrogen at a flow rate of 0.125 ft^3/min at atmospheric pressure and a temperature of 575 °F. Chao claimed that the deactivation was due to oxidation of the catalyst surface and that hydrogen treatment could reverse this effect [18].

Analysis of the two runs published by HRI, lasting 96 and 144 hours, conducted by McCandless, indicated that the catalyst would be completely and irreversibly deactivated despite regeneration after 200 hours of operation [19]. This irreversible catalyst deactivation was believed to be caused by leaching of metals under acidic reaction conditions. HRI believed the acidic conditions were due to the formation of gluconic acid [16], while a 1963 French paper believed it was due to the formation of lactic acid via the Cannizzaro reaction [20].

Despite this concern of acidic conditions, none of the available literature presents data on the pH of the process streams. HRI mentioned adding lime to try to keep the gluconic acid from leaching nickel out of the catalyst, but no data were collected on pH values [16]. Jacot-Guillarmod suggested using a resin to control the undesired Cannizzaro reaction and thus the acid formation [20].

Research conducted by Arena on the acidity problem culminated in two patents awarded to UOP, Inc., [21,22]. Arena determined that the catalyst support was hydrothermally instable because substantial amounts of silica and alumina were dissolved during hydrogenolysis. Arena also found that the active catalytic metal was being leached into the product. Alternate support material and active metal catalyst were developed, for example ruthenium composited on a titanited gamma-alumina, were developed and patented. Again no data were presented as to process stream pH values.

Although significant work has been conducted in the area of hydrogenolysis of sorbitol and other related sugars, substantial investigation is still required to develop a feasible continuous hydrogenolysis process. Areas of concern relate to an extension of production time and maintenance of a high conversion.

CHAPTER 2

RESEARCH OBJECTIVES

The objective of this research was to improve the reaction conditions for the continuous hydrogenolysis of sorbitol to polyhydric alcohols by extending catalyst life, and maintaining a high degree of conversion. The intent was to develop a continuous process as a viable alternate for the production of polyhydric alcohols. The inert packing above the catalyst section of the reactor and the pH of process streams were also studied to determine their contributions to the overall reaction, and/or catalyst deactivation.

To achieve the research objectives it was planned to:

1.) test commercially available catalysts which are reported or suspected to be suitable for this reaction,

2.) test various types of co-catalysts and monitor the pH of product streams,

3.) test different types of inert packing,

4.) and determine an optimum concentration of co-catalyst in the feed solution.

CHAPTER 3

EXPERIMENTAL

Outline of Research

Two stages of experimentation were involved in this research. The first stage consisted of screening commercially available catalysts to find a catalyst that maintained its activity and structural integrity. Experimentation in the second stage attempted to extend the reaction run times from less than 100 hours to more than 300 hours. Throughout both stages of experimentation the concentrations of co-catalyst were varied, and regeneration techniques were tested. In the second stage various types of co-catalyst, and different types of inert packing were tested using the catalyst selected from the first stage. Product stream pH data were collected in both stages in an effort to determine the relation between extent of conversion and type of co-catalyst used to the acidity of the product stream.

Screening of Commercial Catalysts

Catalysts composed of active nickel on an alumina support with a large percentage of silica, and with relatively low silica were tested. The catalysts with the weight percent

$Ca(OH)_2$ and all the experimental runs for screening commercial catalysts are listed in Table 1.

Table 1 Experimental runs for screening commercial catalysts.

Run Number	Catalyst	$Ca(OH)_2$ Conc., wt%
1	United Catalyst G49B	2
2	United Catalyst G49B	2
3	United Catalyst G49B	1
4	United Catalyst G49B	0.5
5	United Catalyst G49B (Crushed)	1
6	United Catalyst C46-8-03 1/16" E	1
7	UOP Inc. XPA-112-90	1

Extending Reaction Run Times

Once a suitable commercial catalyst was found in the first stage of the research, an extensive effort was made to extend the life of the catalyst. Experimental parameters included regeneration techniques, different types of co-catalyst in varying concentrations, and different types of inert packing.

Regeneration

The research conducted by Chao [17] suggested that catalyst activity could be maintained by frequent regeneration. Regeneration techniques using similar conditions as that reported by Chao were used in this study. The regeneration conditions used in this research are listed in Table 2. The experiments which deviated from conditions in Table 2 include a run which used a methanol solution to wash the catalyst after washing with water, a run which used 320 °C for regeneration, and two regeneration attempts utilized only the hydrogen treatment.

Table 2 Regeneration conditions.

Wash:		Hydrogen Treatment:	
Solution:	Water	Hydrogen flowrate:	50-200 SCCM
Pressure:	0-100 psig		1800 psig
Temperature:	100 °C		300 °C
Duration:	3 Hours		4-6.5 hours

Testing of Co-catalysts and Inert Packing

Three types of co-catalysts were studied and are summarized in Table 3. The concentrations are expressed as a percentage of the weight ratio of co-catalyst anion to sorbitol in the feed. $Ca(OH)_2$ was the co-catalyst used in the first stage of experimentation.

Table 4 lists the three types of inert packing used. Inert packing is needed to promote even flow distribution and preheat the feed to the reactor temperature. Table 5 lists the types of inert packing material and the type and concentrations of the co-catalysts tested in the second stage of experimentation.

Table 3 Co-catalysts added to sorbitol feed solution.

Type of Co-Catalyst	Concentration Range
$Ca(OH)_2$	0.1 W% - 2.0 W%
$Ba(OH)_2$	0.1 W% - 5.4 W%
NaOH	0.17 W% - 1.0 W%

Table 4 Inert packing material.

Size	Type	Source
¼" -8 Mesh	Tabular Alumina	Alcoa T-71
1/16"	Spherical Alumina	United Catalyst CS346
⅛"	Stainless "Fenske" Rings	M. R. Fenske Pennsylvania State University

Table 5 Summary of experimental runs for extending reaction run times.

Run #	Co-catalyst	Conc. wt%	Inert Packing
8	$Ba(OH)_2$	5.4	Alcoa T-71
9	$Ba(OH)_2$	0.5	Alcoa T-71
10	$Ba(OH)_2$	0.1	Alcoa T-71
11	$Ba(OH)_2$	0.3	UC CS346
12	$Ca(OH)_2$	0.1	UC CS346
	$Ca(OH)_2/NaOH$	0.1/0.17	
13	$Ca(OH)_2$	0.1	UC CS346
	No co-catalyst	---	
14	No co-catalyst	---	UC CS346
	$Ca(OH)_2$	0.1	
15	No co-catalyst	---	"Fenske" Rings
	$Ca(OH)_2$	0.1	
16	No co-catalyst	---	Alcoa T-71
	$Ca(OH)_2$	0.1	
17	NaOH	1.0	Alcoa T-71
	$NaOH/Ca(OH)_2$	1.0/0.1	
18	$Ca(OH)_2$	0.1	Alcoa T-71
	$NaOH/Ca(OH)_2$	0.17/0.1	
	NaOH	1.0	

Operating Conditions

Operating conditions were similar to those found in the literature [16]. These conditions are summarized in Table 6.

Hydrogenolysis Equipment

The hydrogenolysis of sorbitol was conducted in a trickle bed reactor made of a 24" long, ½" I.D. Schedule 40 type 304 stainless steel pipe. Figure 4 is a diagram of the experimental apparatus. The reactor inlet was connected to a high pressure stainless steel pipe cross. The steel cross contained the mounting for a thermowell that ran axially down the reactor center and inlet valves for sorbitol feed and hydrogen. A Duragauge pressure gauge, attached to the pipe cross was used to measure the pressure at the top of the reactor. The reactor assembly was placed in 3" O.D. aluminum cylindrical block, drilled with a 0.8125" hole on the center axis. This block filled the void space between the reactor pipe and the inside wall of the Lindberg Furnace and helped to distribute heat uniformly to the reactor. The furnace was maintained at the desired temperature with an OMEGA CN382TC temperature controller. A Chromel-Alumel thermocouple placed on the outside of the reactor and its aluminum block was used by the temperature controller to monitor and control the furnace temperature. This thermocouple was placed at the center of catalyst bed of the reactor. Three additional Chromel-Alumel thermocouples were placed in a thermowell to

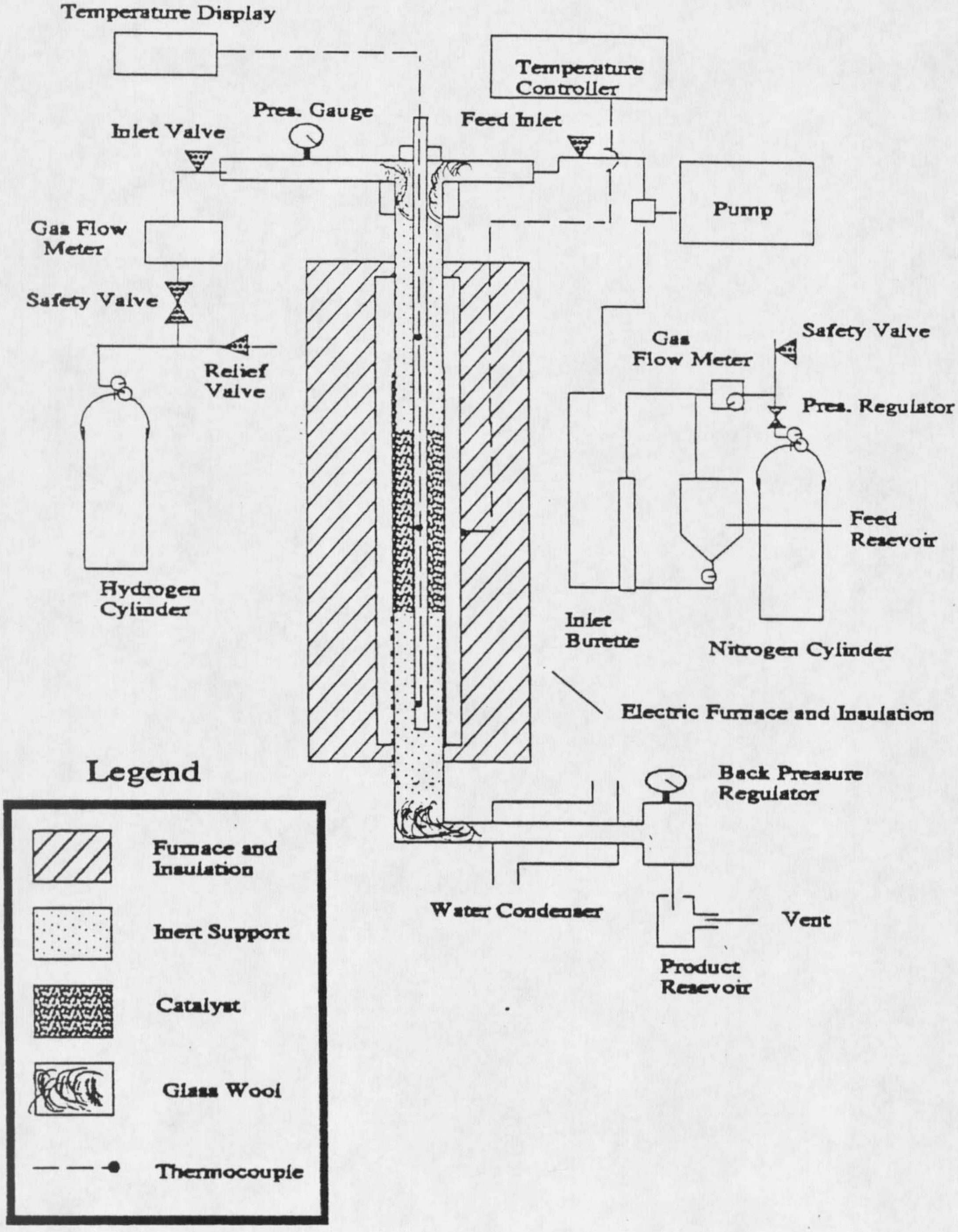


Figure 4 Experimental apparatus.

Table 6 Operating conditions for all experimental runs.

Nominal Reactor Temperature, °C	250 ± 5
Feed Temperature, °C	35 ± 5
Pressure, psig	1780 ± 50
Hydrogen Flow Rate, SCCM	600 ± 50
LHSV	2

monitor the temperatures inside the reactor at three levels, near the top, in the center of the catalyst bed, and near the bottom. The sorbitol feed solution in a glass reservoir was pumped to the top of the reactor with a Milton Roy model MR-1-23-49SM packed piston pump, through ⅛" stainless steel tubing. The pump was equipped with a manually controlled micrometer adjustment for feed rate control. Between the feed reservoir and the pump was an in-line burette for flow rate measurement, and an in-line glass fiber filter to remove insoluble material.

Technical grade nitrogen fed through a pressure regulator, a safety check valve, ⅛" stainless steel tubing, a flowmeter, and valve maintained an inert atmosphere above the feed reservoir.

Technical grade hydrogen was fed through a pressure regulator, a safety check valve, ⅛" stainless steel tubing, a flowmeter, and valve to the reactor head.

At the reactor exit a liquid-gas separation unit was attached. This unit consisted of a water cooled heat exchanger to condense the product, a Grove "Mity Mite" back pressure regulator which maintained the reactor pressure while allowing the products to discharge, a pressure gauge to monitor the back pressure regulator, and a liquid-gas separator. The gases were vented and the liquid was collected in a reservoir.

Procedure

Experimental runs

The reactor was thoroughly cleaned before each run. The reactor was then connected to the reactor head. Loading, from top to bottom, the reactor with glass wool, inert packing, and catalyst was done in the following manner: First the thermowell was centered in the reactor. The top inch of the reactor and void spaces in the head were packed with glass wool, followed with approximately 30 cc of inert packing. 30 cc of catalyst was then added, after which the remaining space was filled with inert packing to within a ½" of the bottom of the pipe. The last ½" of pipe and void space in the elbow was packed with glass wool. All threaded ends of the pipe were wrapped with Teflon tape and tightened to prevent leakage.

The reactor assembly was then placed in the heating unit and connected to the separator and pressure gauge. The back pressure regulator was then set to the desired pressure, after which the hydrogen line was connected.

With the sorbitol inlet valve shut, the system was slowly pressurized to the desired level. All connections were checked for leaks with "snoop", liquid leak detector, and any leaks fixed before proceeding.

Once the reactor was assembled, the heating unit was turned on and maintained for 24 hours with hydrogen flowing through the system. This technique was used to activate the nickel catalyst under a reducing atmosphere. The temperature controller maintained the temperature at 250 °C during the activation process.

