This is to certify that the

dissertation entitled

Biomass Conversion: Sugar Hydrogenolysis, Glycerol
Dehydroxylation and HF Saccharification

presented by

Keyi Wang

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemical Engineering

Mark C Hawley
Major professor

Date September 23, 1999

BIOMASS CONVERSION: SUGAR HYDROGENOLYSIS, GLYCEROL DEHYDROXYLATION AND HF SACCHARIFICATION

By

Keyi Wang

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemical Engineering

1999

BIO

In the

hydrogenolysi

sugar hydroge

glycol; the gly

the HF sacchari

The curren

reaction mecha

mechanism stud

establish the me

experimental wor

retro-aldol reactio

time direct evidenc

carbonyl precurso

possible for one to

the selectivity of su

ABSTRACT

BIOMASS CONVERSION: SUGAR HYDROGENOLYSIS, GLYCEROL DEHYDROXYLATION AND HF SACCHARIFICATION

By

Keyi Wang

In the current research, three biomass conversion processes, namely sugar hydrogenolysis, glycerol dehydroxylation and HF saccharification, are investigated. The sugar hydrogenolysis process converts sugars into glycerol, propylene glycol and ethylene glycol; the glycerol dehydroxylation process converts glycerol to 1,3-propanediol; while the HF saccharification process converts lignocellulosic biomass into sugars.

The current research on sugar hydrogenolysis has focused on understanding of the reaction mechanism and of the factors controlling the reaction selectivity. In the mechanism study, a series of 1,3-diol model compounds have been hydrogenolyzed, to establish the mechanism of C-C and C-O bond cleavage in sugar hydrogenolysis. The experimental work confirmed our theoretical conception that the C-C bond breaks via the retro-aldol reaction of a β-hydroxyl carbonyl precusor, and it also provided for the first time direct evidence that the C-O cleavage is through dehydration of the same β-hydroxyl carbonyl precursor just mentioned. Establishment of the above mechanism makes it possible for one to adopt a more rational approach than the current practice in control of the selectivity of sugar hydrogenolysis.

The s
in sugar h
study, has
concentrati
selectivity.

In the
proposed to
group, and
concept is
tosylates ar
In this work
group are
ruthenium ca

The wo
adsorption p
with a bench
reactor. Two
based on exp
analysis of th
occurring in t
insight into the

The selectivity study in the current work has focused on control of the C-O cleavage in sugar hydrogenolysis. Specifically, an experimental study, as well as a simulation study, has been carried out in this work to investigate the effect of temperature, base concentration, hydrogen pressure, catalyst amount and catalyst type on the C-C v.s C-O selectivity. These studies, both experimental and theoretical, yielded many useful results.

In the research on conversion of glycerol to 1,3-propanediol, a new concept is proposed to selectively transform the second hydroxyl group of glycerol into a tosyloxy group, and then to remove it by hydrogenolysis. The technical feasibility of this new concept is verified experimentally in this work. Before this work, hydrogenolysis of tosylates are generally effected with base metal hydrides, such as $LiAlH_4$ and $LiHBEt_3$. In this work, for the first time, tosylates with a hydroxy group adjacent to the tosyloxy group are hydrogenolyzed with molecular hydrogen in the presence of a nickel or ruthenium catalyst. The mechanism for this hydrogenolysis reaction is also established.

The work on vapor-phase HF saccharification has focused on modeling of the HF adsorption process in a packed-bed reactor. However, experiments were also conducted with a bench-scale reactor to study the behavior of HF adsorption in the packed-bed reactor. Two models of HF adsorption have been developed. One is developed purely based on experimental observations, and the other one is developed based on a detailed analysis of the HF flow, the intrinsic HF adsorption and the heat transfer processes occurring in the reactor during HF adsorption. These models provide a great deal of insight into the HF adsorption process in the packed-bed reactor.

First o
guidance an
he gave me d
Dr. Kris A.
Dale for serv
Scot J. DeAt
Plant Biotec
Bioprocessing
Engineering a
support.

ACKNOWLEDGMENTS

First of all, I wish to thank my academic advisor Dr. Martin C. Hawley for his guidance and support in this investigation. I am especially grateful for the encouragement he gave me during the final stage of my dissertation preparation. I would also like to thank Dr. Kris A. Berglund, Dr. Dannis J. Miller Dr. Rawle I. Howlingsworth and Dr. Bruce E. Dale for serving on my graduate committee, and to thank Mr. Todd D. Furney and Mr. Scot J. DeAthos for their assistance in completing this investigation. The Consortium for Plant Biotechnology Research, the Michigan State University Crop and Food Bioprocessing Center, the Amoco Foundation and the Department of Chemical Engineering at Michigan State University are recognized for their generous financial support.

TABLE OF CONTENTS

PART I. CATALITIC SUGAR HYDROGENOLYSIS

PART II. SELECTIVE DEHYDROXYLATION OF GLYCEROL

PART III. VAPOR-PHASE HF SACCHARIFICATION

APPENDIX

LIST OF TABLES

LIST OF FIGURES

Mathemat

$k_1, k_{-1}, \ldots$

k_i

k_{-i}

K

K_i

$\underline{K}$

$\underline{K}_i$

R_2

R_5

S

t

$X_1, \ldots, X_8$

Special Sym

ΔG^o

$\Delta \underline{G}^o$

[A]

$[A]_0$

LIST OF SYMBOLS AND ABBREVIATIONS

Mathematical Symbols

$k_1, k_{-1}, \ldots\ldots, k_8, k_{-8}$	reaction rate constants defined in Figure 5-5
k_i	forward reaction rate constants of Reaction No. *i* in Figure 5-5
k_{-i}	backward reaction rate constants of Reaction No. *i* in Figure 5-5
K	reaction equilibrium constant
K_i	equilibrium constant of Reaction No. *i* in Figure 5-5
$\underline{K}$	equilibrium constant of dehydrogenation reaction
$\underline{K}_i$	equilibrium constant of dehydrogenation corresponding to Reaction No. *i*
R_2	reversibility parameter of Reaction No. 2, defined by Eq.(37)
R_5	reversibility parameter of Reaction No. 5, defined by Eq.(38)
S	C-C v.s. C-O selectivity
t	reaction time
$X_1, \ldots\ldots, X_8$	reaction flux rate of Reaction No.1 through No.8, respectively

Special Symbols

ΔG^o	free energy change of dehydrogenation reaction
$\Delta \underline{G}^o$	free energy change defined in Page 57.
[A]	concentration of 2,4-pentandiol
$[A]_0$	initial concentration of 2,4-pentanediol

[B]
[C]
[D]
[E]
[F]
[G]
[H]
[I]
[J]
[M]
$[M]_o$
[MH]
[OH]
$[OH]_o$

Chemical

1,2-PD
1,3-PD
2,4-PD
HPA
HPD
HMPD
PTD
TPD

[B]	concentration of 4-hydroxy-2-pentanone
[C]	concentration of acetone
[D]	concentration of isopropanol
[E]	concentration of acetaldehyde
[F]	concentration of ethanol
[G]	concentration of 3-penten-2-one
[H]	concentration of dissolved hydrogen
[I]	concentration of 2-pentanone
[J]	concentration of 2-pentanol
[M]	concentration of metal catalyst
$[M]_0$	initial concentration of metal catalyst
[MH]	concentration of metal hydride
[OH]	concentration of base or hydroxide ion
$[OH]_0$	initial concentration of base or hydroxide ion

Chemical Abbreviations

1,2-PD	1,2-propanediol
1,3-PD	1,3-propanediol
2,4-PD	2,4-pentanediol
HPA	3-hydropropionaldehyde
HPD	5-hydroxy-2-phenyl-1,3-dioxane
HMPD	4-hydroxymethyl-2-phenyl-1,3-dioxolane
PTD	2-phenyl-5-tosyl-1,3-dioxane
TPD	2-tosyloxy-1,3-propanediol

CA

PART I

CATALYTIC HYDROGENOLYSIS OF SUGARS

Curren
natural gas f
resources, th
gas diminis
future. Co
responsible
the biomas
biomass res

The si
of enhanci
occurring m
wastes. It i
these residu
the world is
current tim
portion of
convert bion
of biomass.

CHAPTER 1

GENERAL INTRODUCTION

Currently, a large portion of the chemical process industry depends on petroleum and natural gas for feedstocks. Considering the finite and nonrenewable nature of these fossil resources, this dependence is a severe handicap. As the reserves of petroleum and natural gas diminish, the chemical process industry will possibly face feedstock problems in the future. Consequently, we will face a shortage of synthetic chemicals, which are largely responsible for our current living standard. In light of these possibilities, development of the biomass conversion processes that produce useful chemicals from the renewable biomass resource is of great significance.

The significance of biomass conversion is also comprehensible from the perspective of enhancing biomass utilization. Biomass (lignocellulose) is an abundant material occurring mainly in the form of forestry residues, agriculture residues and municipal solid wastes. It is estimated that each year the U.S. alone generates about 1 billion dry tons of these residues and wastes (Barrier and Bulls, 1992). The annual production of biomass in the world is estimated to be as high as 10^{11} to 10^{12} dry tons (Grohman *et al.*, 1993). At the current time, the greatest use of biomass is to burn it as a low-valued fuel, and a large portion of biomass is simply discarded as waste. Biomass conversion processes can convert biomass into a variety of value-added useful chemicals, and thus upgrade the use of biomass.

In th
hydrogenol
sugar hydro
glycol; the g
HF sacchar
propylene g
while sugar

In spit
to sugar h
hydrogenol
lignocellulos
as sugar cro
is not neces
which also c
which consis
hydrogenoly
conducted as
provided in t

Sugar H
glycerol, pro
Glycerol is us
additives and
deicers and a

In the current research, three biomass conversion processes, namely sugar hydrogenolysis, glycerol dehydroxylation and HF saccharification, are investigated. The sugar hydrogenolysis process converts sugars into glycerol, propylene glycol and ethylene glycol; the glycerol dehydroxylation process converts glycerol to 1,3-propanediol; and the HF saccharification process converts lignocellulosic biomass into sugars. Glycerol, propylene glycol, ethylene glycol and 1,3-propanediol are value-added useful chemicals; while sugar is an important intermediate in the conversion of biomass to useful chemicals.

In spite of the fact that the HF saccharification process naturally provides feedstock to sugar hydrogenolysis, it needs to be noted here that the feedstock of sugar hydrogenolysis is not necessarily from HF saccharification. It may be from other lignocellulose saccharification processes. It may also be from other sugar sources, such as sugar crops and starchy materials. Similarly, the feedstock of glycerol dehydroxylation is not necessarily from sugar hydrogenolysis. It may come from sugar fermentation, which also converts sugars to glycerol, or it may come from processing of fatty materials, which consists of a different type of biomass. In this research, studies on the sugar hydrogenolysis, glycerol dehydroxylation and HF saccharification processes have been conducted as independent sub-projects. A brief discussion on each of these projects is provided in the following.

Sugar Hydrogenolysis. The purpose of sugar hydrogenolysis is to convert sugars to glycerol, propylene glycol and ethylene glycol. These chemicals have extensive uses. Glycerol is used in alkyd resin, ester gums, polyethers, pharmaceuticals, perfumeries, food additives and humectants. Ethylene glycol is used in antifreeze, hydraulic fluids, paints, deicers and alkyd and polyester resins. Propylene glycol has similar applications to

ethylene gl
cosmetic sof
glycerol, pro

At the
as an intern
chlorohydrin
produce glyc
epichlorohyd
glycidol as in
as a by-produc
propanediol a
chemicals and
able to produc
propylene gly
environmentally
methods.

As mention
fermentation, in
some unique adv
carbon atoms in
glycerol yield. T
75% in aerobic f
limitation results

ethylene glycol, and is additionally used as tobacco humectants, food additives and cosmetic softening agents, owing to its non-toxic nature. Because of their extensive uses, glycerol, propylene glycol and ethylene glycol are currently produced in large volumes.

At the current time, ethylene glycol is produced from ethylene with ethylene oxide as an intermediate. Propylene glycol is produced from propylene with propylene chlorohydrin and propylene oxide as intermediates. Several commercial routes exist to produce glycerol from propylene. The major one has ally chloride, dichlorhydrin and epichlorohydrin as intermediates. The more recent one has acrolein, glycidaldehyde and glycidol as intermediates. A small portion of glycerol is also produced from fatty material as a by-product of soap production. Glycerol, propylene glycol, ethylene glycol and 1,3-propanediol are all petroleum-based chemicals. In view of the importance of these chemicals and the inevitability of petroleum depletion in the future, it is significant to be able to produce them from renewable biomass resources. Production of glycerol and propylene glycol by sugar hydrogenolysis also has potential to eliminate the environmentally unfriendly chlorohydrin intermediates from the current production methods.

As mentioned previously, the conversion of sugars to glycerol can also be done by fermentation, in lieu of hydrogenolysis. Nevertheless, the hydrogenolysis process has some unique advantages. Theoretically, the hydrogenolysis reaction preserves all the carbon atoms in the original sugar molecules, and thus can potentially provide a high glycerol yield. The theoretical glycerol yield of fermentation, in contrast, is limited to 75% in aerobic fermentation and to 58% in anaerobic fermentation (Wise, 1983). This limitation results from the carbon loss as carbon dioxide in fermentation. The second

advantag
example.
Consideri
lignocellu
pentose.
The disad
not yet s
glycol, et
envisione
process d

The
reaction
mechanis
plausible
cleavage i
reviewed
performed
retro-aldol
sugar hy
considerati
this work
through d
Establishm

advantage of the hydrogenolysis process is that it can also use pentose, xylose for example, as feedstock. In contrast, the feedstock of fermentation is limited to hexose. Considering that hemicellulose, which is one of the three major components of lignocellulose and accounts for 20 to 30% of its total weight, is composed mainly of pentose, this feature of sugar hydrogenolysis is of great importance to biomass utilization. The disadvantage of the hydrogenolysis process is that, at the current stage, this process is not yet selective. The current hydrogenolysis processes produce glycerol, propylene glycol, ethylene glycol, as well as other polyhydric alcohols, in a mixture. However, it is envisioned that the selectivity of sugar hydrogenolysis can be improved through proper process development.

The current research on sugar hydrogenolysis has focused on understanding of the reaction mechanism and of the factors controlling the reaction selectivity. Reaction mechanism and selectivity control are two major issues of sugar hydrogenolysis. Several plausible mechanisms have been proposed by previous researchers to explain the C-C cleavage in sugar hydrogenolysis. In the current work, these mechanisms are critically reviewed on the theoretical grounds and against the hydrogenolysis experiments performed in this research using 1,3-diol model compounds. This leads us to identify the retro-aldol reaction of a β-hydroxyl carbonyl precursor as the C-C cleavage mechanism of sugar hydrogenolysis. Other mechanisms are excluded based on theoretical considerations and experimental results. The hydrogenolysis experiments performed in this work have also provided for the first time direct evidence that the C-O cleavage is through dehydration of the same β-hydroxyl carbonyl precursor just mentioned. Establishment of the above reaction mechanisms makes it possible for one to adopt a rational approach in control of the selectivity of the sugar hydrogenolysis process.

The selectivity study in the current work has focused on control of the C-O cleavage in sugar hydrogenolysis. It is envisioned that, if the C-O cleavage could be somehow controlled, the reaction products of sugar hydrogenolysis would be significantly simplified, and the reaction would be directed to produce the highest-valued product, glycerol. The selectivity study has also been carried out using a 1,3-diol model compound (2,4-pentanediol). The study on the competition between C-C and C-O cleavage in sugar hydrogenolysis is greatly facilitated by use of this model compound. Thus, an experimental study has been carried out in this work to investigate the effect of temperature, base concentration, hydrogen pressure, catalyst amount and catalyst type on the C-C v.s C-O selectivity, and a simulation study has been conducted to rationalize the experimental results and to look into ways to improve the selectivity. It is found that the temperature has little effect on the selectivity; increasing base concentration can increase the selectivity to certain extent; increase in the amount of catalysts used has an adverse effect on the selectivity; and the selectivity varies widely with the type of catalysts used. The effect of hydrogen pressure on the selectivity is the most interesting. At low pressure, the selectivity increases with the pressure; at medium pressure, the selectivity is not sensitive to the change in the pressure; while at high pressure, the selectivity decreases as the pressure is increased. Of the seven different types of catalysts that has been studied in our experiments, the best one is barium-promoted copper chromite, which has furnished a C-C vs. C-O selectivity of 2.5 in hydrogenolysis of 2,4-PD. Our simulation study also identifies a catalyst with strong capability to hydrogenate ketones and aldehydes but only moderate ability to hydrogenate α,β-unsaturated ketones as the one with high potential to deliver improved selectivity. These results, both experimental and theoretical, point out the possible directions that further selectivity study may follow.

Glycerol Dehydroxylation. The purpose of glycerol dehydroxylation is to convert glycerol to 1,3-propanediol. 1,3-propanediol is a very high-valued specialty chemical, with a current marketing price of $12 per pound. Because of its high price, the use of 1,3-propanediol is limited to specialty polyester fibers, films and coatings. 1,3-propanediol does not impart the stiffness of ethylene glycol, yet avoids the floppiness of 1,4-butanediol and 1,6-hexanediol. Polyesters based on 1,3-propanediol have unique features that are difficult to obtain from other glycols. For instance, polytrimethylene terephthalate (PTT), a new polyester based on 1,3-propanediol has the elastic recovery of nylon and the chemical resistance of polyester (Stinson, 1995). It is positioned by its manufacturers as a rival to tradition nylon in carpet area (Chapman, 1997).

At the current time, the production scale of 1,3-propanediol is small, but is quickly expanding. Dedussa, a German-based company, has just installed 2.2 million lb per year capacity at its plant in Antwerp, Belgium (Stinson, 1995). Shell has also plan to install a 160-million-pound unit at Geiser, Louisiana by early 1999 (Chapman, 1997). The need for 1,3-propanediol is great in production of specialty polymers. Dedussa, Shell and Dupont all have plan to startup or expand their PTT plants (Chapman, 1996). If a low cost process can be found, it is expected that 1,3-propanediol could quickly become a commodity chemical.

Currently, 1,3-propanediol is made by hydration of acrolein to β-hydroxypropionaldehyde, which yields 1,3-propanediol upon hydrogenation. Acrolein is a very dangerous chemicals. It must be synthesized on site. The yield from the acrolein process is very low (Gunzel *et al.*, 1991). The problem is with the first step of the process. Acrolein has a large tendency to polymerize through self-condensation, and hydration must compete with this reaction. 1,3-propanediol may also be made via carbonylation of ethylene oxide to β-hydroxypropionaldehyde. The yield of 1,3-propanediol in this process is also poor, however. Lack of conversion efficiency in the current commercial processes is the main reason for the current high price and small production scale of 1,3-propanediol.

Effort to convert glycerol to 1,3-propanediol has been reported. These processes will be reviewed later in Part 2 of this dissertation. Briefly, these processes are still under investigation and are not yet commercializable.

In the current research, a new concept to convert glycerol to 1,3-propanediol is proposed. This new concept selectively transforms the second hydroxyl group of glycerol into a tosyloxy group with the help of a group protection technique, and then removes it by hydrogenolysis. The technical feasibility of this new concept is verified experimentally in this work. Before this work, hydrogenolysis of tosylates are generally effected with base metal hydrides, such as $LiAlH_4$ and $LiHBEt_3$. In this work, for the first time, tosylates with a hydroxy group adjacent to the tosyloxy group are hydrogenolyzed with molecular hydrogen in the presence of a nickel or ruthenium catalyst.

HF Saccharification. As previously mentioned, in addition to the HF process, other saccharification concepts, including dilute mineral acid, concentrated mineral acid and enzymatic processes, are available to convert lignocellulosic biomass into sugars. The research on HF saccharification in the current project is motivated by the potential advantages it has over other processes. As summarized by Hawley *et al.* (1986) and

Romer
to 95
recov
the H
produ
is rec
and r
HF s

resea
at M
a pa
reac
expe
are
som

nat
beh
the
ads
Thi
reac

Rorrer (1989), the HF saccharification processes is characterized by high sugar yield (85 to 95% of the theoretical yield), easy catalyst recovery (up to 99.6% of the HF may be recovered), and little pretreatment requirement (only drying and chipping). In addition, the HF process operates under ambient reaction time, needs short reaction time and can produce a lignin residue suitable for further conversion. The HF vapor used in the process is recycled internally. The HF residue left with the reacted substrates is dissolved in water and neutralized in post-hydrolysis. Both measures minimize the HF emission from the HF saccharification process.

The current work on vapor-phase HF saccharification is a continuation of the research initiated by Rorrer *et al* (1988), Moring (1989), Rorrer (1989) and Reath (1989) at Michigan State University. It has focused on modeling of the HF adsorption process in a packed-bed reactor. However, experiments have also been performed with a bench-scale reactor to study the behavior of HF adsorption in the packed-bed reactor. Similar experiments has been done previously by Reath (1989), but the experiments in this work are conducted in a broader range of operating conditions, which leads to the finding of some behavior of HF adsorption that has not been observed by Reath.

Two models of HF adsorption have been developed. One is phenomenological nature, and is developed based on experimental observations of the HF adsorption behavior in a bench-scale, packed-bed reactor. The second model is more advanced than the first one. It is developed based on a detailed analysis of the HF flow, the intrinsic HF adsorption and the heat transfer processes occurring in the reactor during HF adsorption. This model provides a great deal of insight into the HF adsorption process in a packed-bed reactor, and it can be used to predict the HF loading distribution, as well as the overall HF

loading. as
modeling w
adsorption p

Results
Part I prese
dehydroxyla

Part I c
Chapter 3 de
of the mecha

Part II c
concept, as
documents th
1,3-propaned
a discussion

Based o
published in
These papers
To avoid re
Therefore, o
briefly desc
saccharificati
in Chapter 10

loading, as functions of the adsorption time and operating conditions. The above modeling work provides a theoretical foundation to design and operation of the HF adsorption process in a packed-bed reactor.

Results from the current research are presented in this dissertation in three parts. Part I presents the work on sugar hydrogenolysis; Part II presents the work on glycerol dehydroxylation; Part III presents the work on HF saccharification.

Part I contains four chapters: Chapter 2 is an introduction to sugar hydrogenolysis; Chapter 3 describes the experimental system and methods; Chapter 4 presents the results of the mechanism study; and Chapter 5 presents the results of the selectivity study.

Part II contains three chapters: Chapter 6 presents the new glycerol dehydroxylation concept, as well as a review of the current glycerol conversion processes; Chapter 7 documents the experimental procedures used to carry out the conversion of glycerol to 1,3-propanediol; and Chapter 8 presents the experimental results. Chapter 8 also includes a discussion on the future work that may be done on glycerol dehydroxylation.

Based on the research on HF saccharification, two papers have been written and been published in *Chemical Engineering Science* (Wang *et al.*, 1994; Wang *et al.*, 1995a). These papers document basically all the work that has been done on HF saccharification. To avoid rewriting, only abstracts of these papers are included in this dissertation. Therefore, only one chapter, Chapter 9, is allocated to Part III in this dissertation, to briefly describe the rationale, scope and accomplishments of the research on HF saccharification. Following Part III, a general summary of the current research is provided in Chapter 10 and recommendations on future work are made in Chapter 11.