After the activation-reduction of the catalyst, the feed reservoir was filled with the sorbitol solution. When either $Ca(OH)_2$ or $Ba(OH)_2$ was added to the sorbitol solution, a nitrogen atmosphere was maintained above the solution in the feed reservoir. This was required because these co-catalysts can react with atmospheric CO_2. Any precipitate that may have formed despite the inert atmosphere was trapped by the in-line glass fiber filter.

With the ⅛" stainless steel tubing disconnected from the reactor head, the pump was turned on to force the feed solution into a beaker. This technique purged the lines of air pockets. After purging, the pump was turned off and the prefilled feed line was connected to the inlet port of the reactor head. With the inlet valve open, the pump was turned on initiating the start of a run. To monitor the flow rate of the sorbitol solution, the feed reservoir valve was shut and the time for a known amount of liquid to be pumped from an in-line burette was timed.

The feed flow rate was continually monitored and adjusted during the first few hours of operation until steady flow rates were attained.

Samples were taken by redirecting the liquid product into a sampling beaker. Sample times varied but ranged from 2-24 hours. Each sample was collected in a 4 dram sample vial. The pH of each sample was measured using an Altex Φ30 pH meter. Other data collected at the same time included, temperature readings of the three thermocouples, system pressure, feed flow rate, and hydrogen flow rate. To prevent plugging, the in-line filter between the reservoir and the pump required constant checking to maintain proper feed flow rates.

At the completion of a run, the pump was turned off and the sorbitol inlet valve was shut. The temperature controller was set to allow the reactor to cool to ambient temperature. While the reactor system was cooling, hydrogen was passed through the system to dry the catalyst and the inert packing.

Analytical

A Shimadzu high performance liquid chromatography (HPLC) unit was used for quantitative analysis. Corrected area normalization was used to correlate the output of the refractive index detector (RID) to known standards. A detailed description of operating procedures for the HPLC is given in the appendix. For qualitative confirmation of product components, a Shimadzu Gas Chromatography 14-A (GC) with a Flame Ionization Detector (FID) was used. The GC used an Alltech 25M x 0.53MM Bonded FSOT SuperoxII (Carbowax 20M, DB-Wax) column. The components in the product stream samples were determined by comparing the retention times of the components peaks from both the HPLC and GC to the retention times of peaks in standards.

CHAPTER 4

RESULTS AND DISCUSSION

The main concern in this research was maintaining the reaction for extended periods of time. The two most significant problems were catalyst deactivation and reactor plug-up. Several theories have been found in the literature in regard to catalyst deactivation [16,19,20,21]. Reactor bed plug up was a new problem encountered in this research and not discussed in the literature.

Results of Screening Commercial Catalysts

Initial runs encountered significant problems with catalyst deactivation and reactor bed plug-up. The first two experimental reaction runs, listed in Table 8, resulted in catalyst bed plug-up. The frequent bed plug-ups encountered with relatively high concentrations of co-catalyst seemed to be a problem only in this research, as other experiments utilizing co-catalyst did not encounter bed plug-ups [10,11,12,15]. When other types of continuous reactors, such as CSTR or stirred batch reactors were used, plug-up due to highly insoluble co-catalysts was not a problem. This is due to the different mechanical nature of these reactors. However, HRI used a reactor system very similar to the system in this study with a relatively high concentration of co-catalyst without plugging their reactors [16]. It is speculated that this was accomplished with frequent regeneration and washing.

Table 7 Experimental runs for testing commercial catalyst.

Run Number	Catalyst	$Ca(OH)_2$ Conc., wt%	Length of Run, Hrs	Result
1	UC G49B	2	16.3	Plug-up
2	UC G49B	2	12.5	Plug-up
3	UC G49B	1	43.25	Low Conversion
4	UC G49B	0.5	26.5	Low Conversion
5	UC G49B (Crushed)	1	20	Low Conversion
6	UC C46	1	85	Moderate Conversion
7	UOP XPA	1	28	Low Conversion

Since the objective of this research was to find a catalyst and co-catalyst system which maintained its activity for long periods of time, shut downs due to reactor bed plugging had to be avoided. Therefore in an effort to overcome the problem of bed plug-up, lower concentrations of co-catalyst in the feed were tried. Run number 3, listed in Table 8, was operated for 16 hours without the use of a co-catalyst. After 16 hours of operation 1.0 wt% $Ca(OH)_2$ was added, followed by two regeneration cycles at 22 hours and

36.25 hours. This was done in an attempt to increase overall conversion. Despite these efforts conversion for United Catalysts UC G49B remained low-to-moderate based on GC analysis.

Run number 4, with united catalyst G49B and 0.5 wt% $Ca(OH)_2$ had a high-to-moderate initial conversion which dropped off very rapidly. The run was terminated after 26.5 hours because of low conversion.

In an effort to increase the surface area of the catalyst and thus activity, crushed UC G49B catalyst (-8+12 Mesh) was used with 1.0 wt% $Ca(OH)_2$ in run number 5. The conversion was moderate to low and regeneration after 17 hours did not appear to increase the conversion.

Archer Daniel Midland conducted metal analysis of samples from this product stream in an effort to detect nickel, which would signify that the acidic conditions were leaching the nickel out of the catalyst. The analysis did not detect nickel in the product stream samples. However, in a personal communication it was reported that a significant amount of silica was present in samples of the product stream when United Catalyst G49B was used [23]. The catalyst used, United Catalyst G49B, had a high SiO_2 content of 40 wt%. This could explain the decline in activity as the catalyst would lose its structural integrity and high metal surface area. This was also reported by Arena, under the acidic hydrogenolysis conditions [21,22]. Therefore a switch was made to catalysts which were reported to be able to withstand the acidic conditions, such as UOP Inc, XPA-112-90, or a catalyst with low silica content.

UC C46-8-03 1/16" E which has a silica content of 3±1 wt% was used a run number 6. 1.0 wt% $Ca(OH)_2$ was added to the sorbitol feed stream as a co-catalyst. The conversion from this run remained relatively high, but did decline with time. This run ended after 85 hours, while the overall conversion of the sorbitol fed to the reactor was still approximately 46 percent (46 %).

Run number 7 lasted only 28 hours with UOP Inc., XPA-112-90 catalyst. The conversion was poor and quickly declined.

Based on the low to moderate conversion, the leaching of silica from the Kielseguhur support, and the subsequent lose of activity, UC G49B was not a suitable commercial catalyst. UOP XPA-112-90 had such poor conversion and rapid deactivation that it proved to be unsuitable. United catalyst C46-8-03 was chosen for further testing due to low silica content in the support material and high to moderate conversion obtained in run number 7.

Results of Extending Reaction Run Times

After selecting the catalyst, the following parameters were tested in an effort to extend the length of reaction times; regeneration technique, type and concentration of co-catalyst, and type of inert packing above the catalyst section of the reactor. For all experiments data on the pH of the process stream were collected in an effort to determine its effect on conversion and catalyst deactivation.

Regeneration

Catalyst regeneration was extensively tried in the first experimental stage, as it was believed that regeneration was required to maintain high conversion. However, regeneration techniques did not appear to restore activity to catalyst that had deactivated.

reg-
not useful
to restore
activity
of catalyst

Once lower concentrations of co-catalyst were used in the second stage of experimentation, regeneration failed to reactivate the catalyst. Near the conclusion of run number 10, an attempt was made to regenerate the catalyst after 435.5 hours service. Since bed plug-up was not a problem for this run, washing the catalyst was considered unnecessary. Thus the regeneration utilized only the hydrogen treatment listed in Table 3. A sample taken 14.5 hours after regeneration showed no improvement in the overall sorbitol conversion.

The last attempt to improve conversion via regeneration was conducted in run number 12. This run used 0.1 wt% $Ca(OH)_2$ as the co-catalyst. After a run time of 246.5 hours, regeneration was attempted utilizing only the hydrogen treatment at a temperature of 300 °C. A sample collected 4 hours after regeneration showed no improvement in conversion. Hydrogen treatment was attempted after 291.5 hours of operation with a hydrogen treatment temperature of 320 °C. Again no improvement in conversion was observed.

Since these attempts did not use a wash cycle in the regeneration but only the hydrogen treatment, this author speculates that the regeneration conducted by HRI resulted in an increase of conversion because of the wash cycle. A possible explanation could be that the high concentration of co-catalyst began to plug the reactor bed and occupy active sites on the catalyst. HRI's frequent wash cycles would then prevent catalyst bed plug-up and re-expose active sites in the catalyst bed. A slight increase in conversion of sorbitol would be seen but the overall conversion would still decrease. F.P. McCandless in his analysis of HRI data, showed that despite repeated regeneration the overall conversion would decrease and that the catalyst would irreversibly deactivate [19]. However, this was not the scope of this research and no attempt was made to confirm these speculations. With the success of extending the reaction run times without regeneration to more than 200 hours, regeneration was no longer considered an important parameter in this research.

Co-Catalyst, Inert Packing, and Product Stream pH

The use of $Ca(OH)_2$ was extensively reported in literature, therefore initial efforts focused on its use as a co-catalyst. A significant problem with $Ca(OH)_2$ is that its solubility decreases with increasing temperature [24]. This could explain why even low concentrations of $Ca(OH)_2$ in the hot reactor would eventually plug-up the catalyst bed. In an attempt to increase the solubility of the co-catalyst in the feed solution, the co-catalyst was switch to $Ba(OH)_2$, which has a higher solubility than $Ca(OH)_2$ and increases with higher temperatures [25].

Run number 8, with 5.4 wt% $Ba(OH)_2$ showed a very high degree of sorbitol conversion, however after only 36.5 hours of operation the catalyst bed showed signs of plugging. The final conversion was still 80 %, with the majority of the product being propylene glycol. A white precipitate was noticed in the feed reservoir. Further investigation led to the discovery that the $Ba(OH)_2$ was reacting with atmospheric CO_2 and forming insoluble $BaCO_3$. With the addition of an inert atmosphere and an in-line filter to the experimental apparatus, this difficulty was resolved.

The removal of precipitate from the feed and a lower concentration of 0.5 wt% $Ba(OH)_2$ in the feed led to the first run of significant duration. Figure 5 and 6 show the conversion of sorbitol and the composition of the product stream on a sorbitol free basis versus time, respectively for run number 9.

This run lasted for 190 hours before mechanical problems with the thermowell forced a shut down. The overall conversion at the end of the run was approximately 40 %. The overall conversion was increasing at the time of shut down as shown in Figure 5. Approximately equal amounts of glycerol and propylene glycol were formed during this run as shown in Figure 6. Figure 7 shows how the product stream pH remained fairly constant throughout the run.

Run number 10 with 0.1 wt% $Ba(OH)_2$ had the longest run time. The goal was to operate the reactor for more than 300 hours, while still maintaining reasonable conversion. After 460 hours the conversion was still 23% as shown in Figure 8. The product distribution had equal amounts of glycerol and propylene glycol as shown in Figure 9. Figure 10 shows how the product streams pH decreased with time. Figures 8 and 10 show a decrease in conversion and a decrease in the product stream pH.

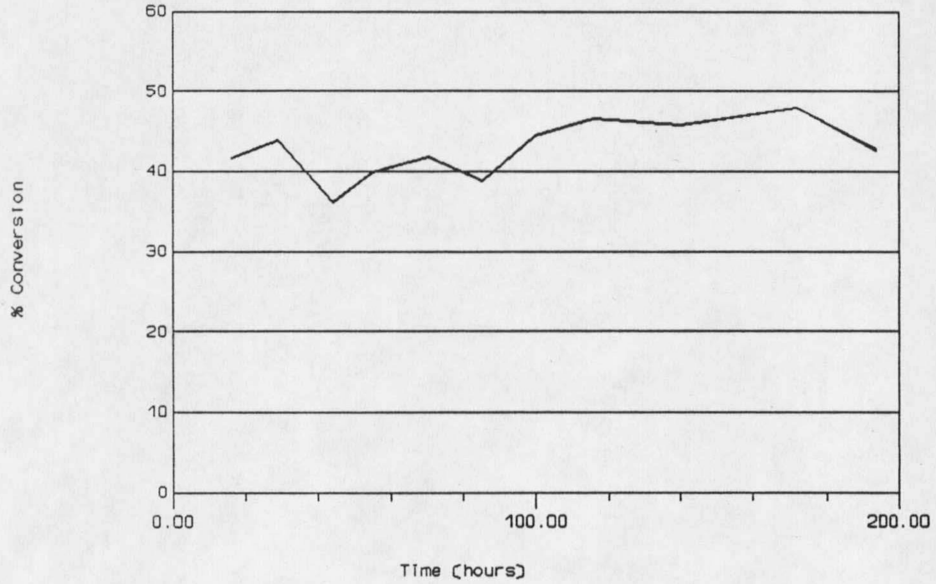


Figure 5 Conversion of sorbitol versus time for run #9, 0.5 wt% $Ba(OH)_2$, Alcoa T-71.

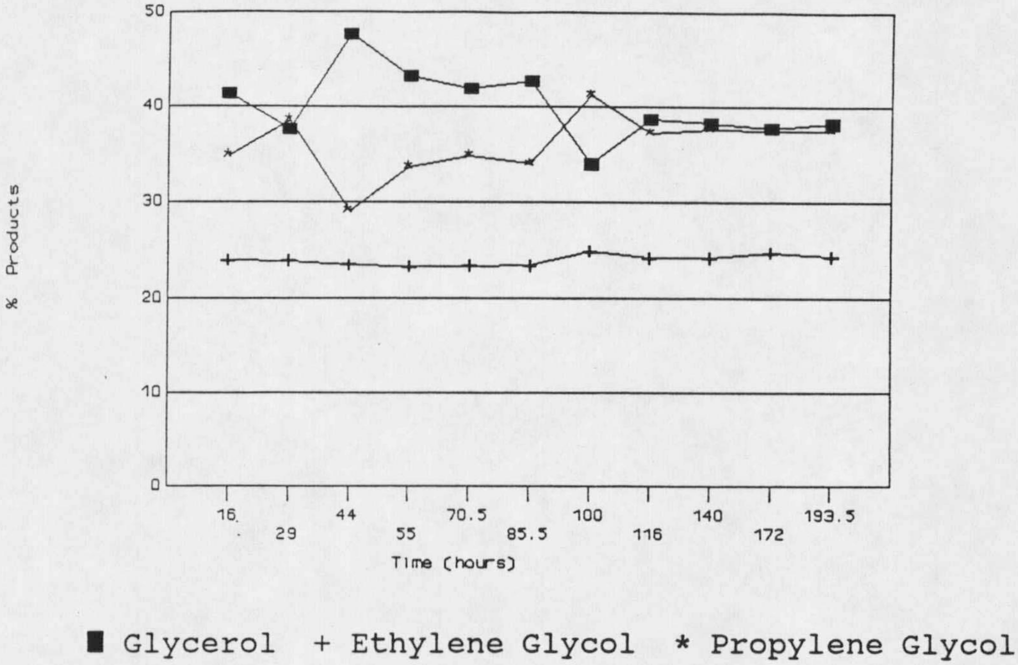


Figure 6 Product distribution versus time on a sorbitol free basis for run #9, 0.5 wt% $Ba(OH)_2$, Alcoa T-71.