2.1

hydr

This

accor

Suga

poter

propy

alcoh

Sugar

condi

bond

fact,

hydro

CHAPTER 2

INTRODUCTION: SUGAR HYDROGENOLYSIS

2.1 Literature Review

Under high temperature and high hydrogen atmosphere, sugars can be catalytically hydrocracked into lower polyhydric alcohols in the presence of transition metal catalysts. This process is called hydrogenolysis, because the bond cleavage reactions are accompanied with hydrogen addition as shown below:

$$R_3C-CR'_3 + H_2 \longrightarrow R_3CH + HCR'_3$$

$$R_3C-OH + H_2 \longrightarrow R_3CH + H_2O$$

Sugars are available from a variety of biomass raw materials. Hydrogenolysis provides a potential process to convert sugars to synthetically important polyols, including glycerol, propylene glycol and ethylene glycol.

In the literature, sugar hydrogenolysis is discussed indistinguishably from sugar alcohol hydrogenolysis, because of the close relationship between these two reactions. Sugar hydrogenolysis and sugar alcohol hydrogenolysis take place under the same conditions, yield the same products and have identical bond cleavage mechanisms and bond cleavage precursors (sugars), as will be shown later in Chapter 4. As a matter of fact, in sugar hydrogenolysis, a significant portion of the starting sugar will be hydrogenated to sugar alcohol before being finally hydrogenolyzed into lower polyhydric

alcohols. I
hydrogenolys
understood a
context indic

The sug
(Connor and
was started n
Laboratory (
been increas
sugar hydrog
interest in bi
hydrogenoly
this process.
studies on p
selectivity ar

2.1.1 Studie

In the
purpose of
experiments,
nickel on kies
reaction was
to 240 °C, an

alcohols. In some occasion, sugar alcohols have been used to study the sugar hydrogenolysis process. In the following, references to sugar hydrogenolysis should be understood as the hydrogenolysis of both sugars and sugar alcohols, except where the context indicates otherwise.

The sugar hydrogenolysis reactions have been performed since as early as the 1930's (Connor and Adkins, 1932). However, the research for the purpose of biomass conversion was started much later. The first one was reported in 1950's, at the U.S. Forestry Products Laboratory (Clark, 1958). Since then, the body of literature on sugar hydrogenolysis has been increasing steadily. Like many other biomass conversion projects, the research on sugar hydrogenolysis underwent a "boom" period in the 1980's, as a result of the general interest in biomass conversion stimulated by the oil crisis in 1970's. The research on sugar hydrogenolysis has been conducted in many countries, and has covered various aspects of this process. In the following, the available literature is reviewed according to four topics: studies on process development, studies on reaction mechanism, studies on reaction selectivity and studies on reaction kinetics.

2.1.1 Studies on Process Development

In the 1950's, Clark (1958) started the first research on sugar hydrogenolysis for purpose of biomass conversion at the U.S. Forestry Products Laboratory. In his experiments, sorbitol was reacted under the hydrogenolysis conditions in the presence of a nickel on kieselguhr catalyst. Calcium hydroxide was added to promote the reaction. The reaction was carried out in aqueous phase in a batch reactor. The temperature was at 215 to 240 °C, and the hydrogen pressures was at 2000 to 5600 *psi*. The identified products inc

com

gly

max

expe

and

(Boel

of cat

and B

perfor

range

and 2

glycer

covere

believe

Va

hydroge

was don

100-300

ethylene

hexitols

included glycerol, propylene glycol, ethylene glycol, erythritol and xylitol. The product composition varied with the reaction time. The concentration of xylitol, erythritol, glycerol increased during the initial period of an experimental run, but after reaching a maximum, they started declining. The maximum yield of glycerol obtained in Clark's experiments was 40%.

At about the same time as Clark's work, according to Boelhouwer *et al.*, Geerards and co-workers investigated the hydrogenolysis of sucrose with HI as a catalyst (Boelhouwer *et al.*, 1960). The products they obtained had very low oxygen contents.

In their own work, Boelhouwer *et al.* (1960) hydrogenolyzed sucrose with a variety of catalysts, including nickel on kieselguhr, nickel-thorium oxide on kieselguhr, and MgO and BeO promoted copper chromite. Calcium oxide was also added. The reaction was performed in a rotating autoclave with methanol as the reaction medium. The temperature range was between 195 and 250 °C, and the hydrogen pressure range was between 150 and 200 atm. The products were fractionated by distillation. In one experiment, the glycerol fraction was reported to account for 61% of the product. Since each fraction covered a broad boiling range, exact products were not determined. However, it was believed that glycerol, propylene glycol and ethylene glycol were included in the products.

Van Ling and co-workers (van Ling *et al.*, 1967; van Ling and Vlugter, 1969) hydrogenolyzed sucrose, glucose, fructose and inulin with CuO-CeO_2-SiO_2. The reaction was done in a 250 mL autoclave, at a temperature of 200-250 °C, a hydrogen pressure of 100-300 atm, with addition of caladium hydroxide. In the hydrogenolysis of sucrose, ethylene glycol, propylene glycol, glycerol, teritols, pentinols, hexitols and dehydrated hexitols were obtained. In hydrogenolysis of other sugars, the products were similar.

Van Li

process to p

first was a tu

cm. The rea

Because of s

yield (below

tank reactors

operating vol

reaction syste

(CuO-CeO$_2$-S

A great

hydrogenolyze

hydrogenolyze

platinum on ca

carbonaceous p

using a sulfur-

64.6% in one e

ruthenium and

sorbitol in both

work by the Mo

1991), various s

were subject to

Ranney Cu and ot

Van Ling *et al.* (1970) further developed a continuous pilot-scale hydrogenolysis process to produce glycerol from sucrose. Two reactor configurations were studied. The first was a tubular reactor, composed of a 2 *m* long stainless steel tube with a diameter of 2 *cm*. The reactor was filled with 1/8-inch Raschig rings to promote the gas-liquid contact. Because of sucrose decomposition, this reaction system furnished only a poor glycerol yield (below 20%). The second reaction system was composed of two continuous stirred-tank reactors (CSTR) in series. Each reactor had a total volume of 500 *ml* and an operating volume of 250 *ml*. Sucrose was fed in 75% methanol-water solution. With this reaction system, a glycerol yield up to 30% was obtained. The catalyst used in this study ($CuO-CeO_2-SiO_2$) was the same as in their previous research.

A great deal of work was accomplished in the 1980's. Chao *et al.* (1982) hydrogenolyzed sorbitol with a supported nickel catalyst in aqueous phase. Arena (1983) hydrogenolyzed sorbitol, glucose and sucrose in the presence of nickel on kieselguhr, platinum on carbon, or metals (including palladium, rhenium and copper) deposited on a carbonaceous pyropolymer structure. Duback and Knapp (1984) hydrogenolyzed sorbitol using a sulfur-modified ruthenium catalyst, and achieved a propylene glycol yield of 64.6% in one experiment. Ariono *et al.* (1986) hydrogenolyzed glucose with palladium, ruthenium and rhodium supported on carbon. Tanikella (1983a; 1983b) hydrogenolyzed sorbitol in both aqueous and non-aqueous solutions to produce ethylene glycol. In the work by the Motassier group (Sohounloue *et al.*, 1983; Montassier *et al.*, 1988, 1989 and 1991), various sugar alcohols, including sorbitol, xylitol, erythritol and even glycerol, were subject to the hydrogenolysis conditions. The catalysts used included Ru/SiO_2, Ranney Cu and other metal based catalysts.

In all t
heterogeneou
(Andrews an
and *manno*-
pyrrolidinone
atm. The r
heterogenous
With fructose
glycerol relat
hydrogenation
to the previous
favored than in

Studies o
al., 1975; Pikk
two-stage, low
products. The
equilibrium.

2.1.2 Studies

In sugar hy
are promoted b
Montassier *et al*

In all the work reviewed above, the hydrogenolysis has been carried out with heterogeneous catalysts, but a process was also reported using homogenous catalysts (Andrews and Klaeren, 1989). Andrews and Klaeren hydrogenolyzed fructose, glucose and *manno*-heptulose with $H_2Ru(PPh_3)$. The reaction was done in *N*-methyl-2-pyrrolidinone solvent, at a temperatures of 50 to 100 °C and a hydrogen pressures of 20 *atm*. The reaction conditions were significantly less severe than those used with heterogenous catalysts. In most of the experiments, KOH was added as a co-catalyst. With fructose as the starting compound, this process provided very good selectivity toward glycerol relative to other degradation products. However, because of the rapid simple hydrogenation of fructose (to sorbitol and mannitol), the overall glycerol yield was similar to the previous processes. With glucose as the starting compound, glycerol was much less favored than in the case of fructose.

Studies on separation of the hydrogenolysis products were also reported (Sokolvo *et al.*, 1975; Pikkov *et al.*, 1973; Solkovo *et al.*, 1977). Sokolvo *et al.*, (1975) developed a two-stage, low pressure distillation process to separated glycerol from other reaction products. They also determined the activity coefficients for the glycerol-water vapor equilibrium.

2.1.2 Studies on Reaction Mechanism

In sugar hydrogenolysis, both C-C and C-O are subject to cleavage. These reactions are promoted by transition metals and base co-catalysts. Cleavage of C-O bonds, as Montassier *et al.* (1988 and 1989) proposed, is through dehydration of a β-hydroxyl carbonyl:

The structure

molecule, and

The direct pro

carbonyl, whic

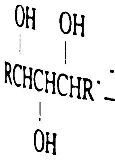
just discussed.

hydrogenation s

The origin

explain the C-C

reaction:



Andrews and Kla

that the primary

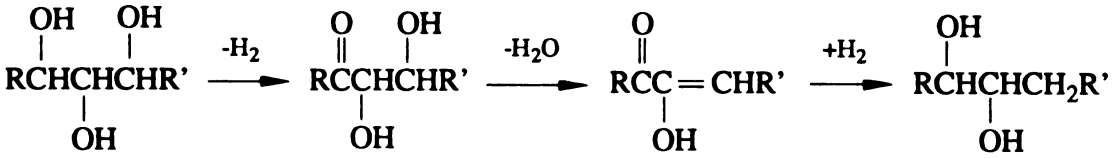
According to this

Cleavage of this

subsequently hydro

Later, howeve

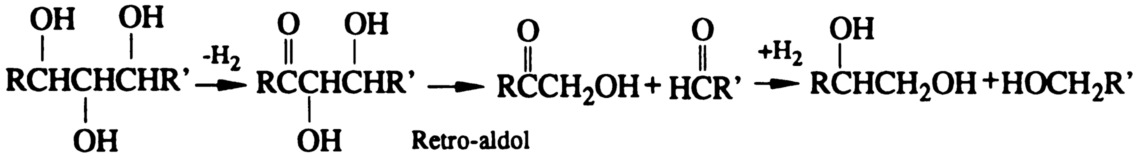
carbonyl:



$$R\overset{OH}{C}H\underset{OH}{C}H\overset{OH}{C}HR' \xrightarrow{-H_2} R\overset{O}{\overset{\|}{C}}\underset{OH}{C}H\overset{OH}{C}HR' \xrightarrow{-H_2O} R\overset{O}{\overset{\|}{C}}\underset{OH}{C}=CHR' \xrightarrow{+H_2} R\overset{OH}{C}H\underset{OH}{C}HCH_2R'$$

The structure of this β-hydroxyl carbonyl is already contained in an open-chain sugar molecule, and it may be generated from a sugar alcohol molecule by dehydrogenation. The direct product from dehydration of the β-hydroxyl carbonyl is an α,β-unsaturated carbonyl, which yields a polyhydric alcohol upon hydrogenation. In the reaction scheme just discussed, the dehydration step is catalyzed by bases, and the dehydrogenation and hydrogenation steps are catalyzed by transition metal catalysts.