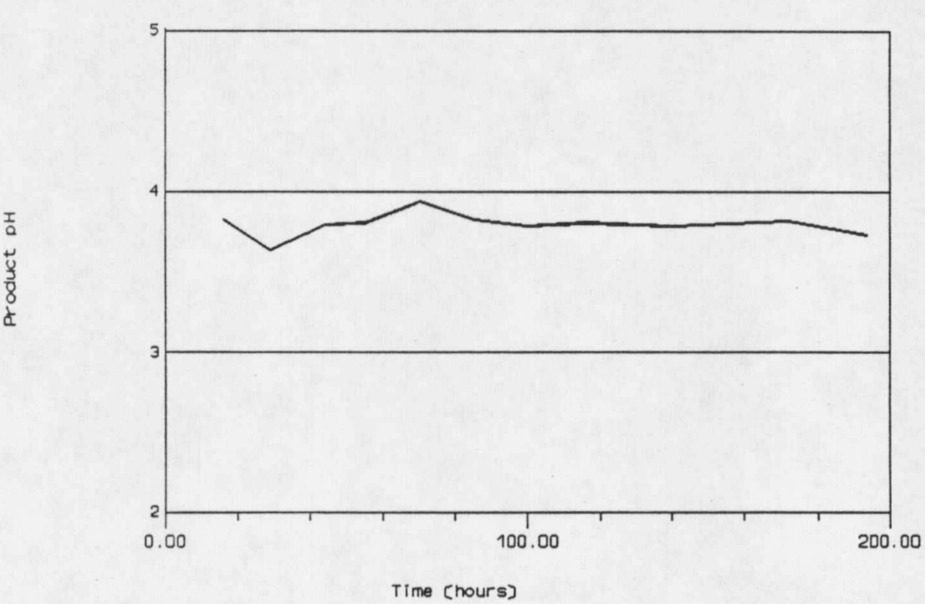


Figure 7 Product stream pH versus time for run #9, 0.5 wt% $Ba(OH)_2$, Alcoa T-71.

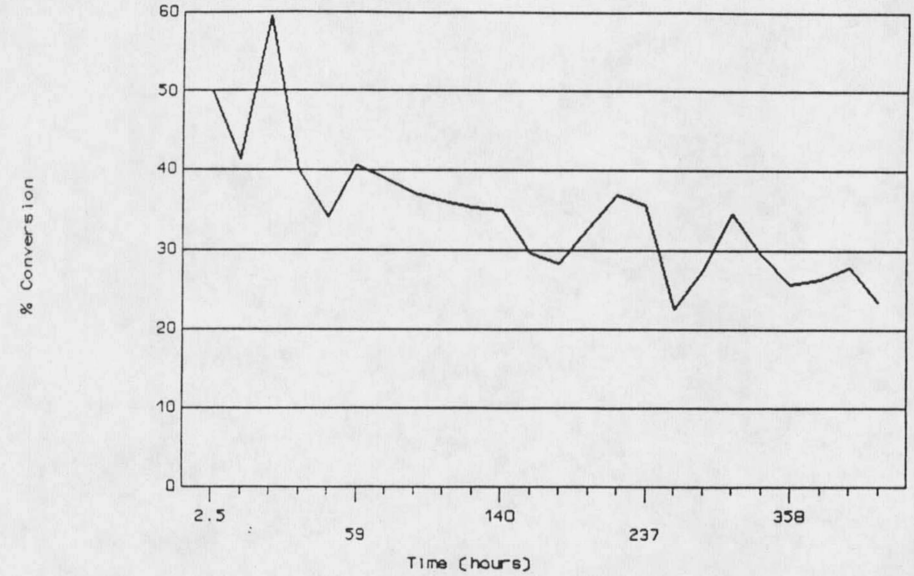
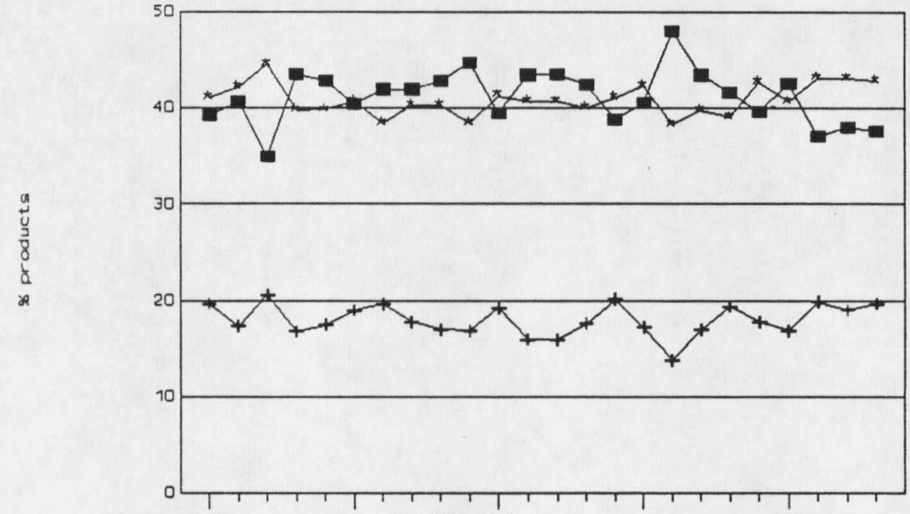


Figure 8 Conversion of sorbitol versus time for run #10, 0.1 wt% $Ba(OH)_2$, Alcoa T-71.



■ Glycerol + Ethylene Glycol * Propylene Glycol

Figure 9 Production distribution versus time on a sorbitol free basis for run #10, 0.1 wt% $Ba(OH)_2$, Alcoa T-71.

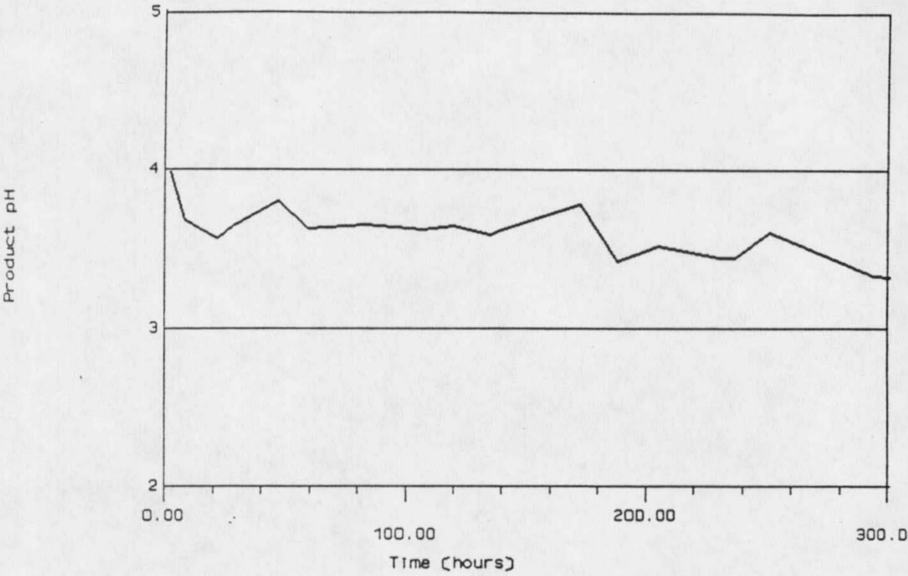


Figure 10 Product stream pH versus time for run #10, 0.1 wt% $Ba(OH)_2$, Alcoa T-71.

Run number 11 was the last run using $Ba(OH)_2$. The co-catalyst concentration was 0.3 wt%. The total run time was 192.5 hours. The conversion at the end of this run was still approximately 27 % as shown in Figure 11. Figure 12 initially shows the predominate component was propylene glycol and later glycerol. Figure 13 shows a decreasing pH while the conversion was decreasing.

Because of the toxicity of $Ba(OH)_2$, subsequent work was conducted with $Ca(OH)_2$ and NaOH. Since initial attempts with $Ca(OH)_2$ as the co-catalyst used a concentration greater than 0.5 wt%, 0.1 wt% $Ca(OH)_2$ was used in run 12. Figure 14 shows how the conversion changed with time. Once the conversion appeared to be dropping off at 319 hours, NaOH was added in a three to one molar ratio. The first and only sample collected

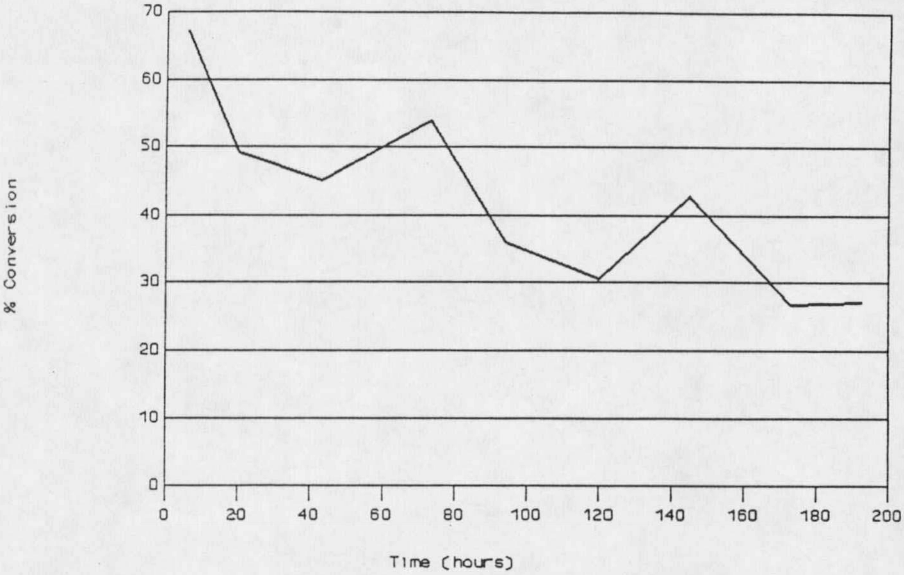
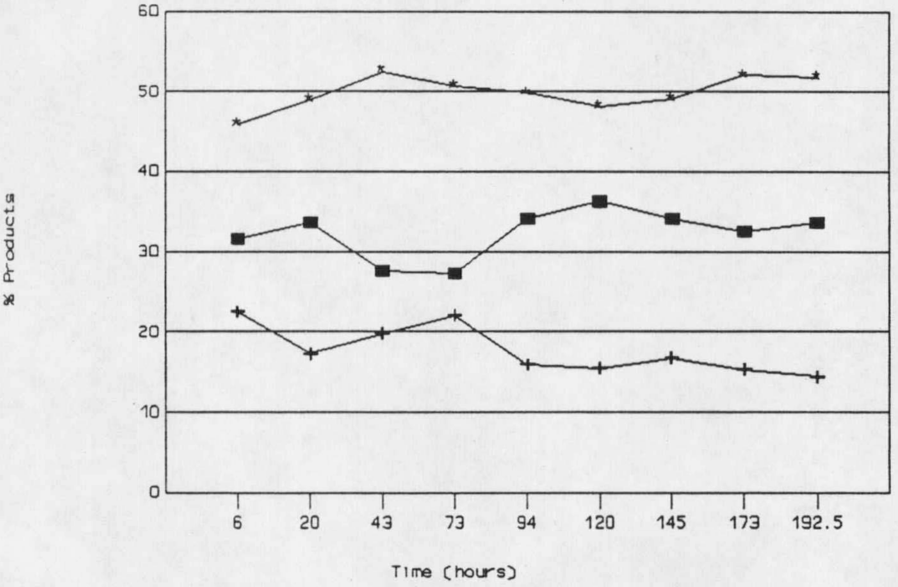


Figure 11 Conversion of sorbitol versus time for run #11, 0.3 wt% $Ba(OH)_2$, UC CS346.



■ Glycerol + Ethylene Glycol * Propylene Glycol

Figure 12 Product distribution versus time on a sorbitol free basis for run #11, 0.3 wt% $Ba(OH)_2$, UC CS346.

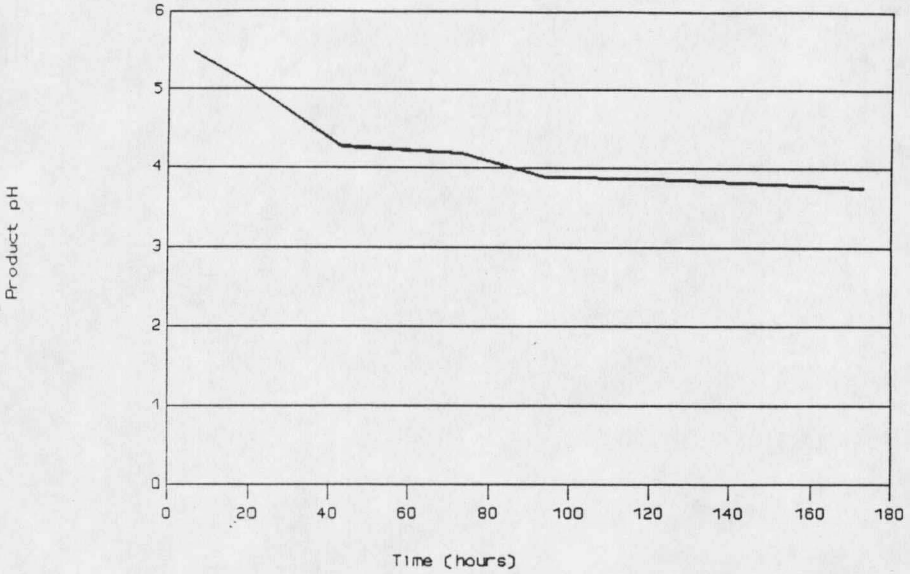


Figure 13 Product stream pH versus time for run #11, 0.3 wt% $Ba(OH)_2$, UC CS346.

after the feed change indicated a very slight increase in the overall conversion. However, the run was shut down before sufficient evidence could be collected to confirm this possibility. Figure 15 shows how the product distribution on a sorbitol free basis started out with nearly equal proportions of glycerol and propylene glycol. But, as the run progressed the amount of propylene glycol increased, while the amount of glycerol decreased. As anticipated the pH of the product stream changed when the NaOH was added, as shown in Figure 16. Before the NaOH was added the pH was decreasing gradually with time while the conversion was decreasing.

Run number 13 attempted to duplicate run number 12, with the exception of switching the feed from 0.1 wt% $Ca(OH)_2$ to a feed with no co-catalyst. Figure 17 shows the change in the

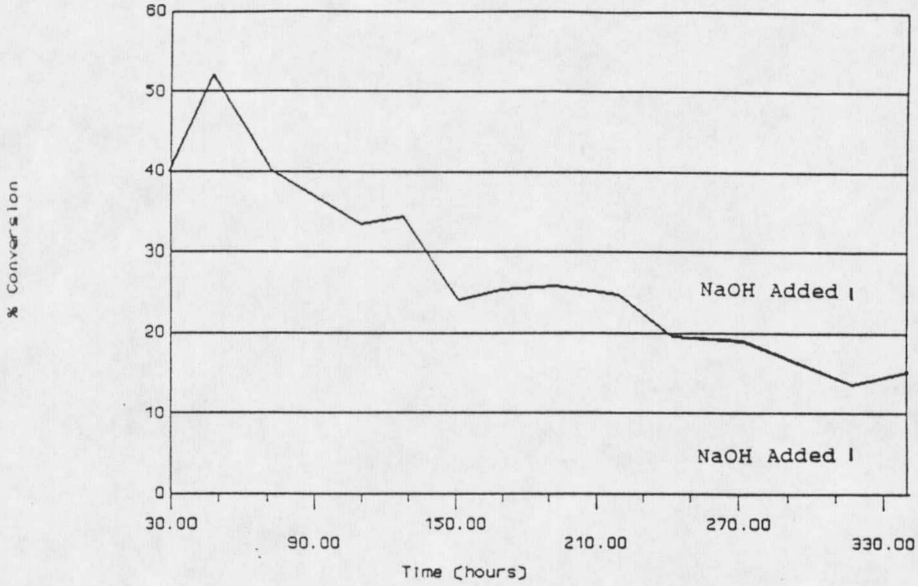


Figure 14 Conversion of sorbitol versus time for run #12, 0.1 wt% $Ca(OH)_2$ - 0.17 wt% NaOH/ 0.1 wt% $Ca(OH)_2$, UC CS346.

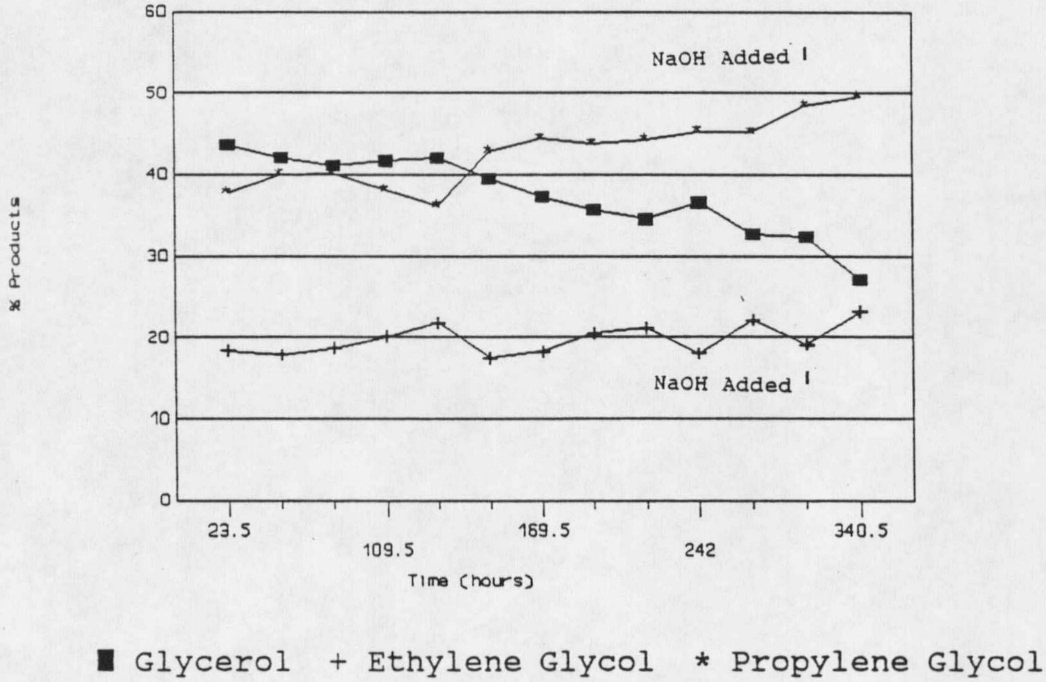


Figure 15 Product distribution versus time on a sorbitol free basis for run #12, Ca(OH)2 - NaOH/$Ca(OH)_2$, UC CS346.

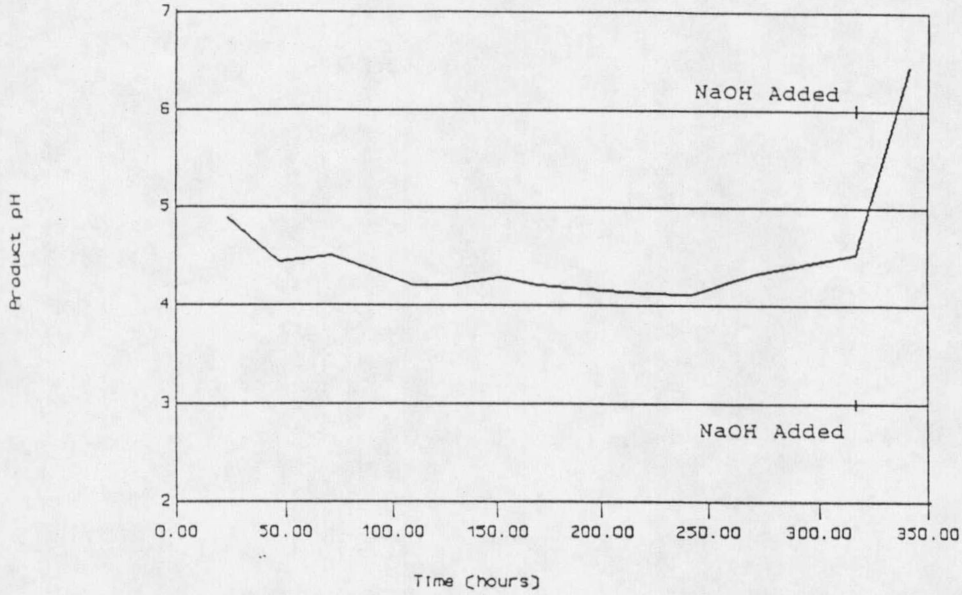


Figure 16 Product stream pH versus time for run #12, 0.1 wt% $Ca(OH)_2$ - 0.17 wt% NaOH/ 0.1 wt% $Ca(OH)_2$, UC CS346.

conversion of sorbitol versus time which resulted in a conversion of approximately 17 % at termination. Figure 18 shows the product distribution versus time with the predominate components being glycerol and propylene glycol. The feed switch was made after 246 hours, but no apparent change in the conversion was observed. However, the product distribution shifted towards a greater percentage of glycerol. Figure 19 shows the decline in the product stream pH with time.

Because no apparent change in sorbitol conversion was observed when the feed was switched in run number 13, run number 14 used no co-catalyst initially and then after 255.5 hours, 0.1 wt% $Ca(OH)_2$ was added to the feed solution. The

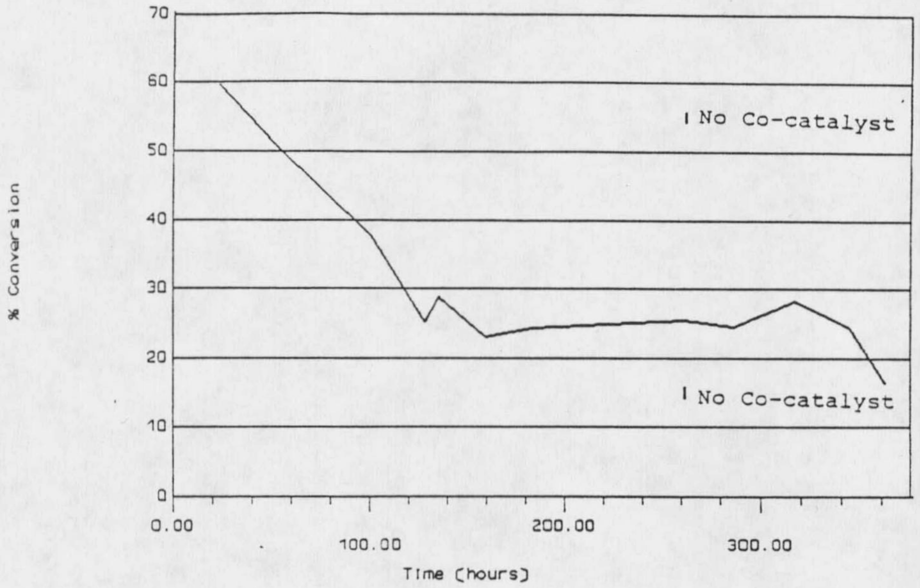


Figure 17 Conversion of sorbitol versus time for run #13, 0.1 wt% $Ca(OH)_2$ - No co-catalyst, UC CS346.

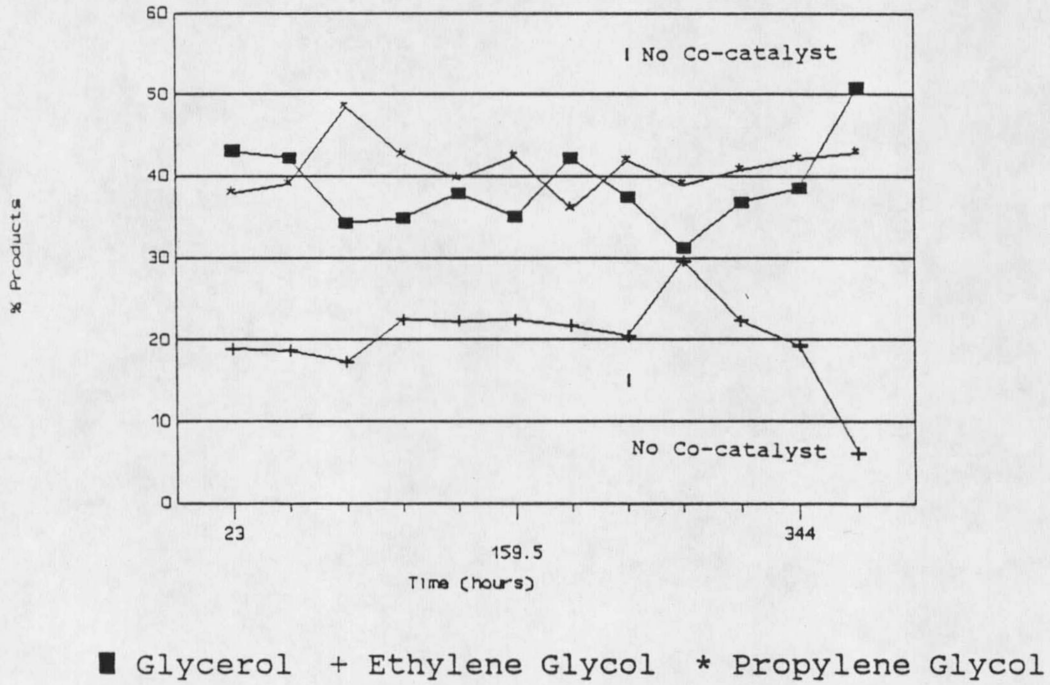


Figure 18 Product distribution versus time on a sorbitol free basis for run #13, 0.1 wt% $Ca(OH)_2$ - No co-catalyst, UC CS346.

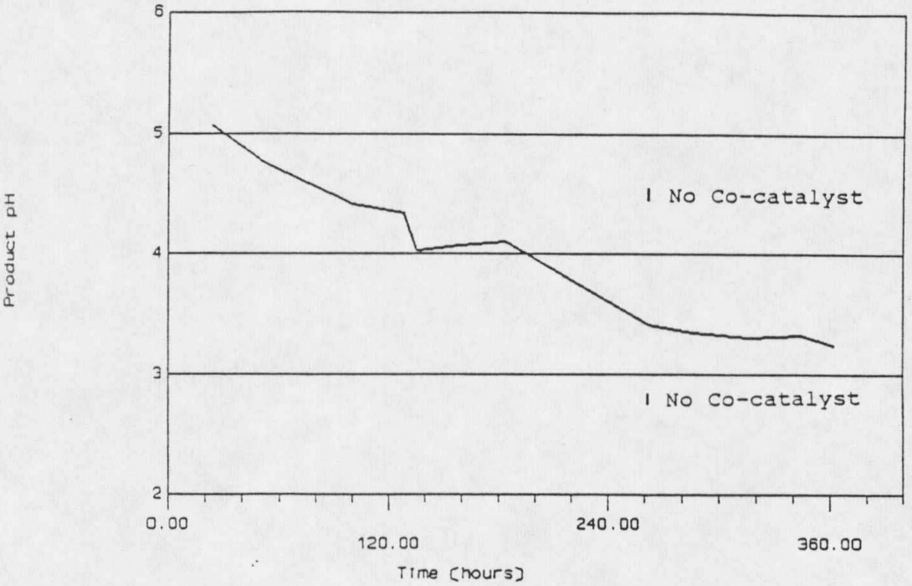


Figure 19 Product stream pH versus time for run #13, 0.1 wt% $Ca(OH)_2$ - No co-catalyst, UC CS346.

run lasted 320.5 hours, as shown in Figure 20. At run termination the conversion was still about 35 %. No apparent change was observed in the overall conversion when the co-catalyst was changed at 255 hours. But, the product distribution changed as shown in Figure 21. The change in co-catalyst increased the proportion of ethylene glycol and lowered the proportion of glycerol and propylene glycol. The pH of the product increased when the feed was switched, which is shown in Figure 22.