The original mechanism proposed by the Montassier group (Sohounloue, 1983) to explain the C-C cleavage in sugar and sugar alcohol hydrogenolysis is the retro-aldol reaction:



$$R\overset{OH}{C}H\underset{OH}{C}H\overset{OH}{C}HR' \xrightarrow{-H_2} R\overset{O}{\overset{\|}{C}}\underset{OH}{C}H\overset{OH}{C}HR' \xrightarrow[\text{Retro-aldol}]{} R\overset{O}{\overset{\|}{C}}CH_2OH + H\overset{O}{\overset{\|}{C}}R' \xrightarrow{+H_2} R\overset{OH}{C}HCH_2OH + HOCH_2R'$$

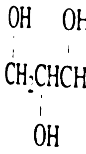
Andrews and Klaeren (1989) suggested the same mechanism, based on their observation that the primary C-C cleavage site is β to the carbonyl group in sugar hydrogenolysis. According to this mechanism, the C-C cleavage precursor is again a β-hydroxyl carbonyl. Cleavage of this β-hydroxyl carbonyl leads to an aldehyde and a ketone, which are subsequently hydrogenated to alcohols.

Later, however, Montassier *et al.* (1988) felt that it was difficult to explain the absence of m

and other su

another mech

hydrogenolys



$$\overset{OH}{CH_2}\underset{OH}{CH}\overset{OH}{CH}$$

This mechan

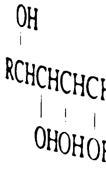
hydrogenolysis

allows format

formaldehyde

xylitol and sort

the mechanism



$$R\overset{OH}{CH}\underset{OH}{CH}\underset{OH}{CH}\underset{O}{CH}$$

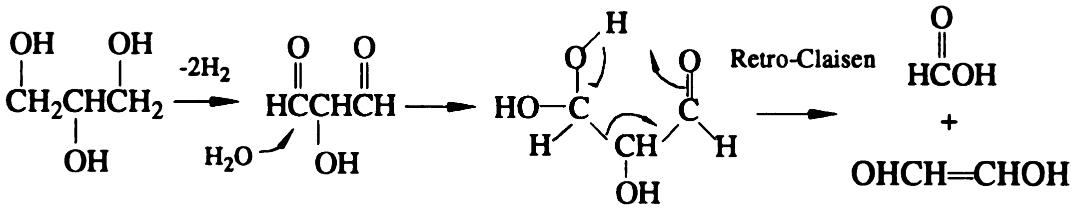
This mechanism

The reactio

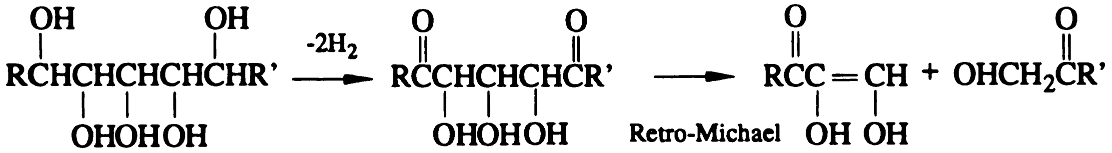
in sugar hydroge

support any of the

absence of methanol and the presence of CO_2 in the hydrogenolysis products of glycerol and other sugar alcohols with the retro-aldol mechanism. Therefore, they proposed another mechanism, namely the retro-Claisen reaction, for the C-C cleavage in glycerol hydrogenolysis:



This mechanism allows formation of formic acid which decomposes under the hydrogenolysis conditions to form CO_2. The mechanism based on the retro-aldol reaction allows formation of formaldehyde rather than formic acid. Upon hydrogenation, formaldehyde yields methanol. To explain the C-C cleavage in the hydrogenolysis of xylitol and sorbitol, Montassier *et al.* (1988) also proposed the retro-Michael reaction as the mechanism:



This mechanism requires a δ-dicarbonyl as the bond cleavage precursor.

The reaction mechanisms just reviewed are all consistent with the products obtained in sugar hydrogenolysis. Other than that, no direct experimental evidence is available to support any of the bond cleavage mechanisms proposed.

2.1.3 Studi

Studies

Sohounloue

sucrose, glu

selectivity p

representing

glycol) in the

the percentag

percentage, re

products inclu

that the C.S

variables, such

dependent on t

increased. It w

that it is promo

Sohounlo

sorbitols. He

increased. He a

glycerol to prop

increased in a ne

were experiment

not well reflected

2.1.3 Studies on Reaction Selectivity

Studies on the reaction selectivity have been reported by van Ling *et al.* (1969) and Sohounloue *et al.* (1983). Ling *et al.* studied the effect of the starting sugars, including sucrose, glucose, fructose and inulin, on the reaction selectivity. He defined three selectivity parameters for sugar hydrogenolysis: 1) C.S., or cleavage selectivity, representing the percentage of the C3-C3 cleavage products (glycerol and propylene glycol) in the total cleavage products; 2) H.S., or hydrogenation selectivity, representing the percentage of glycerol in the total C3-C3 cleavage products; and 3) C.P., or cleavage percentage, representing the percentage of the bond cleavage products in all reaction products including hexitols from the starting sugar via simple hydrogenation. He found that the C.S varies with the starting sugar, but was independent of the other reaction variables, such as catalyst type and base concentration. The H.S, as he reported, is also dependent on the starting sugar, and in addition it decreases as the reaction temperature is increased. It was also found that the C.P increases with decreasing hydrogen pressure, and that it is promoted by small addition of $Ca(OH)_2$.

Sohounloue *et al.* (1983) studied the reaction selectivity in the hydrogenolysis of sorbitols. He observed that the C-C cleavage became random as the temperature increased. He also observed that the C-C v.s. C-O selectivity, as defined by the ratio of the glycerol to propylene glycol, decreased with temperature in a basic reaction medium but increased in a neutral medium. Both of the studies by Ling *et al.* and by Sohounloue *et al.* were experimental in nature, and the mechanisms controlling the reaction selectivity were not well reflected.

2.1.4 Studi

The fir
(1958), who
hydrogen pre
in a pressure
activation ene
determined to

Chang *e*
slightly differ
Raney nickel a
in the concentr
minus 0.8 orde
amount of cata
experiments by
was sufficiently
Chang *et al.* (
reaction was als

The work
modeling of su
hydrogenolysis
model had been
hydrogenolysis (
subsequently adop

2.1.4 Studies on Reaction Kinetics

The first empirical kinetic study on sugar hydrogenolysis was reported by Clark (1958), who found that the hydrogenolysis of sorbitol is first-order in the substrate. The hydrogen pressure does have effect on the reaction rate, but this effect has been considered in a pressures dependent activation energy. For a hydrogen pressure of 5600 psi, the activation energy was determined to be 44 kcal; for a hydrogen pressure of 2900 psi, it was determined to be 33 kcal.

Chang *et al.* (1985) studied the kinetics of sorbitol hydrogenolysis also, but used a slightly different catalyst. Instead of nickel on kieselguhr as in Clark' work, they used Raney nickel as the catalyst. They found that the hydrogenolysis of sorbitol is first order in the concentration of sorbitol, as Clark did. In addition, they found that this reaction is minus 0.8 order with respect to the hydrogen pressure and second order with respect to the amount of catalyst. The activation energy was determined to be about 22 kcal/mol. The experiments by Chang *et al.* were conducted in an one-liter autoclave. The agitation rate was sufficiently high to eliminate the effect of external mass transfer. In the work of Chang *et al.* (1985), the kinetics of glycerol hydrogenolysis was also studied. The reaction was also found to be first-order in the substrate.

The work by Tronconi *et al.* (1992) was the only one reportedly on mathematical modeling of sugar hydrogenolysis. This work provided a kinetic model for sorbitol hydrogenolysis which was different from the previous work. The authors claimed that this model had been developed based on their analysis of the whole reaction network of hydrogenolysis (which is not shown in the paper). The developed model was subsequently adopted in a simple pseudo-homogeneous non-isothermal plug flow reactor model. Com

and pilot-sca

kinetic expre

A kinet

(1973). How

2.2 Object

A major

control. As di

generally non-

glycol are proc

levels. It is cle

hydrogenolysis

Another r

Knowledge of h

importance for

Review, three

Michael, have b

dehydration mec

is basically non-e

the C-C cleavage

verified.

In view of th

model. Comparison of this reactor model against their experimental data from their micro and pilot-scale reactors allowed them to determine the model parameters present in the kinetic expression.

A kinetic study on sugar hydrogenolysis was also reportedly done by Stefoglo *et al.* (1973). However, the detail of this study is not clear.

2.2 Objective and Scope of Current Research

A major issue in development of the sugar hydrogenolysis process is selectivity control. As discussed in the Literature Review, current sugar hydrogenolysis processes are generally non-selective. In these processes, glycerol, propylene glycol and ethylene glycol are produced in a mixture, along with other polyhydric alcohols occurring at lower levels. It is clear that a more selective process needs to be developed, in order for sugar hydrogenolysis to be commercially viable.

Another major issue of sugar hydrogenolysis concerns the reaction mechanism. Knowledge of how the C-C and C-O bonds are broken in sugar hydrogenolysis is of great importance for control of the reaction selectivity. So far, as discussed in the Literature Review, three competing mechanisms, namely retro-aldol, retro-Claisen and retro-Michael, have been proposed to explain the C-C cleavage in sugar hydrogenolysis. The dehydration mechanism of C-O cleavage is not disputed, but direct experimental evidence is basically non-existent. Before a useful strategy for selectivity control can be developed, the C-C cleavage mechanism must be clarified and the C-O cleavage mechanism must be verified.

In view of the above situation, the objectives of the current research are determined as: 1) to carry out a mechanism study to discriminate and verify the existing bond cleavage mechanisms of sugar hydrogenolysis; and 2) to carry out a selectivity study to investigate the factors controlling the selectivity of sugar hydrogenolysis. In this capacity, a series of 1,3-diol model compounds are hydrogenolyzed, to establish the mechanism of C-C and C-O bond cleavage in sugar hydrogenolysis. The experimental work confirmes our theoretical conception that the C-C bond breaks via the retro-aldol reaction of a β-hydroxyl carbonyl precusor, and it also provides for the first time direct evidence that the C-O cleavage is through dehydration of the same β-hydroxyl carbonyl precursor just mentioned.

In the selectivity study, the research focuses on control of the C-O cleavage in sugar hydrogenolysis. It is envisioned that the reaction products of sugar hydrogenolysis would be considerably simplified, and the reaction would be directed to produce the highest-valued glycerol, if the C-O cleavage can be controlled somehow. Thus in this work, the competition between the C-C and C-O cleavage is studied again using a 1,3-diol model compound (2,4-pentanediol). Experiments, as well as computer simulation, are conducted to investigate the effects of temperature, base concentration, hydrogen pressure, catalyst amount and catalyst type on the selectivity, as well as possible ways to improve this selectivity to C-C bond cleavage.

CHAPTER 3

EXPERIMENTAL SYSTEM AND METHODS

3.1 Experimental System and Procedure

In this work, 1,3-diols with various structural features were hydrogenolyzed as model compounds to study the reaction mechanism and selectivity of sugar hydrogenolysis. These hydrogenolysis experiments were performed in a specially designed, stainless steel reactor of 50 mL capacity. The detailed design of this reactor is given in Figure 3-1.

This hydrogenolysis reactor is basically a pressure vessel (note that hydrogenolysis is effected at high temperature and high hydrogen pressure), and is equipped with a magnetic stirring bar. Because of the need to regularly take samples during the reaction, a sampling port is provided with the reactor. This sampling system is composed of a sampling valve, a sampling tubing and an inlet filter emerged in the reaction medium. This filter has a 0.45 μ rating. It can prevent solid catalyst particles from entering the sampling system and generate clean samples suitable for direct HPLC and GC injection. This filter also reduces the pressure exerted on the sampling valve, which levitates the requirement on the sampling valve. The sampling tubing is very thin, with an inner diameter of about 0.1 mm. The dead volumes of the sampling valve and the inlet filter are 0.2 and 0.4 μL, respectively. The whole sampling system has a total hold volume of only several microliters. This guarantees that the samples taken from this system always

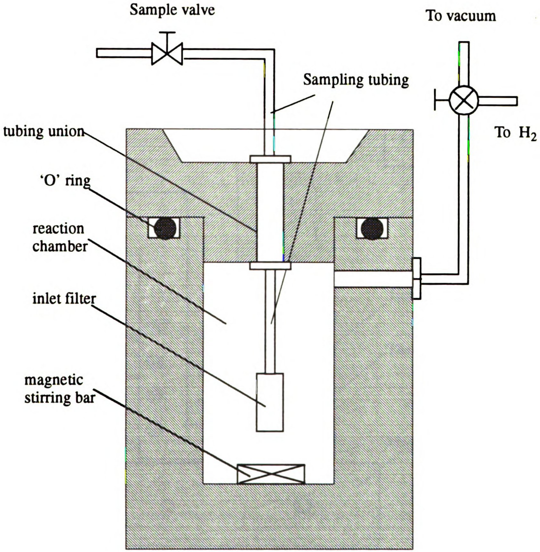


Figure 3-1. Illustration of Hydrogenolysis Reactor

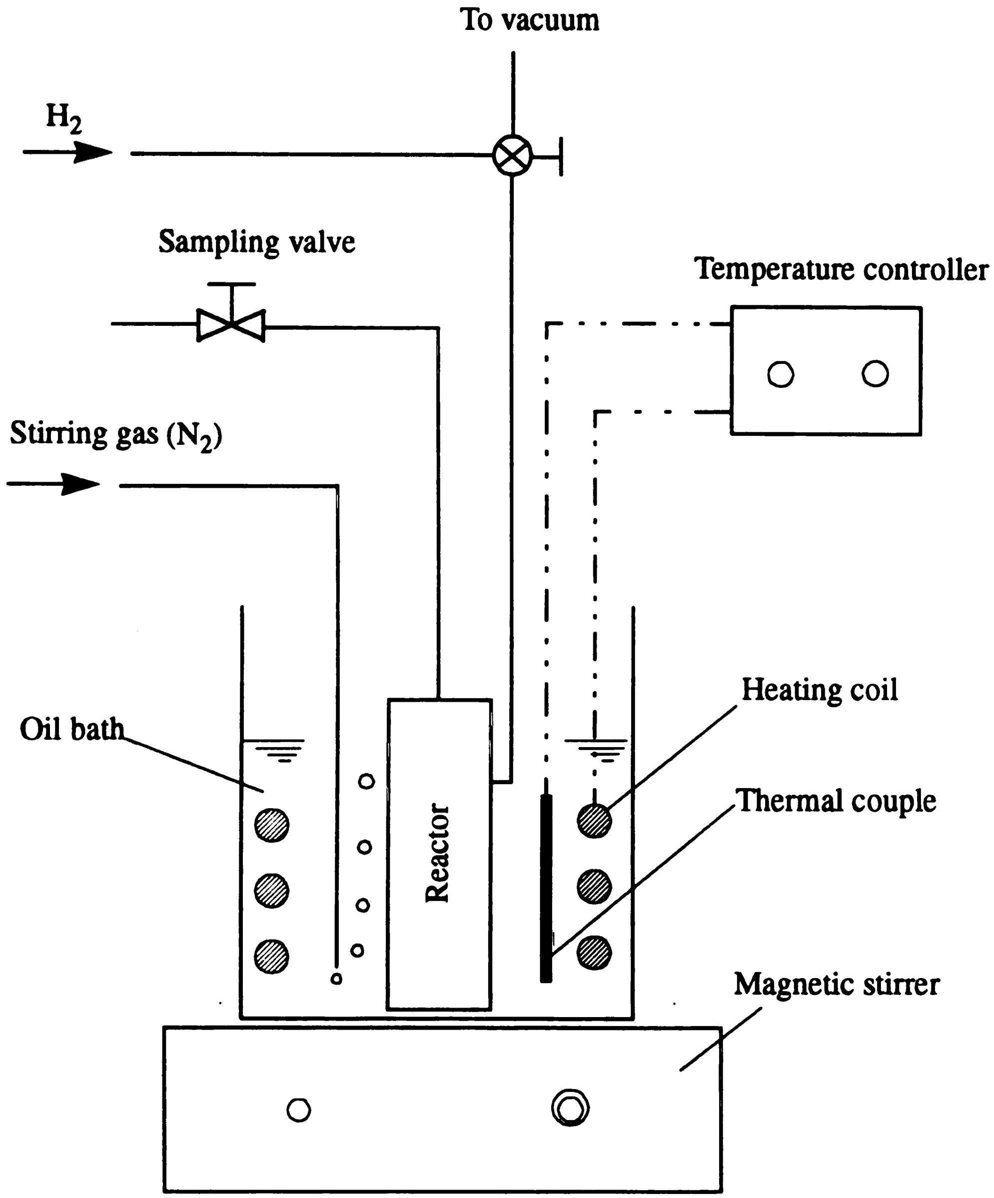


Figure 3-2. Schematic Illustration of Experimental System

represent the current condition in the reactor.

The reactor is heated in a silicone oil bath. The heat is provided by an electric heating coil emerged in the oil bath, which is constantly stirred by bubbling a nitrogen flow into it. The temperature of the oil bath is controlled by a temperature controller, which controls the oil temperature within ± 3 °C of the set point. The reaction medium is stirred by the magnetic stirring bar inside the reactor. To provide the magnetic force to the stirring bar, the whole oil bath is placed on a magnetic stirrer.

The hydrogen pressure is provided to the reactor by a hydrogen cylinder with high pressure regulator for pressure control. To prevent over-pressurization, a pressure relief valve is installed in the H_2 supply line as a safety device. A vacuum line is also connected to the reactor for the purpose of initial reactor purging. A schematic illustration of the whole experimental system is provided as Figure 3-2.

To carry out the hydrogenolysis reaction, the starting diol, the catalyst, a certain amount of sodium hydroxide (if needed) and a proper amount of distilled water are placed in the reactor. The reactor is purged by alternately connecting it to hydrogen and vacuum. After purging, the reactor is pressurized with hydrogen, and heating and stirring (both inside and outside of the reactor) are started. Thereupon, the reaction starts. During the reaction course, reaction samples are taken regularly from the reactor and are analyzed for composition of reaction products. After the the desired conversion has occurred the reaction is stopped by shutting off the heater and hydrogen supply.

3.2 Reaction Regents and Product Analysis

All the 1,3-diols and catalysts used in this work are purchased from Aldrich and are used as received. The hydrogen (99.9% pure) is obtained from Purity Cylinder Gases and AGA Gas Products.

The hydrogenolysis products from the mechanism study are analyzed by GC and HPLC. The GC column used in this work is a non-polar DB624 column, supplied by J&W Scientific Company. With this column, samples can be injected in the aqueous phase. The HPLC column used in this work is a 25 x 0.46 *cm* C18 column obtained from Whatman (Cat.# 4621-1502). The detectors used with GC and HPLC are a FID detector and a differential refractometer, respectively. In both cases, samples taken from the reactor are injected directly.

In the mechanism study, seven different 1,3-diols are hydrogenolyzed, giving seven different sets of products. GC and HPLC methods are developed for each set of these products, and are documented here in Table 3-1 and Table 3-2, respectively. However, the hydrogenolysis products from the selectivity study are analyzed by GC only. Since the selectivity study demands more accurate measurement of the product concentrations, calibration curves are prepared for all the products from 2,4-pentanediol hydrogenolysis (2,4-pentanediol is the model compound used in selectivity study).

In the HPLC chromatograms of actual reaction products, a skewed peak has often been seen at a retention time well earlier than those for the expected reaction products. This peak is identified as the impurities introduced into the reaction medium with Raney Cu and Ni catalysts. An experiment without any 1,3-diol substrate was performed. Samples taken from this experiment are found to give the same skewed peak. Since no

Table 3-1. HPLC Methods for 1,3-Diol Hydrogenolysis Products .

Conditions	Retention Time
Product Set #1: 2,4-dimethyl-2,4-pentanediol	
solvent: 25% acetonitrile/water flow rate: 1.5 ml/min (isocratic) temperature: 40 °C	1. 2,4-dimethyl-2,4-pentanediol: 2.92 min
Product Set #2: 2-methyl-2,4-pentanediol	
solvent: 42% methanol/water flow rate: 0.8 ml/min (isocratic) temperature: 40 °C	1. acetone: 3.98 min 2. isopropanol: 4.25 min 3. 2-methyl-2,4-pentanediol: 4.91 min 4. 4-methyl-2-pentanol: 11.85 min
Product Set #3: 2,2,4-trimethyl-1,3-pentanediol	
solvent: 25% acetonitrile/water flow rate: 2.0 ml/min (isocratic) temperature: 40 °C	1. methanol: 1.30 min 2. isobutanol: 2.31 min 3. 2,2,4-trimethyl-1,3-pentanediol: 3.62 min 4. 2,4-dimethyl-3-pentanol: 9.98 min
Product Set #4: 2,2-dimethyl-1,3-propanediol	
solvent: 10% acetonitrile/water flow rate: 1.5 ml/min (isocratic) temperature: 60 °C	1. methanol: 1.80 min 2. 2,2-dimethyl-1,3-propanediol: 2.70 min 3. isobutanol: 5.15 min
Product Set #5: 2,4-pentanediol	
solvent: 42% methanol/water flow rate: 0.8 ml/min (isocratic) temperature: 40 °C	1. ethanol: 3.62 min 2. 2,4-pentanediol: 3.84 min 3. isopropanol: 4.22 min 4. 2-pentanone: 6.54 min 5. 2-pentanol: 8.21 min
Product Set #6: 1,3-butanediol	
solvent: 3% acetonitrile/water flow rate: 1.2 ml/min (isocratic) temperature: 60 °C	1. methanol: 2.58 min 2. ethanol: 3.15 min 3. 1,3-butanediol: 3.23 min 4. acetone: 4.50 min 5. isopropanol: 5.00 min 6. 2-butanone: 9.48 min 7. 2-butanol: 10.98 min 8. n-butanol: 13.85min
Product Set #7: 1,3-propanediol	
solvent: 0.3% acetonitrile/water flow rate: 1.5 ml/min (isocratic) temperature: 60 °C	1. methanol: 2.04 min 2. 1,3-propanediol: 2.32 min 3. ethanol: 2.90 min 4. n-propanol: 5.51 min

Table 3-2. GC Methods for 1,3-Diol Hydrogenolysis Products.