In order to study the effect of the inert packing above the catalyst section of the reactor, the packing was changed to stainless steel "Fenske" rings, while the type and concentration of the co-catalyst remained the same. The

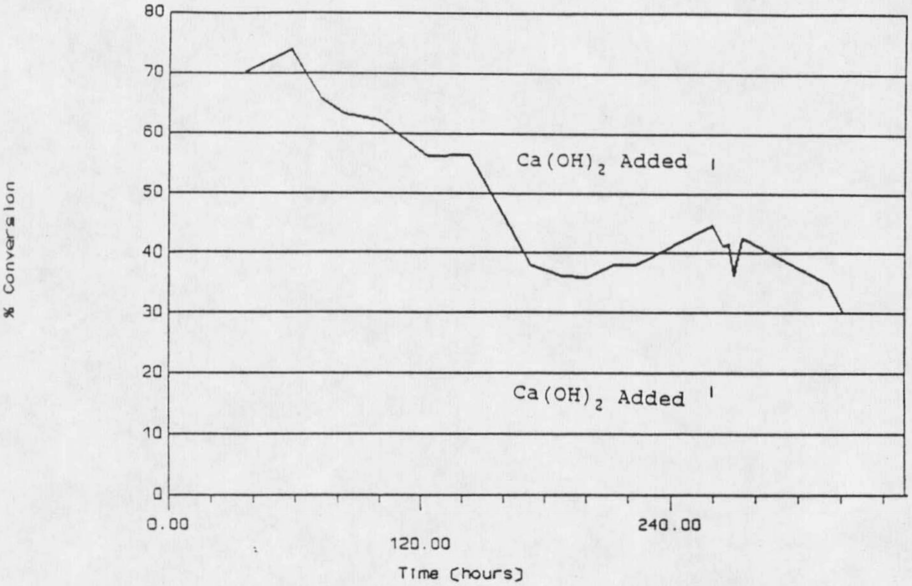
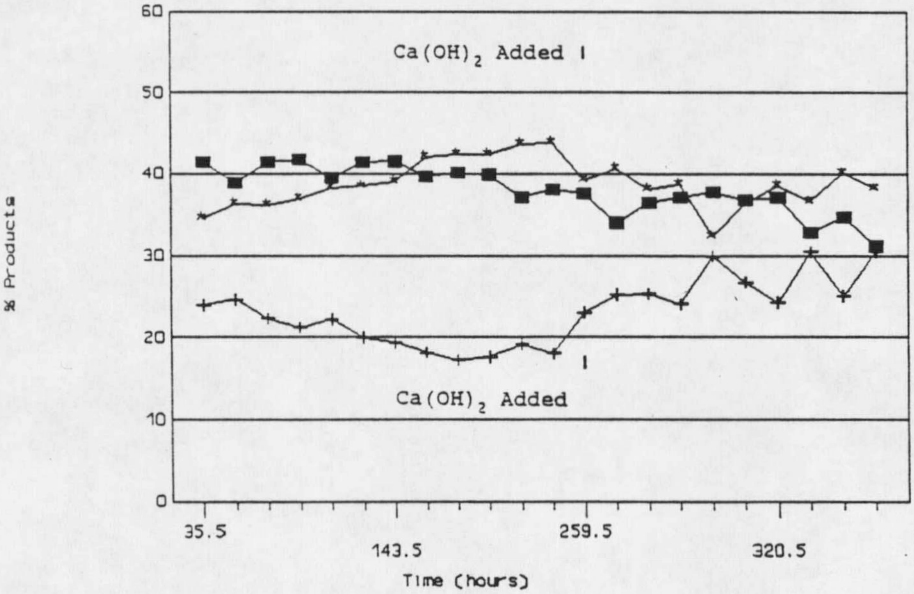


Figure 20 Conversion of sorbitol versus time for run #14, No co-catalyst - 0.1 wt% Ca(OH)$_2$, UC CS346.



■ Glycerol + Ethylene Glycol * Propylene Glycol

Figure 21 Product distribution versus time on a sorbitol free basis for run #14, No co-catalyst - Ca(OH)$_2$, UC CS346.

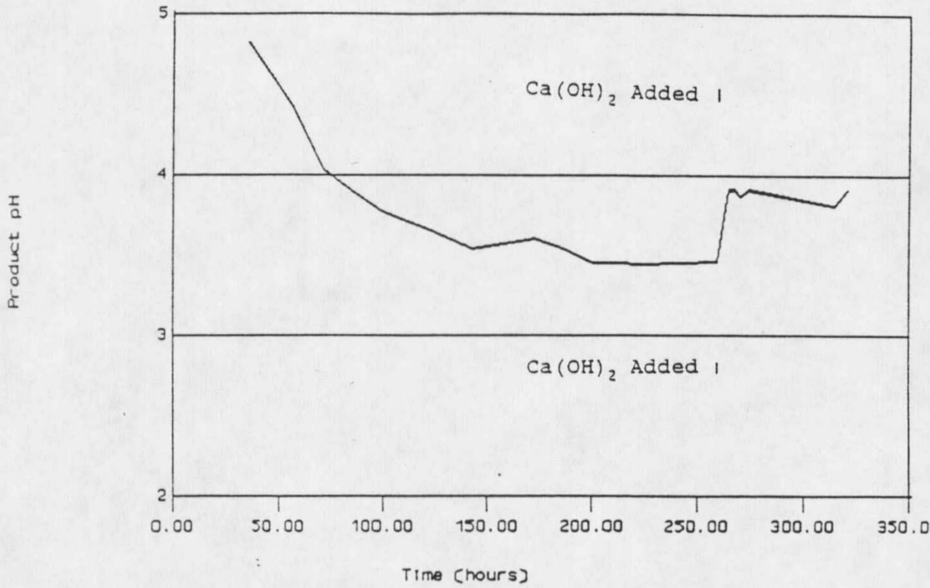


Figure 22 Product stream pH versus time for run #14, No co-catalyst - 0.1 wt% $Ca(OH)_2$, UC CS346.

conversion of sorbitol versus time for the run number 15 is shown in Figure 23. A significant shift in the product distribution toward more propylene glycol can be seen in Figure 24. Figure 25 shows the product stream pH versus time. The type of co-catalyst in the feed was changed after 151.5 hours which can be seen in the change in pH value. The total run time was 188.5 hours at which time the reactor was shut down and cleaned. While cleaning the reactor, crystalline formations of sorbitol were observed on the "Fenske" rings, which could possibly lead to problems with catalyst bed fouling.

Although the Alcoa T-71 inert packing had been previously used, another run was made with this packing with similar conditions as runs 14 and 15. Run number 16 only lasted 104.3

hours, so no change in the co-catalyst was made. The conversion of sorbitol and the product distribution versus time are shown in Figures 26 and 27 respectively. The predominate product was propylene glycol. The pH value quickly decreased to around 3.5 and then decreased gradually as shown in Figure 28. For run number 16 there is a corresponding decrease in pH of the product stream with a decrease in the sorbitol conversion.

Run number 17 was conducted to test NaOH as a co-catalyst. The conversion of sorbitol was very high as shown in Figure 29. The conversion was 94 % after 142.5 hours but, dropped rapidly when 0.1 wt% $Ca(OH)_2$ was added to the feed solution. The product stream also changed from a clear liquid

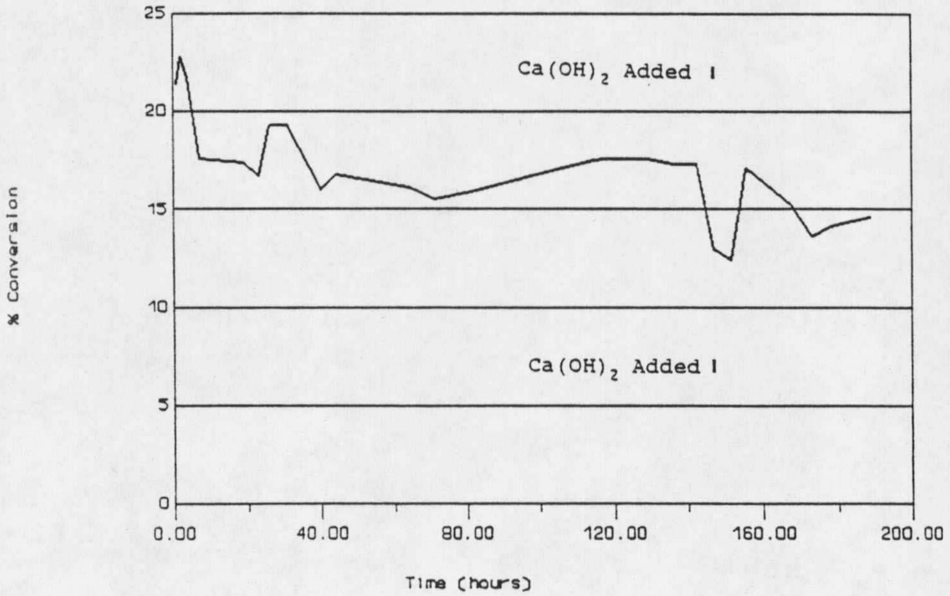
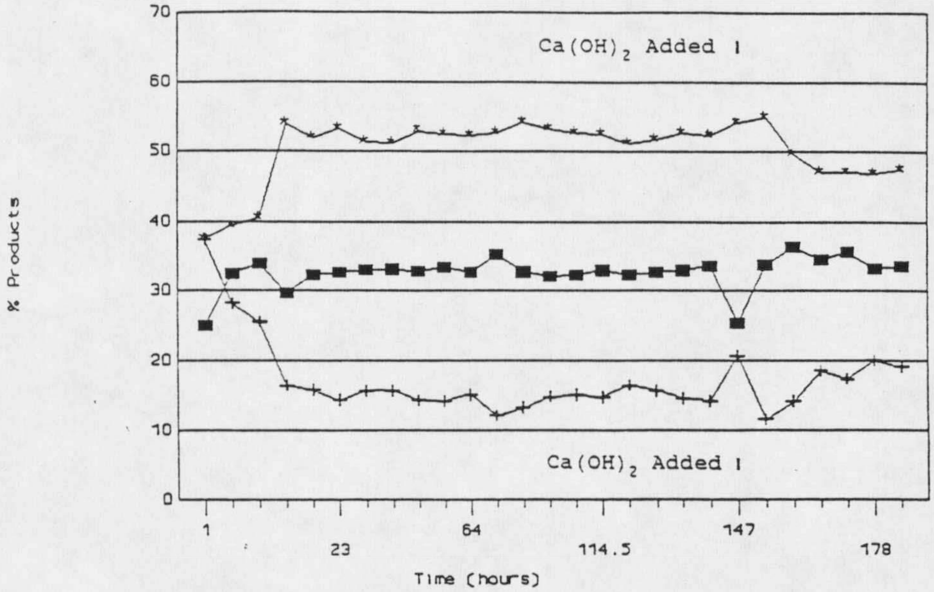


Figure 23 Conversion of sorbitol versus time for run #15, No co-catalyst - 0.1 wt% $Ca(OH)_2$, "Fenske" Rings.



■ Glycerol + Ethylene Glycol * Propylene Glycol

Figure 24 Product distribution versus time on a sorbitol free basis for run #15, No co-catalyst - $Ca(OH)_2$, "Fenske" Rings.

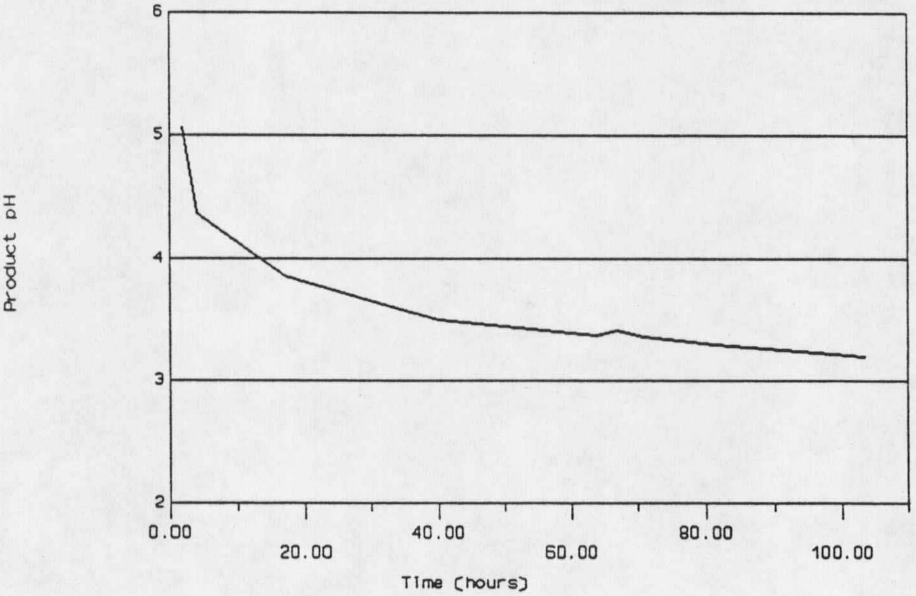


Figure 25 Product stream pH versus time for run #15, No co-catalyst - 0.1 wt% $Ca(OH)_2$, "Fenske" Rings.

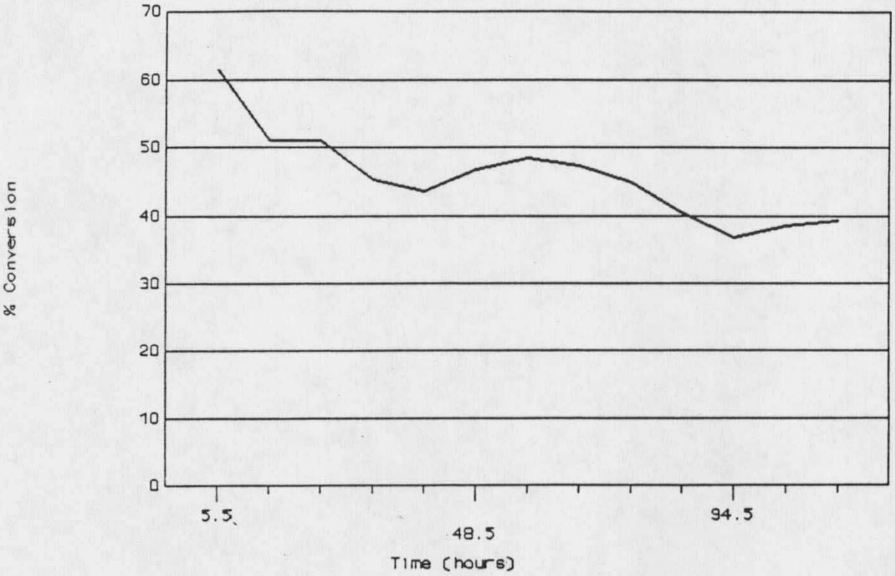
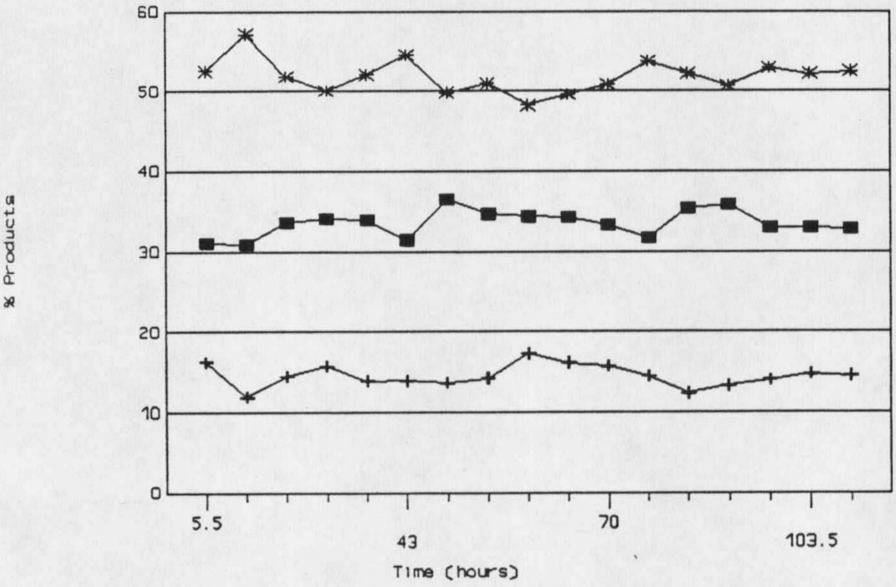


Figure 26 Conversion of sorbitol versus time for run #16, No co-catalyst, Alcoa T-71.