Conditions	Retention Time
Product Set #1: 2,4-dimethyl-2,4-pentanediol	
initial temperature/time: 150 °C/1 min temperature ramp: 40 °C/min final temperature/time 260 °C/3 min	1. 2,4-dimethyl-2,4-pentanediol: 2.10 min
Product Set #2: 2-methyl-2,4-pentanediol	
initial temperature/time: 80 °C/1 min temperature ramp: 40 °C/min final temperature/time 260 °C/10 min	1. isopropanol: 1.14 min 2. acetone: 1.20 min 3. 4-methyl-2-pentanol: 2.50 min 4. 2-methyl-2,4-pentanediol: 3.76 min
Product Set #3: 2,2,4-trimethyl-1,3-pentanediol	
initial temperature/time: 150 °C/1 min temperature ramp: 30 °C/min final temperature/time 260 °C/10 min	1. methanol: 0.91 min 2. isobutanol: 1.11 min 3. 2,4-dimethyl-3-pentanol: 1.57 min 4. 2,2,4-trimethyl-1,3-pentanediol: 3.35 min
Product Set #4: 2,2-dimethyl-1,3-propanediol	
initial temperature/time: 150 °C/1 min temperature ramp: 30 °C/min final temperature/time 260 °C/10 min	1. methanol: 0.92 min 2. isobutanol: 1.11 min 3. 2,2-dimethyl-1,3-propanediol: 2.16 min
Product Set #5: 2,4-pentanediol	
initial temperature/time: 40 °C/1 min temperature ramp: 40 °C/min final temperature/time 260 °C/3 min	1. ethanol: 1.43 min 2. isopropanol: 1.69 min 3. 2-pentanone: 3.09 min 4. 2-pentanol: 3.19 min 5. 2,4-pentanediol: 4.68 min
Product Set #6: 1,3-butanediol	
initial temperature/time: 40 °C/1 min temperature ramp: 40 °C/min final temperature/time 260 °C/3 min	1. methanol: --- min 2. ethanol: 1.49 min 3. 1,3-butanediol: --- min 4. acetone: --- min 5. isopropanol: 1.69 min 6. 2-butanone: --- min 7. 2-butanol: --- min 8. n-butanol: --- min
Product Set #7: 1,3-propanediol	
initial temperature/time: 120 °C/1 min temperature ramp: 30 °C/min final temperature/time 260 °C/10 min	1. methanol: 0.90 min 2. ethanol: 0.96 min 3. n-propanol: 1.09 min 4. 1,3-propanediol: 2.32 min

1,3-diol is added to the reactor in this experiment, this skewed peak can only result from the catalyst added.

4.1 The

As r

Claisen a

hydrogen

either re

retro-ald

require a

further

unfavor

carbon

mono-c

dehydra

favorab

resulte

domina

reaction

the dehy

CHAPTER 4

MECHANISM OF SUGAR HYDROGENOLYSIS

4.1 Theoretical Considerations

As reviewed in the previous chapter, three competing mechanisms (retro-aldol, retro-Claisen and retro-Michael) have been proposed for the C-C cleavage in sugar hydrogenolysis. However, two theoretical considerations prevent us from believing that either retro-Claisen or retro-Michael is a dominating C-C cleavage mechanism over the retro-aldol in hydrogenolysis. First, both the retro-Claisen and retro-Michael mechanisms require a dicarbonyl precursor. The formation of a dicarbonyl presumedly occurs through further dehydrogenation of a mono-carbonyl. As dehydrogenation is thermodynamically unfavorable, the dicarbonyl formed is unlikely to be significant relative to the mono-carbonyl, the precursor of the retro-aldol reaction. Second, the dehydrogenation of the mono-carbonyl is in competition with dehydration, the C-O cleavage reaction. Since the dehydration is both thermodynamically and kinetically (in presence of bases) much more favorable than the dehydrogenation, the hydrogenolysis products would have exclusively resulted from C-O cleavage, had either the retro-Claisen or the retro-Michael been the dominating mechanism of C-C cleavage in hydrogenolysis. In contrast, the retro-aldol reaction shares the same precusor as the dehydration, and has the ability to compete with the dehydration. Based on these reasons, we tend to believe that the C-C cleavage occurs through th

The

absence o

Montassie

not have

reaction

hydrogen

formic a

catalyzed

catalysts

F

through the retro-aldol reaction.

The need for a formic acid intermediate to explain the formation of CO_2 and the absence of methanol in the hydrogenolysis of glycerol was the direct motivation for Montassier *et al.* to propose the retro-Claisen mechanism. However, this formic acid does not have to be from the retro-Claisen reaction. It may be produced from the Cannizzaro reaction of formaldehyde, which is expected by the retro-aldol mechanism in the hydrogenolysis of glycerol. In the Cannizzaro reaction, formaldehyde is oxidized to formic acid while other carbonyl compounds are reduced to alcohols. This reaction is catalyzed by bases, but has been reported to be greatly enhanced by transition metal co-catalysts (Cook and Mailis, 1981). The Cannizzaro reaction enhanced by the transition

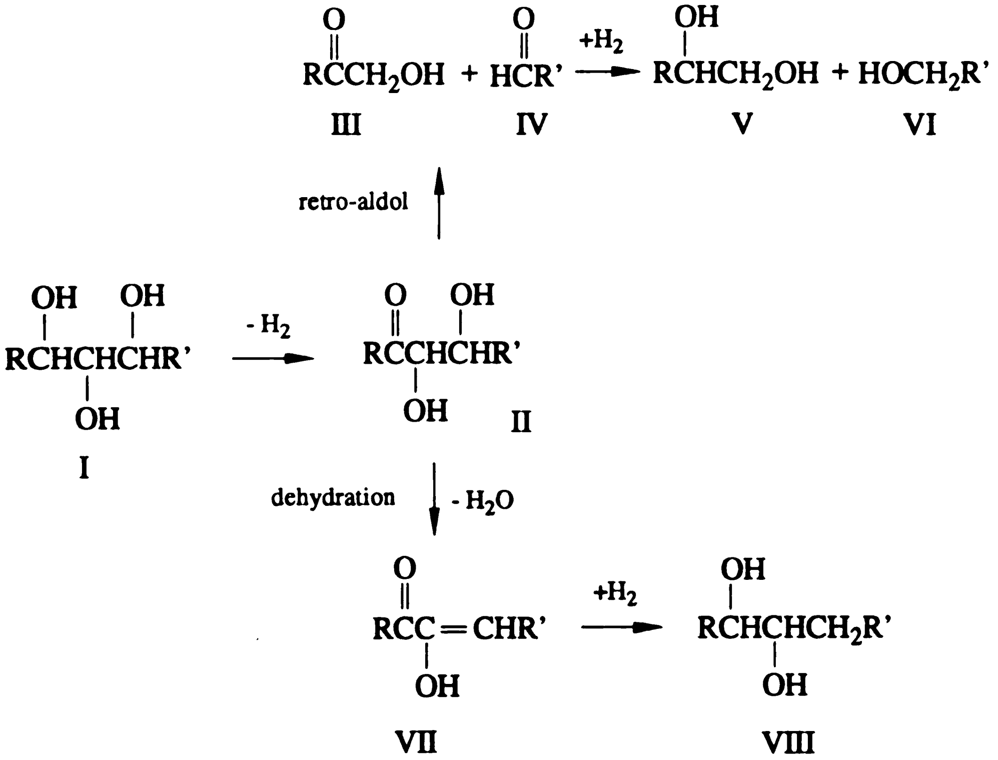


Figure 4-1. Mechanism of Sugar and Sugar Alcohol Hydrogenolysis

metal is lil
in the hyd
absence of

The
dehydrati
mechanis
processe
In Figure
the bond
alcohol l

4.2 Ex

Th
found s
verifica
dehydra
that deh
unavaila
alcohol
al., *198*
the prima
strong sug
However,

metal is likely to be the side reaction competing with the hydrogenation of formaldehyde in the hydrogenolysis of glycerol and other sugar alcohols, which is responsible for the absence of methanol and the presence of CO_2 in the hydrogenolysis product.

The retro-aldol mechanism needs a β-hydroxyl carbonyl precursor. Considering that dehydration is a well-known reaction of β-hydroxyl carbonyls. The dehydration mechanism of C-O cleavage is very sound, at least in theory. Thus, the bond-cleaving processe in the hydrogenolysis of sugars and sugar alcohols can be pictured as Figure 4-1. In Figure 4-1, sugars are represented by II and sugar alcohols by I. Based on Figure 4-1, the bond cleavage mechanisms in sugar hydrogenolysis ought to be the same as in sugar alcohol hydrogenolysis.

4.2 Experimental Verification

The reaction mechanism described in Figure 4-1 can explain all the reaction products found so far in sugar hydrogenolysis. Nevertheless, it is still subject to experimental verification. The currently available data provide no clue that the C-O bond is broken by dehydration of a β-hydroxyl carbonyl in sugar hydrogenolysis. Experimental evidence that dehydrogenation is a necessary step in the hydrogenolysis of sugar alcohols is also unavailable, and no sugar intermediate has been identified so far in any of the sugar alcohol hydrogenolysis experiments (Clark, 1958; Sohounloue *et al*, 1983; Motassier *et al.*, 1988 and 1989; Chang *et al.*, 1985). Andrew and Klaeren's (1989) observation that the primary C-C cleavage site is β to the carbonyl group in sugar hydrogenolysis may be a strong suggestion that the C-C cleavage has occurred through the retro-aldol reaction. However, bond breakage at this site is also expected by the retro-Claisen mechanism.

Clearly, t

In t

accompli

dehydrog

sugar alc

pursued

mechani

compou

the start

1,3-diol

underga

As a re

in the s

have to

results

necessa

results.

for inst

the mec

can be

The

pentaned

dimethyl-

Clearly, more evidence is desired to validate the mechanism described in Figure 4-1.

In the current research, verification of the reaction mechanism in Figure 4-1 is accomplished using 1,3-diol model compound. According to Figure 4-1, a 1,3-diol or its dehydrogenation product is the basic structural unit giving the reactivity to sugar and sugar alcohol molecules. Therefore, a mechanism study of sugar hydrogenolysis can be pursued with 1,3-diol model compounds. Using 1,3-diol model compounds in the mechanism study has several advantages over direct use of the sugar or sugar alcohol compounds. First, the bond cleavage pattern is indicated by the reaction products, since the starting molecule undergoes only one bond-cleaving reaction in the hydrogenolysis of 1,3-diols. In the hydrogenolysis of sugars and sugar alcohols, the starting molecule can undergo a chain of bond-cleaving reactions before further hydrogenolysis is impossible. As a result, the bond cleavage pattern is difficult to recognize based on the final products in the sugar and sugar alcohol hydrogenolysis. Second, sugar and sugar alcohol molecules have too many functional groups, which makes it possible to interpret the experimental results in a variety of ways. In contrast, 1,3-diols possess only the functional groups necessary for the hydrogenolysis to occur, which minimizes the ways to interpret the results. The retro-Michael mechanism is excluded from the hydrogenolysis of 1,3-diols, for instance, because 1,3-diols are incapable of forming the δ-dicarbonyl as required by the mechanism. Last and the most important, 1,3-diols with special structural features can be used, to verify the role played by individual reaction steps in the hydrogenolysis.

The 1,3-diols model compounds used in this work include 2,4-dimethyl-2,4-pentanediol (**1**), 2-methyl-2,4-pentanediol (**2**), 2,2,4-trimethyl-1,3-pentanediol (**3**), 2,2-dimethyl-1,3-propanediol (**4**), 2,4-pentanediol (**5**), 1,3-butanediol (**6**) and 1,3-propanediol

(7). The st

2,4-dimeth
2-methyl-2
2,2,4-trim
2,2-dimet
2,4-penta
1,3-butan
1,3-propa

Al

hydroga

transiti

catalys

et al.,

4-2, to

Figure

mass is

where

attribu

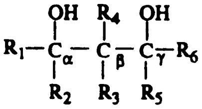
formald

Ac

dehydrog

(7). The structures of these compounds are provided in Table 4-1.

Table 4-1. Structures of 1,3-diols Used in Mechanism Study

Name	R_1	R_2	R_3	R_4	R_5	R_6	1,3-diol
2,4-dimethyl-2,4-pentanediol (1)	CH_3	CH_3	H	H	CH_3	CH_3	
2-methyl-2,4-pentanediol (2)	CH_3	CH_3	H	H	H	CH_3	
2,2,4-trimethyl-1,3-pentanediol (3)	H	H	CH_3	CH_3	H	$CH(CH_3)_2$	
2,2-dimethyl-1,3-propanediol (4)	H	H	CH_3	CH_3	H	H	
2,4-pentanediol (5)	CH_3	H	H	H	H	CH_3	
1,3-butanediol (6)	H	H	H	H	H	CH_3	
1,3-propanediol (7)	H	H	H	H	H	H	

All the hydrogenolysis experiments in this work are performed at 210 °C and 5 MPa hydrogen pressure in the aqueous phase. NaOH is added to promote the reaction. The transition catalysts used in this work are Raney Cu and Raney Ni, two of the typical catalysts used in sugar and sugar alcohol hydrogenolysis (Montassier *et al.*, 1988; Chang *et al.*, 1985; Sohounloue *et al.*, 1983). The experimental results are summarized in Table 4-2, together with a documentation of the expected products from each 1,3-diol based on Figure 4-1. The yields presented in Table 4-2 are based on the reacted 1,3-diols. The mass is not balanced perfectly, but is within the experimental error. In all the experiments where methanol is an expected product, it is found only in a trace amount. The reason is attributed to the transition-metal-catalyzed Cannizzaro reaction, which intercepts formaldehyde, the hydrogenation precusor to methanol, as discussed earlier.

According to Figure 4-1, the hydrogenolysis of a 1,3-diol is initiated by dehydrogenating one of its hydroxyl groups. This postulation is strongly supported by the

Table 4-2. Results of 1,3-Diol Hydrogenolysis [a]

Table 4-2. Results of 1,3-Diol Hydrogenolysis [a]

Run No.	Diol/ grams	Raney Catalyst[b]		Time (min)	Conv. (%)	Expected Products[c]				Identified Products/Yield (%)[c,d]					Selectivity[e]			
		Cu (g)	Ni (g)			C_α-C_β	C_β-C_γ	C_α-O	C_γ-O	C_α-C_β	C_β-C_γ	C_α-O	C_γ-O	addi- tional	S_1	S_2	S_3	S_4
1	1/1.10	9.08	—	360	none	none	none	none	none	none	none	none	none	none	—	—	—	—
2	2/1.06	9.05	—	240	71	11	none	19	none	11/75	none	19/7	none	12/20	10.7	—	—	—
3	3/1.03	9.81	—	200	51	8, 20	15	none	none	8/tr. 20/13	15/91	none	none	none	—	—	0.14	—
4	4/1.05	8.99	—	180	15	8 & 15		none	none	8/tr. & 15/99		none	none	none	—	—	—	—
5	5/2.25	12.2	—	190	81	9 & 11		17		9/10 & 11/15		17/46		18/42	0.17		—	—
6	6/1.02	9.75	—	240	73	8, 11	9	14	13	8/tr. 11/27	9/3	14/61	13/6	12/3 16/4	0.46	0.50	10.0	10.8
7	7/1.07	9.67	—	240	34	8 & 9		10		8tr. & 9/24		10/81		none	0.30		—	—
8	1/0.97	—	11.4	240	none	none	none	none	none	none	none	none	none	none	—	—	—	—
9	2/1.05	—	9.91	150	71	11	none	19	none	11/97	none	19/3	none	none	32.3	—	—	—
10	3/1.07	—	11.7	180	51	8, 20	15	none	none	8/tr. 20/51	15/52	none	none	none	—	—	0.98	—
11	4/0.94	—	9.02	210	32	8 & 15		none	none	8/tr. & 15/98		none	none	none	—	—	—	—
12	5/1.59	—	9.66	180	97	9 & 11		17		9/43 & 11/53		17/26		18/25	1.04		—	—
13	7/1.16	—	10.5	250	55	8 & 9		10		8/tr. & 9/51		10/48		none	1.06		—	—

Table 4.3. (Cont'd)

Table 4-2. (Cont'd)

a. All reactions were performed at 210 °C and 5 MPa hydrogen pressure in water. In addition to the Raney catalyst, 0.4 mL 1 N NaOH was added as a co-catalyst in each run. The total volume of the reaction solution was 40 mL. *b*. Both Raney Cu and Ni were added in the form of 50% slurry. *c*. **8**=methanol, **9**=ethanol, **10**=n-propanol, **11**=isopropanol, **12**=acetone, **13**=n-butanol, **14**=2-butanol, **15**=isobutanol, **16**=2-butanone, **17**=2-pentanol, **18**=2-pentanone, **19**=4-methyl-2-pentanol, **20**=2,4-dimethyl-3-pentanol. *d*. Yields are based on the reacted diols; tr. = trace. *e*. S_1, S_2, S_3 and S_4 are defined as the ratios of C_α-C_β cleavage to C_α-O cleavage, of C_β-C_γ cleavage to C_γ-O cleavage, of C_α-C_β cleavage to C_β-C_γ cleavage and of C_α-O cleavage to C_γ-O cleavage, respectively.

results fro
α and γ ca
inactive u
to be inac
as a catal
products
used in th
undergo
hydroger
can not
to be b
hydroge
carbon,
2 and 9

Th
against
reaction
dicarbo
in hydro
rate of
shown by

In c
the C-C bo

results from hydrogenolysis of **1**. Because of the absence of a hydrogen atom on both the α and γ carbons, **1** is incapable of undergoing dehydrogenation, and thus is expected to be inactive under the hydrogenolysis conditions. As indicated in Table 4-2, **1** is indeed found to be inactive. The hydrogenolysis of **1** has been carried out for six hours with Raney Cu as a catalyst (Run 1) and for four hours with Raney Ni as a catalyst (Run 8). No reaction products have been identified at the end of either reaction. For comparison, other 1,3-diols used in this work are all found to be reactive under the same conditions, because they can undergo the dehydrogenation reaction. That dehydrogenation is a necessary step for hydrogenolysis is additionally supported by the results from hydrogenolysis of **2**. As **2** can not be dehydrogenated at the α carbon, the C-C and C-O bonds of **2** are not expected to be broken between the β and γ carbons and at the γ carbon, respectively, during hydrogenolysis, although they may be broken between the α and β carbons and at the α carbon, respectively. The experimental results turned out again exactly as expected (Runs 2 and 9).

The results from hydrogenolysis of **2** (Runs 2 and 9) also provide good evidence against the retro-Claisen as the dominating C-C cleavage mechanism. The retro-Claisen reaction requires a dicarbonyl precursor. Since **2** is incapable of forming such a dicarbonyl, the retro-Claisen mechanism predicts that the C-C bonds of **2** are unbreakable in hydrogenolysis. However, the experimental results show otherwise: the hydrogenolysis rate of **2** is not impaired by its incapability of undergoing the retro-Claisen reaction, as shown by the conversion data in Table 4-2.

In contrast to the retro-Claisen mechanism, the retro-aldol mechanism predicts that the C-C bond of **2** may be broken between the α and β carbons to form two isopropanol

molecul
predicts
4-2, iso
domina
identifi
Aceton
Raney
in the
hydrog

T
aldol
consi
again

a ca
they
our
repo
hydr
in t
react

cleava

molecules, as **2** can be dehydrogenated at the γ carbon. The retro-aldol mechanism also predicts that the isopropanol is formed through an acetone intermediate. As seen in Table 4-2, isopropanol is not only found at the end of the reaction (Runs 2 and 9), but is a dominating product of 2-methyl-2,4-pentanediol hydrogenolysis. Furthermore, acetone is identified in the reaction when Raney Cu is used as the hydrogenolysis catalyst (Run 2). Acetone is not detected in the reaction when Raney Ni is used as the catalyst, because Raney Ni is a more efficient hydrogenation catalyst than Raney Cu. The acetone formed in the hydrogenolysis of **2** may be quickly hydrogenated to isopropanol. The results from hydrogenolysis of **2** are very supportive of the retro-aldo mechanism.

The results from hydrogenolysis of **3**, **4**, **5**, **6** and **7** are also supportive of the retro-aldol mechanism. In all these experiments, the C-C bond cleavage patterns are found to be consistent with the retro-aldol mechanism. In hydrogenolysis of **6** (Run 6), acetone is again identified as an intermediate as predicted by the retro-aldol mechanism.

Hydrogenolysis of **2**, **6** and **7** has been carried out by Conner and Adkins (1932) with a catalyst prepared by precipitation of Ni carbonates. However, in hydrogenolysis of **2**, they identified only the end products, isopropanol (**11**) and 4-methyl-2-pentanol (**19**), as in our experiment with Raney Ni as the catalyst. In hydrogenolysis of **6** and **7**, they did not report the C-C cleavage at all. The successful identification of C-C bond cleavage in hydrogenolysis of **6** and **7** and of the retro-aldo intermediates in hydrogenolysis of **2** and **6** in this work strengthens the theory that the C-C cleavage is through the retro-aldol reaction.

Also according to Figure 4-1, the dehydration reaction is responsible for the C-O cleavage in hydrogenolysis. This postulation is strongly supported by the results from hydr

attac

such

occu

O c

the

bo

o

w

t

The

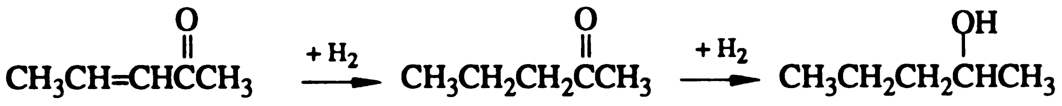
hydrog

C=C do

The

hydrogenolysis of **3** and **4**. Based on the dehydration mechanism, a hydrogen atom attached to the β carbon is necessary for the hydrogenolysis of C-O bonds to occur. Since such a hydrogen does not exist in **3** and **4**, cleavage of the C-O bonds is not expected to occur in the hydrogenolysis of these compounds. Indeed, as indicated in Table 4-2, no C-O cleavage is found in hydrogenolysis of either **3** or **4**.

The dehydration mechanism is also supported by the C-O cleavage pattern found in the hydrogenolysis of **2** (Runs 2 and 9). The dehydration mechanism expects the C-O bond to be broken only at the α carbon in hydrogenolysis of **2**, as **2** can be dehydrogenated only at the γ carbon. The results from hydrogenolysis of **2** shows that this expectation is well founded. The additional products 2-pentanone (**18**) and 2-butanone (**16**) identified in the hydrogenolysis of **5** (Runs 5 and 12) and **6** (Run 6), respectively, provide additional evidence to the dehydration mechanism. These compounds are not the direct products of dehydration, or VII in Figure 4-1, but intermediates from VII to VIII. The hydrogenation of VII to VIII is believed to take place in two sequential steps, as shown in the following with hydrogenolysis of **5** as an example:



$$CH_3CH{=}CH\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{+H_2} CH_3CH_2CH_2\overset{\overset{O}{\|}}{C}CH_3 \xrightarrow{+H_2} CH_3CH_2CH_2\overset{\overset{OH}{|}}{C}HCH_3$$

VII = 3-pentene-2-one

2-pentanone

VIII = 2-pentanol

The accumulation of 2-pentanone in hydrogenolysis of **5** and of 2-butanone in hydrogenolysis of **6** suggests that, with Raney Cu and Ni as catalysts, the hydrogenation of C=C double bonds is faster than the hydrogenation of C=O double bonds.

The mechanism pictured in Figure 4-1 is supported additionally by the selectivity dat

clea

C_3

doe

an

Th

al

C

t

o

sc

exp

aldeh

conde

1,3-dic

As

strongly

data collected from our experiments. In hydrogenolysis of a 1,3-diol, typically four bond cleavage selectivities can be defined, namely; C_α-C_β vs. C_α-O, C_β-C_γ vs. C_γ-O, C_α-C_β vs. C_β-C_γ, and C_α-O vs. C_γ-O. These selectivities are calculated for each experiment and are documented in Table 4-2.

According to Figure 4-1, the retro-aldol reaction responsible for the C-C cleavage and the dehydration reaction responsible for the C-O cleavage share the same precursor. Therefore, the C-C v.s. C-O selectivities should be affected by relative rate of the retro-aldol reaction to the dehydration reaction. This expectation is justified by the C-C v.s. C-O selectivity data in Table 4-2. In hydrogenolysis of straight-chain 1,3-diols (**5**, **6** and **7**), the reaction is found to favor the C-O cleavage products, because the dehydration is faster than the retro-aldo reaction in this case. In hydrogenolysis of a branched-chain 1,3-diol (**2**), the reaction is found to greatly favor the C-C cleavage products, because the retro-aldol reaction is faster than the dehydration in this case (Neilson and Houlihan, 1968).