■ Glycerol + Ethylene Glycol * Propylene Glycol

Figure 27 Product distribution versus time on a sorbitol free basis for run #16, No co-catalyst, Alcoa T-71.

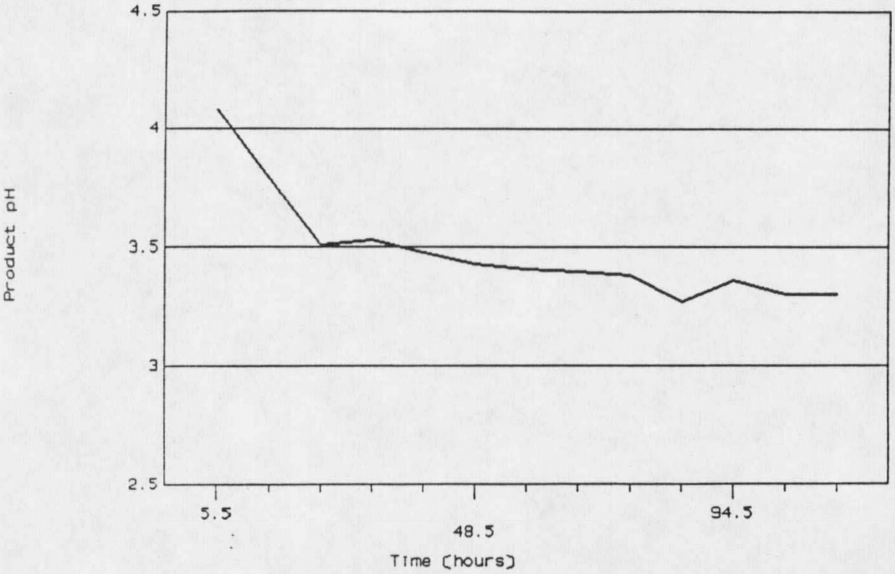


Figure 28 Product stream pH versus time for run #16, No co-catalyst, Alcoa T-71.

to a brown, "charred" liquid. Using NaOH as a co-catalyst, although effective, shifted the product distribution significantly towards more propylene glycol. The product stream had high concentrations of propylene glycol and ethylene glycol and decreased amounts of glycerol as shown in Figure 30. When the $Ca(OH)_2$ was added, the product distribution changed. The proportion of propylene glycol began to decrease and the proportion of ethylene glycol and glycerol began to increase. Figure 31 shows how the pH of the product stream fluctuated with time. The range of pH values for other co-catalyst was 3-5 but the product stream from the reaction using NaOH as a co-catalyst had a pH range of 6-8. When the $Ca(OH)_2$ was added no significant change in the pH occurred.

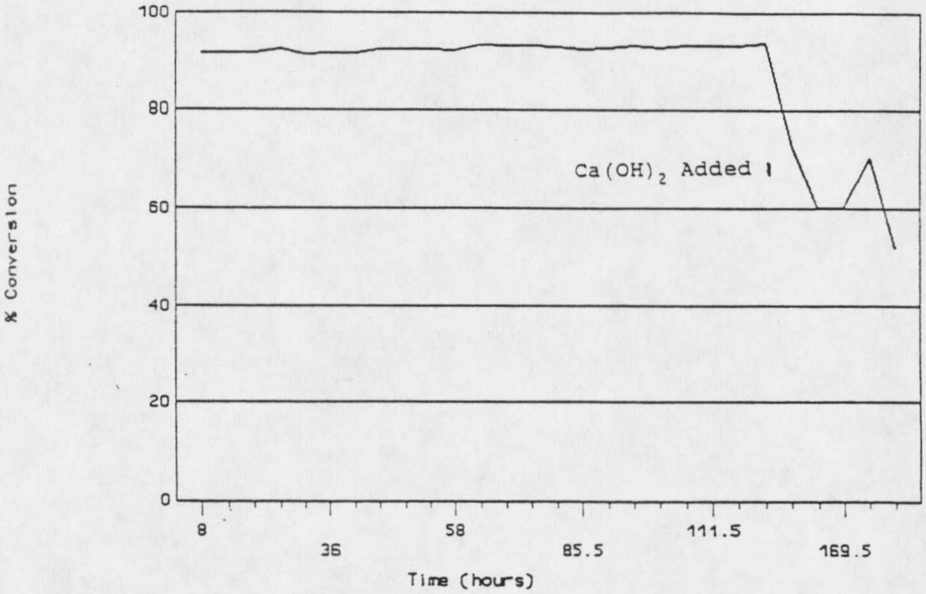


Figure 29 Conversion of sorbitol versus time for run #17, 1.0 wt% NaOH - 1.0 wt% NaOH/ 0.1 wt% Ca(OH)$_2$, Alcoa T-71.

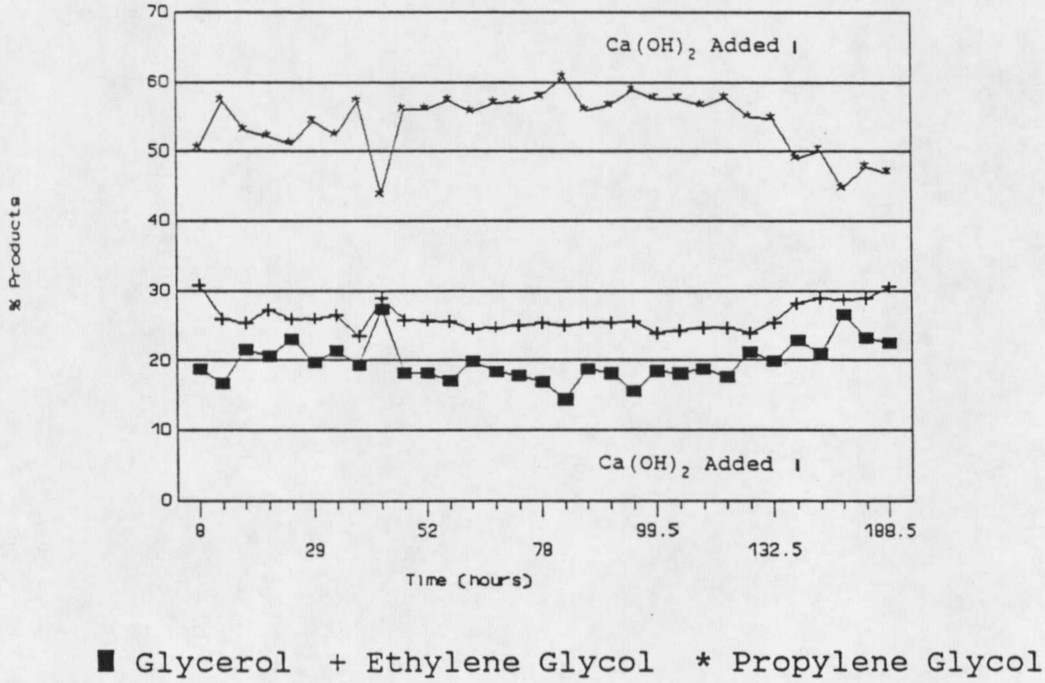


Figure 30 Product distribution versus time on a sorbitol free basis for run #17, NaOH - Ca(OH)$_2$/NaOH, Alcoa T-71.

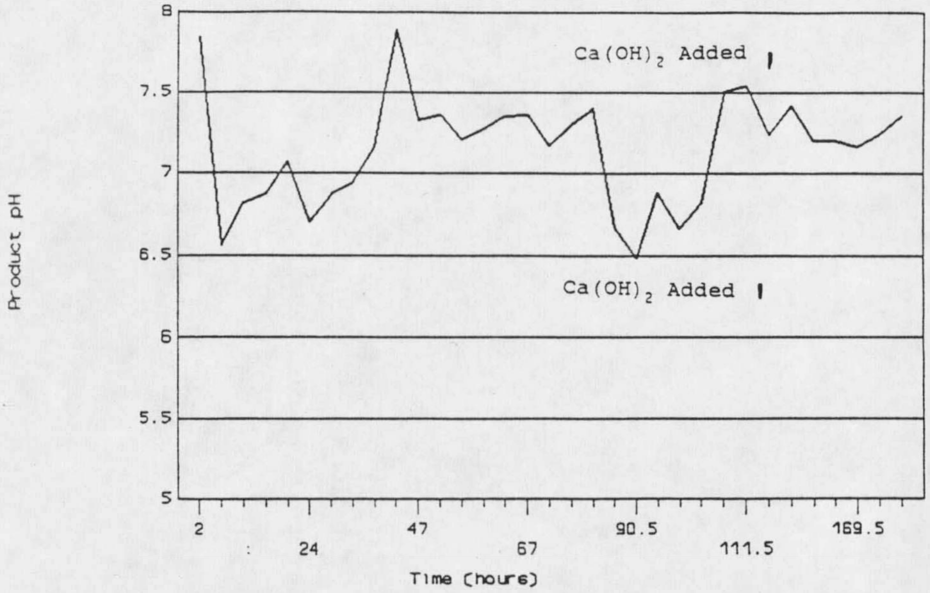


Figure 31 Product stream pH versus time for run #17, 1.0 wt% NaOH - 1.0 wt% NaOH/ 0.1 wt% Ca(OH)$_2$, Alcoa T-71.

Run number 18 was conducted to investigate the use of NaOH and Ca(OH)$_2$ together as co-catalysts. Since the conversion in run number 17 decreased when Ca(OH)$_2$ was added, this run started with 0.1 wt% Ca(OH)$_2$ and then NaOH was added after 48 hours. The NaOH was added in a three to one molar ratio to the Ca(OH)$_2$ contained in the feed. After 20 additional hours of operation, the co-catalyst in the feed was switched to just 1.0 wt% NaOH. Figure 32 shows the conversion of sorbitol versus time. Despite the addition of NaOH no increase in the conversion was observed. Figure 33 shows the product distribution which is initially similar to other runs with 0.1 wt% Ca(OH)$_2$, but when the NaOH was added the product composition changed. The glycerol concentration decreased slowly after 0.17 wt% NaOH was added and then abruptly when

1.0 wt% NaOH was added. The Propylene glycol concentration increased slightly with the first change in co-catalyst and then significantly with the second change of co-catalyst. Ethylene glycol became more predominate than glycerol after the switch to 1.0 wt% NaOH. Figure 34 shows a jump in the pH when 0.17 wt% NaOH was added to the 0.1 wt% Ca(OH)2 and shows a second jump when the feed was switched to 1.0 wt% NaOH.

General Discussion

Runs 1 through 8 failed in their attempt to establish a catalyst and co-catalyst system which maintained its activity for extended periods of time. However, runs 9 through 18

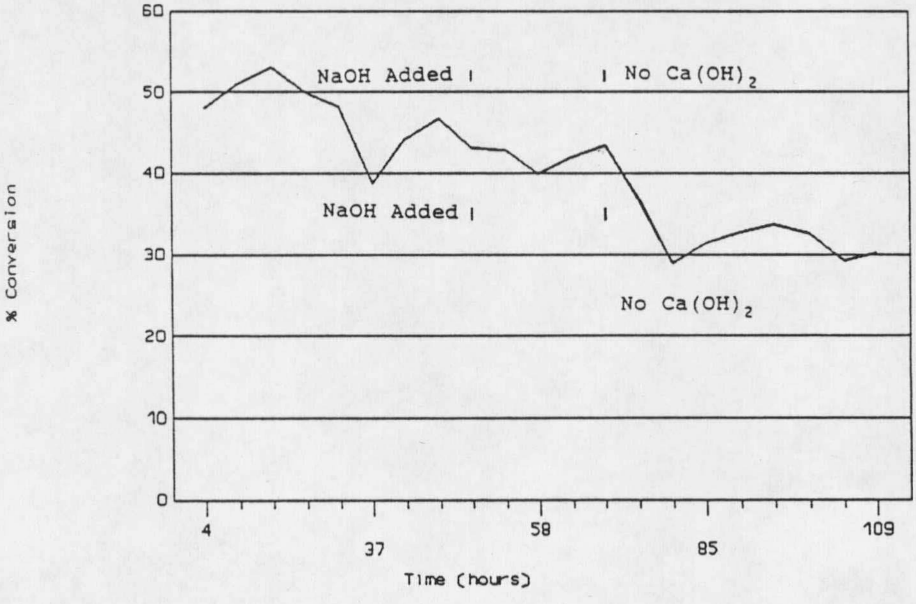


Figure 32 Conversion of sorbitol versus time for run #18, 0.1 wt% $Ca(OH)_2$ - 0.17 wt% NaOH/0.1 wt% $Ca(OH)_2$ - 1.0 wt% NaOH, Alcoa T-71.

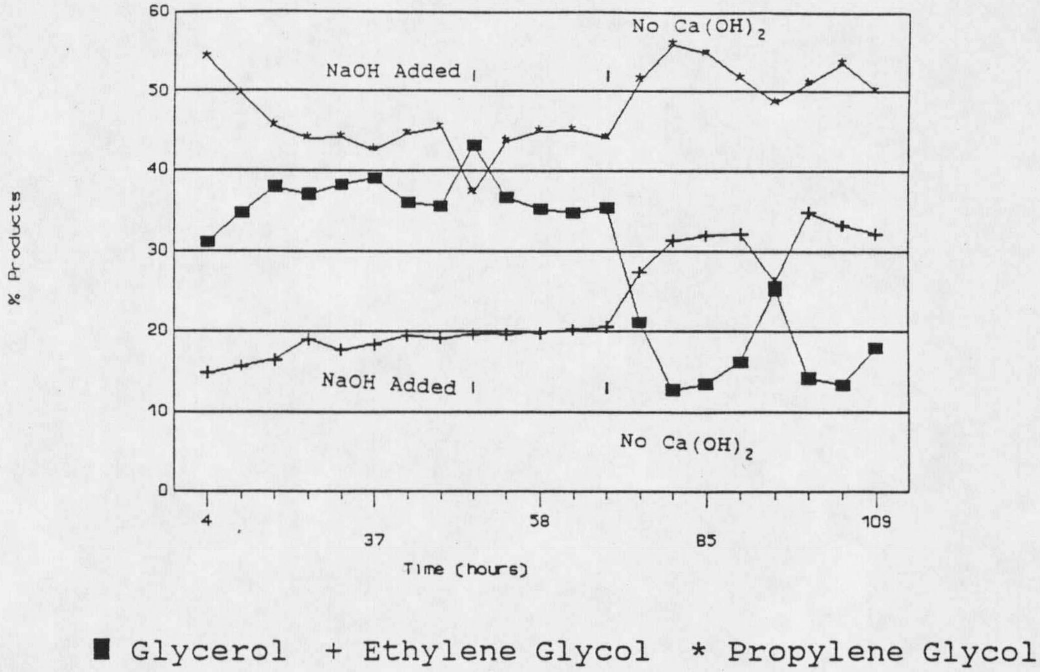


Figure 33 Product distribution versus time on a sorbitol free basis for run #18, $Ca(OH)_2$ - NaOH/ $Ca(OH)_2$ - NaOH, Alcoa T-71.

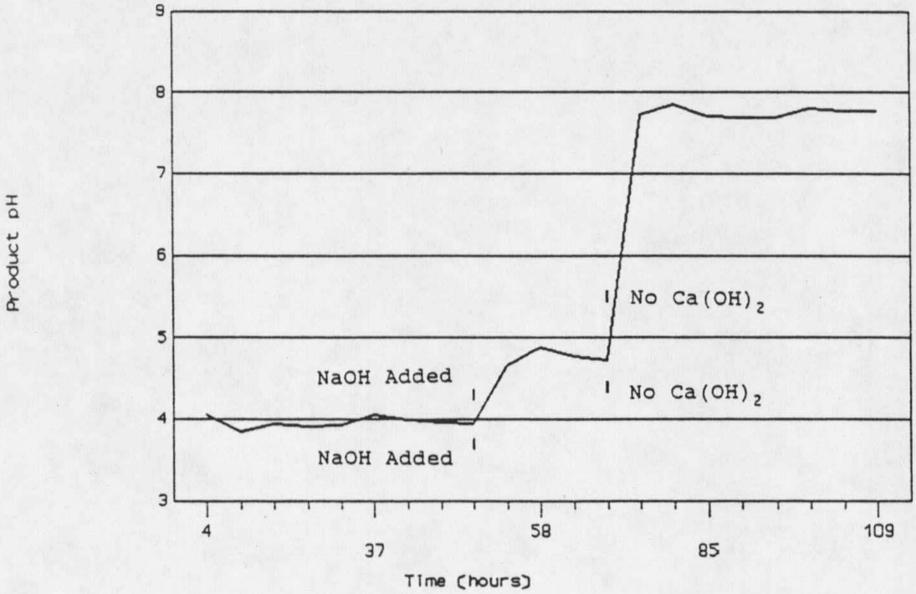


Figure 34 Product stream pH versus time for run #18, 0.1 wt% $Ca(OH)_2$ - 0.17 wt% NaOH/0.1 wt% $Ca(OH)_2$ - 1.0 wt% NaOH, Alcoa T-71.

succeeded in extending the catalyst life time, while maintaining a moderate conversion. This was a significant accomplishment since the available published literature reported only marginal success in continuous hydrogenolysis of sorbitol [15,16]. Van Ling claimed that a continuous hydrogenolysis would have a lower percent conversion and less glycerol in the product [15]. However, run number 17 with NaOH as the co-catalyst maintained a 90 % conversion.

From the literature for batch processes, success was obtained in using well documented types of co-catalyst, such as $Ca(OH)_2$. In this work not all of the batch type co-catalysts could be used since solubility of the co-catalyst in the feed solution was critical in continuous hydrogenolysis. Therefore techniques for co-catalyst application had to be improved, by maintaining an inert atmosphere over the feed reservoir to prevent the co-catalyst from reacting with air and adding an in-line filter to remove remaining insoluble materials. Three runs were started without the initial addition of a co-catalyst resulting in sustained catalytic activity. The majority of the runs which did use a co-catalyst used a significantly lower concentration than reported in the literature.

Of all the experiments the longest run lasted 460 hours, while yielding a final conversion of about 23%. This significantly exceeded any of the reported or predicted results for continuous hydrogenolysis [15,16]. Also achieved were moderate conversions and a high percentage of glycerol in the product stream. Three other reactions times greater than 300 hours and four runs lasted almost 200 hours. These extended runs were obtained without the use of regeneration.

After obtaining extended activity in the runs, a closer look at the rates of deactivation was possible for longer actual run times. Based on the data collected while operating with the initial co-catalyst, a linear correlation was developed to compare the different runs.

A least squares method was used to derive equations for the best fit lines through the data of each run. Figure 35 shows an example of the best fit line through natural log of conversion versus time data for run number 12. The regression coefficient of 0.93 indicates a good fit of the line to the data. This linear model can then be used to predict the conversion at 500 hours. Figures 36 and 37 show the linear models extrapolated to 500 hours. This model can also be used to predict the time required for the conversion to drop below 20%. A summary of these calculated values is listed in Table 9. Run number 17 is listed first despite the poor model because of the high actual conversion, 94 %, obtained after 142.5 hours of service.

Table 9 lists the corresponding regression coefficients for each run. Since the linear correlations were based on the initial feed, some of the data used were related to the unsteady start-up periods. This along with possible

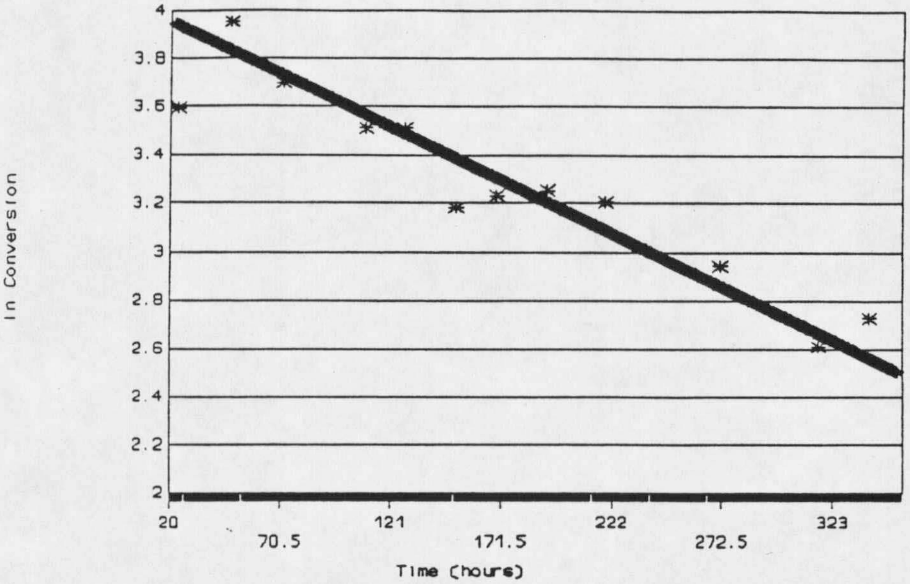


Figure 35 An example of the natural log of conversion versus time with the best fit line, run # 12, R = 0.93.

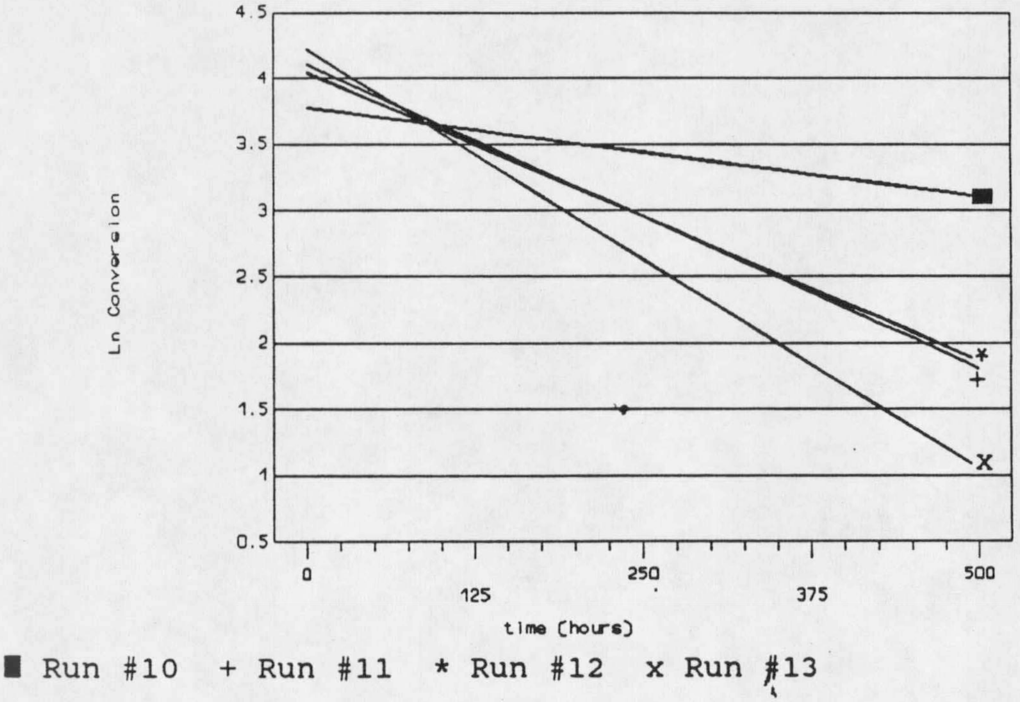


Figure 36 Best fit lines for the natural log of conversion versus time for runs 10, 11, 12, and 13.

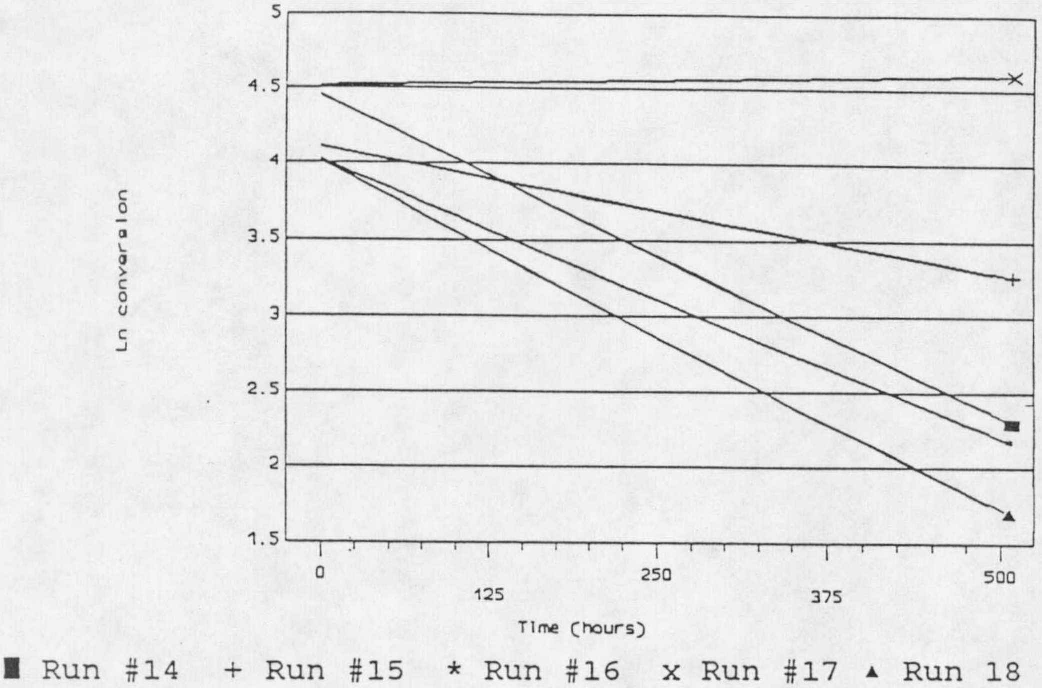


Figure 37 Best fit lines for the natural log of conversion versus time for runs 14, 15, 16, 17, and 18.

experimental errors in analysis could explain some of the poor regression coefficients in Table 9.

The effect of different types of co-catalyst on the product distribution has been well documented in the literature for batch type reactions. The effect of co-catalyst on product distribution in the runs conducted in this continuous reaction research correspond to those found in literature for batch processes [12,26]. The use of no co-catalyst and $Ba(OH)_2$ seemed to keep the proportion of propylene glycol and glycerol in the product stream approximately equal, while using $Ca(OH)_2$ and NaOH decreased the percentage of glycerol in the product stream. Van Ling et al., had similar results in his work with NaOH and $Ca(OH)_2$

Table 8 Summary of experimental runs based on linear correlations.

Run Number	Initial co-catalyst/ conc., wt%	Conversion at 500 hrs.	Time to 20 % Conversion	R
17	NaOH/ 1.0	--	---	0.66
15	No co-catalyst	24	600	0.46
10	$Ba(OH)_2$ / 0.1	22	600	0.71
14	No co-catalyst	13	400	0.91
16	No co-catalyst	9	275	0.81
11	$Ba(OH)_2$ / 0.3	6	250	0.85
12	$Ca(OH)_2$ / 0.1	6	250	0.93
18	$Ca(OH)_2$ / 0.1	5	225	0.75
13	$Ca(OH)_2$ / 0.1	3	200	0.93

[12]. Therefore the high conversion obtained with NaOH is not the best co-catalyst if a larger proportion of glycerol is needed. This was also observed when the co-catalyst system was changed during the reaction. When either $Ca(OH)_2$ or NaOH was added to a run, the proportion of glycerol in the product stream decreased and the proportion of propylene glycol and ethylene glycol increased.

Figure 38 shows the linear correlations for runs 14, 15 and 16, in which the three types of inert packing were tested using a constant concentration of co-catalyst. From Figure 38 the catalyst used in run 15 appears to deactivate much slower than in runs 14 and 16. This indicates that "Fenske" rings appear to either enter into the reaction, transfer heat better or improve the feed flow conditions.

Figure 39 shows the linear correlations for runs 12, 13, and 18. These three runs had the same type and concentration of co-catalyst. Runs 12 and 13 used United Catalyst spherical alumina (UC CS346), while run 18 used Alcoa tabular alumina (Alcoa T-71). Figure 39 does not show any significant difference between the two types of alumina packing.

In most runs as the conversion decreased, the acidity of the product stream increased. Chang et al., found that batch reactions were more acidic at the end of a run. Chang also had some success in controlling the product pH by using

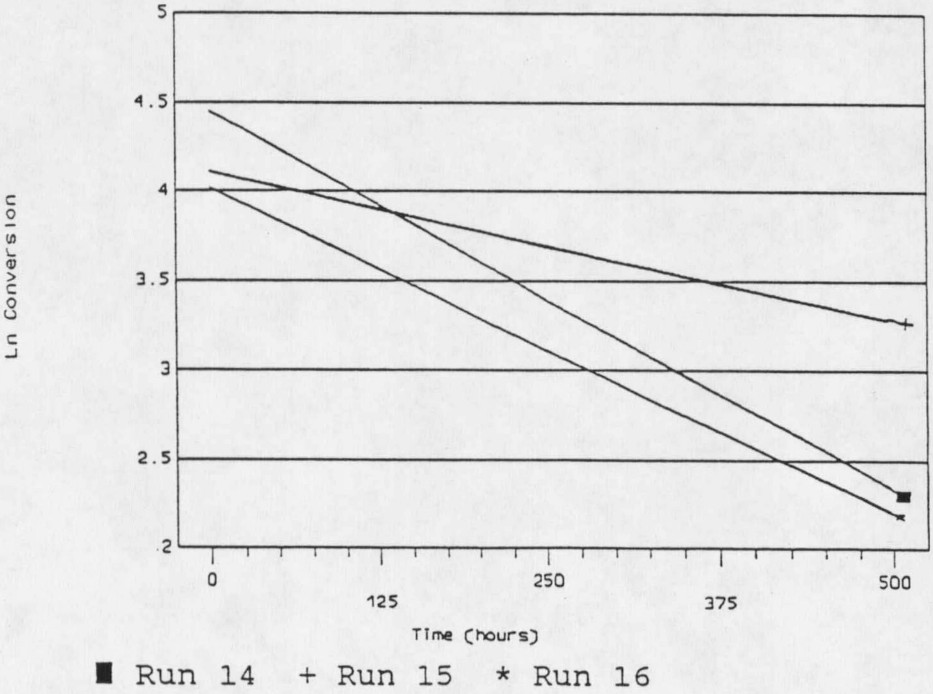
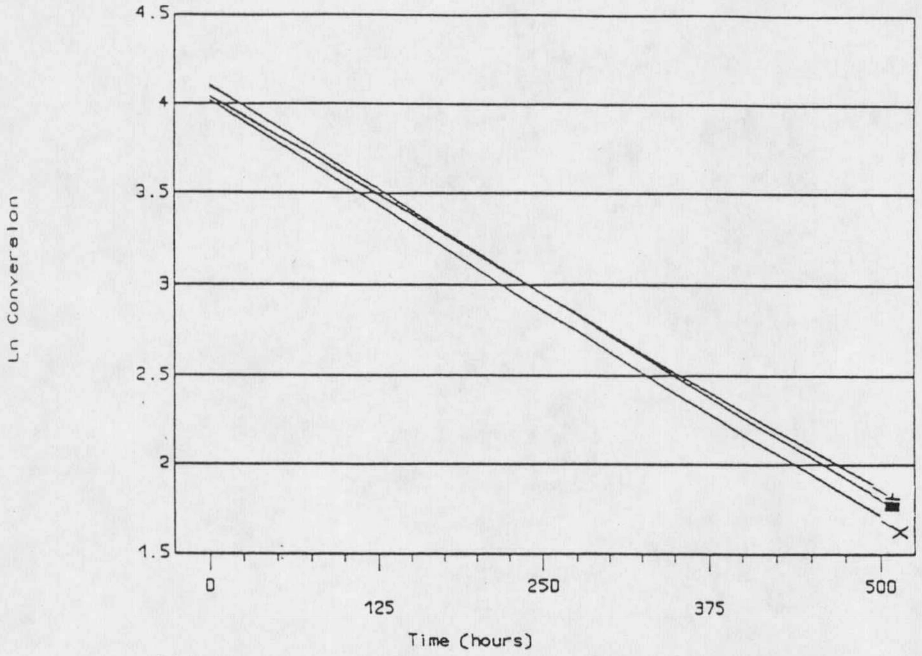


Figure 38 Linear correlations for runs 14, 15, and 16 for the comparison of inert packing.



■ Run 12 + Run 13 x Run 18

Figure 39 Linear correlations of runs 12, 13, and 18 for the comparison of inert packing.

calcium oxide and zinc oxide [13]. Based on the runs using NaOH it appears that if the feed is more basic then conversion of sorbitol will remain higher. Unfortunately the attempts to increase the conversion by increasing the feed pH during the run failed. The pH of the product stream did increase, but from runs 12 and 18 it appears that the conversion did not. In run number 18 the overall sorbitol conversion dropped when the co-catalyst was switched to 1.0 wt% NaOH.

One analytical difficulty encountered during this study was the presence of an unknown compound in the product stream. This compound had a retention time through the HPLC greater than that of sorbitol. Because corrected area normalization was used, the response of the RID for this compound could not be compared to a standard. Quantitative analysis could not be conducted for this compound. This compound did not appear in runs using NaOH as the co-catalyst but did appear in runs using $Ca(OH)_2$ and $Ba(OH)_2$. Runs with no co-catalyst also had a detectable amount of this unknown compound. Analysis of feed samples in which either $Ca(OH)_2$ or $Ba(OH)_2$ were present did not show an unknown compound. Therefore the unknown compound is a suspected reaction product which had a concentration ranging from 1 to 10 wt% depending on experimental conditions. Qualitative analysis was conducted to determine the unknown by comparing its retention time to known standards. A list of the chemicals tested which were reported in literature as possible reaction products can be found in the Appendix.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based on initial experimentation the best commercial catalyst of those tested was United Catalyst C46-8-03 1/16" E. This catalyst was used in reactions up to 460 hours, and could feasibly be used for more than 500 hours. The best co-catalyst system was NaOH, if a significant amount of propylene glycol can be tolerated in the product. When a greater proportion of glycerol is desired, the use of 0.1 wt% $Ba(OH)_2$ is preferable, although the conversion will be significantly less. If toxicity of $Ba(OH)_2$ is a problem then not using a co-catalyst appears best based on run number 14. The effects of co-catalyst type on product distribution for the continuous reaction was similar to those reported for batch processes. No difference was found between the two types of alumina packing tested. Although not observed in every run, the pH of the product stream decreased as the overall sorbitol conversion decreased. The pH of the product stream can be modified by varying the type and concentration of co-catalyst.

Recommendations

The unknown component in the product stream should be identified. This might be accomplished with the use of Chromatography and Mass Spectrometry.

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APPENDICES

APPENDIX A

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OPERATING PROCEDURES

In an effort to enhance reproduction of the analytical technique used in this hydrogenolysis study, a detailed description of high performance liquid chromatography (HPLC) equipment and operating procedures is given.

Equipment

The Shimadzu HPLC system is shown in Figure 40. The operating parameters that maximized the resolution of component peaks was a column temperature of 75°C and a carrier flow rate of 0.6 ml/min.

Procedures

Contamination is the largest problem associated with analysis. Careful start-up, operation, injection, and sample preparation procedures were developed to minimize the effect of contamination.

Start-up and Operation

Start-up procedures begin with purification of the mobile phase, or carrier. For the analysis of polyhydric alcohols and saccharides, water was the best carrier. After distillation and deionizing, the water was boiled and then degassed under a vacuum in an ultrasonic cleaner. At the mobile phase intake, a 0.3 micron suction filter was used to remove suspended particles. An in-line Whatman Aqueous IFD filter/degasser was added to remove the remaining gas. At the pump outlet, another in-line filter removes particles that may have entered the system in the pump. The carrier then passes

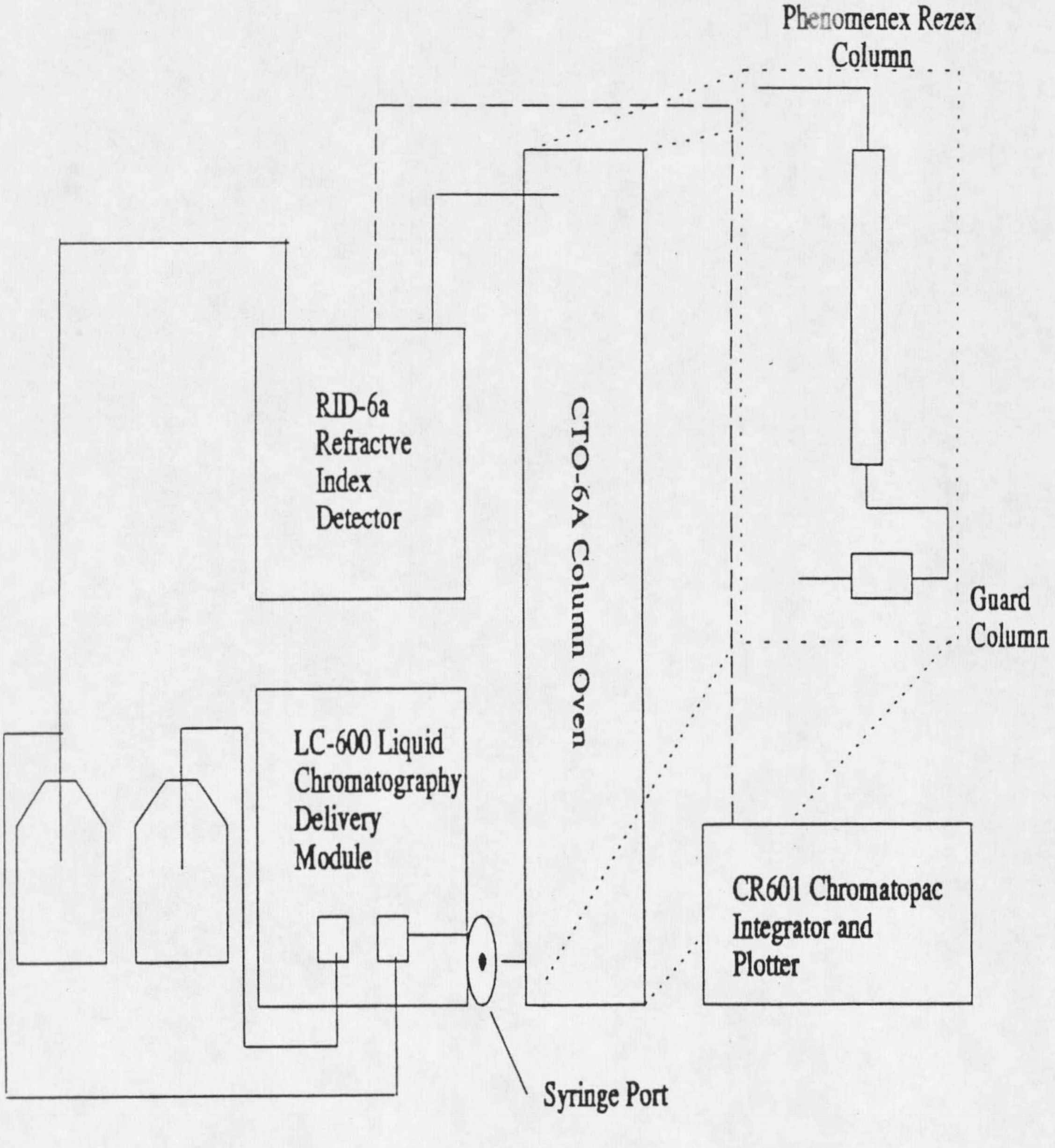

Figure 40 High Performance Liquid Chromatography system.

through the injection port and then into the column oven. Inside the column oven, a guard column was installed as the last line of protection for the analytical column. The guard column also removed substances that may have been injected with the sample, or chemicals harmful to the column found in the samples.

In addition to the above mentioned start-up and operating procedures, stabilization of the RID for a period of 24 hours was required. The column oven was turned on early to allow the column to reach its operating temperature of 75 °C before the mobile phase was pumped through the column. To purge the lines of the old mobile phase, the drain valve on the LC-600 pump was opened. This allowed fresh carrier to replace the old carrier in the lines up to the pump outlet. Once the carrier was allowed to flow through the whole system, another period of approximately 30 to 60 minutes was needed to achieve a stable base line. The optimum flow rate for this analysis was 0.6 ml/min. Once a stable base line had been reached, the samples were prepared and analyzed.

Sample Preparation and Analysis

The HPLC with the Shimadzu RID-64 refractive index detector (RID) was sensitive enough to detect a change in mobile phase, therefore careful sample preparation was required, as well as injection procedures. The sample was diluted approximately 1000:1 with water taken straight from the mobile phase reservoir. For example, 10 micro-liters (ul) of sample was drawn into a well rinsed 10 ul syringe and injected into a clean vial, rinsed and filled with 1 ml of water from the mobile phase reservoir. The vial was then shaken and the syringe was rinsed again. A 10 ul diluted sample was then drawn for injection. Prior to injection, the injection port in the "inject" position was rinsed with 1 ml of water from the mobile phase reservoir. The last step before injection was to initialize the integrator with a Self-Test function. Self-Test is a function incorporated in the Shimadzu Chromatopac CR601, which automatically determine the peak processing parameters [27].

The knob of the injection port valve was then switched to the load position and the syringe was inserted into the needle port. The sample was then injected into the 20 ul sample loop. While holding the syringe in the needle port, the knob is then rotated back to the inject position. The syringe was removed and rinsed.

The use of the Shimadzu CR601 Chromatopac integrator greatly enhanced analysis when quantitative calculation methods incorporated in the integrator were used. Description of each method, and detailed programming is available in the chromatopac CR601 instruction manual [28]. In this study corrected area normalization method was used to calibrate the response of the RID to standards. Once again caution was needed to ensure that proper sample dilution, sample injection, and operating procedures are followed, when standards were used.

APPENDIX B

CHEMICAL STANDARDS TESTED FOR UNKNOWN PRODUCT

The following list contains all the chemicals used in an effort to determine the unknown component in the product stream. Several were listed in the research conducted by HRI [17]. Others on this list were chemicals suspected to be in the product stream by the author.

Lactic Acid
Gluconic Acid
Methanol
Ethanol
Isopropanol
1,3 Butanediol
1,2 Butanediol
1,4 Butylene Glycol
1,5 Pentanediol
1,6 Hexylene Glycol
1,2,6 Trihydroxyhexane
1,2,4 Butanetriol

Erythritol
Xylitol
Mannitol
Mannose
Lactitol
Lactose
Diethylene Glycol
Triethylene Glycol
Tetraethylene Glycol
Dipropylene Glycol
Tripropylene Glycol