When the retro-aldol reaction occurs, the aldol reaction is also possible, which often leads to scrambling of the retro-aldol fragments. Thus, in the hydrogenolysis of 1,3-diols, one might expect 1,3-diols other than the starting ones to be formed as the result of the scrambling aldol reaction. However, no such by-products have been observed in any experiments carried out in this work. The reason is attributed to the fast hydrogenation of aldehydes intermediates under the hydrogenolysis conditions and the unfavorable condensation between ketone intermediates, which minimize the formation of any new 1,3-diols.

As discussed above, the hydrogenolysis mechanism described in Figure 4-1 is strongly supported by the results from hydrogenolysis of 1,3-diol model compounds. To sum

and

the

prop

resp

pen

cle

C

2.

e

e

n

Ra

stro

and C

contro

summarize the experimental results, the hydrogenolysis of 2,4-dimethyl-2,4-pentanediol and 2-methyl-2,4-pentanediol demonstrates that the dehydrogenation is a necessary step in the hydrogenolysis of sugar alcohols. The hydrogenolysis of 1,3-dimethyl-1,3-propanediol and 2,2,4-trimethyl-1,3-pentanediol demonstrates that the dehydration is responsible for the C-O cleavage in hydrogenolysis. The hydrogenolysis of 2-methyl-2,4-pentanediol also provides good evidence against the retro-Claisen as the dominating C-C cleavage mechanism. The likelihood of the retro-Michael reaction being a dominating C-C cleavage mechanism is all but eliminated by the capability of all the 1,3-diols (except 2,4-dimethyl-2,4-pentanediol) to undergo hydrogenolysis. On the other hand, these experimental results are very supportive to the retro-aldol mechanism. In all the experiments but hydrogenolysis of 2,4-dimethyl-2,4-pentanediol, where no reaction is supposed to occur, the C-C cleavage is found to follow the patterns predicted by the retro-aldol mechanism. In addition, some ketone intermediates expected by this mechanism are identified in the hydrogenolysis of 2-methyl-2,4-pentanediol, 2,4-pentanediol and 1,3-butanediol. In no reaction, has a product other than the expected been found, and in no reaction, has an expected product not been found.

The experiments have been performed with two different catalysts (raney Cu and Raney Ni), the reaction patterns are not affected by the change of catalysts. These results strongly support the mechanism described in Figure 4-1. Now that the mechanism of C-C and C-O cleavage is known, it becomes possible for one to adopt a rational approach in control of the selectivity of sugar hydrogenolysis.

5.1

th

v

s

I

c

su

m

is. hy

C-O c

to con

hydrogen

our mech

CHAPTER 5

SELECTIVITY OF SUGAR HYDROGENOLYSIS

5.1 Selectivity Study Using 2,4-PD Model Compound: Rationale

Because of the multiple bond-cleavage reactions involved in sugar hydrogenolysis, three types of selectivities can be defined for this process, namely the C-C vs. C-C, C-O vs. C-O and C-C vs. C-O selectivities. In the current work, the C-C v.s. C-O selectivity of sugar hydrogenolysis is studied using 2,4-pentanediol (2,4-PD) model compounds. The purpose is to find a way to minimize C-O cleavage in sugar hydrogenolysis. As the C-O cleavage is to a great extent responsible for the complication of sugar hydrogenolysis products, minimizing C-O cleavage is expected to make the reaction more selective. Reduction of C-O cleavage in sugar hydrogenolysis is also expected to increase the yield of glycerol. As mentioned in Chapter 3, glycerol is the highest-valued major product of sugar hydrogenolysis, and it preserves all the oxygen atoms in the starting sugar molecules.

Using 2,4-PD model compound in the selectivity study has a major advantage, that is, hydrogenolysis of 2,4-PD gives only one pair of C-C cleavage products and one pair of C-O cleavage products, and these products do not undergo further bond cleavage reactions to complicate the process. Figure 5-1 shows the reaction pathway of 2,4-PD hydrogenolysis, which is derived based on the hydrogenolysis mechanism established in our mechanism study. From this figure, it is seen that aldehyde, ethanol, acetone and

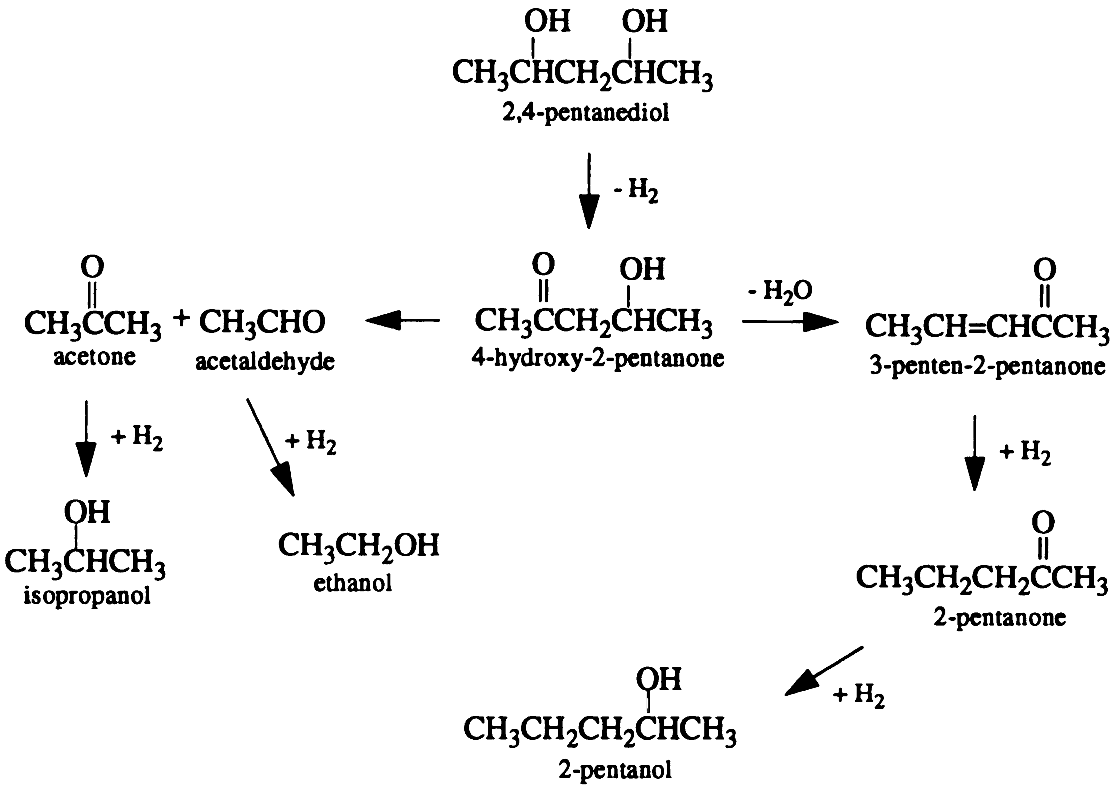


Figure 5-1. Reaction Pathway of 2,4-Pentanediol Hydrogenolysis

isopropanol result only from the C-C cleavage, and that 3-penten-2-one, 2-pentanone and 2-pentanol result only from the C-O cleavage. Therefore, the C-C cleavage in 2,4-PD hydrogenolysis can be quantified by the sum of acetone and isopanol, and the C-O cleavage by the sum of 3-penten-2-one, 2-pentanone and 2-pentanol, which makes the selectivity study easy to carry out. In contrast, in hydrogenolysis of real sugars, it is difficult to tie any reaction products to a specific bond-cleavage reaction, because of the general existence of more than one pathway to the same product.

In spite of the convenience of using 2,4-pentanediol model in selectivity study, a difference between 2,4-pentanediol and sugars needs to be noted. Compared to 2,4-PD,

sugar and sugar alcohol are characterized by a third hydroxy group at the β position, which will slightly alter the hydrogenation pathway of the α,β-unsaturated ketone from the C-O cleavage, or dehydration, reaction. In the presence of a hydroxy group at the β position, the α,β-unsaturated ketone can tautomerize to give a 1,2-diketone, as shown in Figure 5-2. Therefore, hydrogenation of the α,β-unsaturated ketone may occur via two pathways in the hydrogenolysis of real sugars.

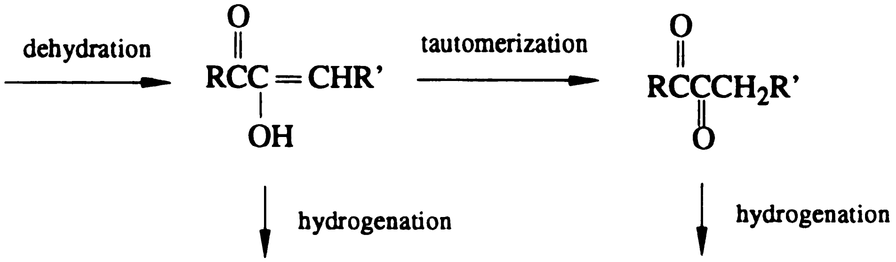


Figure 5-2. Alternate Hydrogenation Pathway of α,β-Unstaurated Ketone in Sugar Hydrogenolysis

At 25 °C, the equilibrium ratio of the α,β-unsaturated ketone to the 1,2-diketone is about 1:99 (Alexander, 1954). At 220 °C, a typical temperature used in hydrogenolysis, this ratio still remains at about 1:20. However, because the hydrogenation of an α,β-unstaurated ketone is generally much faster than the hydrogenation of an 1,2-diketone, direct hydrogenation of the α,β-unstaurated ketone intermediate is still expected to be a major pathway, even in sugar hydrogenolysis.

The C-O cleavage in sugar hydrogenolysis is expected to be less favorable than in 2,4-PD hydrogenolysis. The tautomerization reaction following the dehydration converts a better hydrogenation precursor to a worse one, and thus may reduce the hydrogenation rate of the dehydration product in sugar hydrogenolysis. Based on this reason, a catalyst wh

de

5.

co

c

r

n

ne

As se

initia

follow

which gives a good C-C v.s. C-O selectivity in 2,4-PD hydrogenolysis is expected to also deliver a good selectivity in sugar hydrogenolysis.

5.2 Experimental Study

In the current work, 2,4-PD has been hydrogenolyzed under various reaction conditions to investigate the effects of temperature, hydrogen pressure, base concentration, catalyst amount and catalyst type on the C-C v.s C-O selectivity. Figure 5-3 presents the result from a typical experiment run, carried out at 220 °C, 5 MPa H_2 pressure and with Ni on kieselguhr as the catalyst. In addtion to the end products, ethanol, isopropanol and 2-pentanol, two intermediate products, acetone and 2-pentanone, are normally observed at a significant level in 2,4-PD hydrogenolysis. Other intermediate products, including 4-hydroxy-2-pentanone, acetaldehyde and 3-penten-2-one, are sometimes detected during the initial period of reaction, but generally exist only at low levels. These products are not quantified and therefore are not shown in Figure 3.

Figure 5-4 shows how the C-C v.s C-O selectivity changes during the hydrogenolysis. This selectivity is defined as the ratio of the mole of C-C bonds to the mole of C-O bonds broken in the reaction. Since the amount of 3-penten-2-one is negligible in the reaction product, the selectivity is calculated as:

$$S = \frac{[acetone] + [isopropanol]}{[2-pentanone] + [2-pentanol]}$$

As seen from Figure 5-4, the selectivity is typically stabilized at a constant level after the initial period of the reaction. It is this stabilized selectivity that is compared in the following for different reaction conditions.

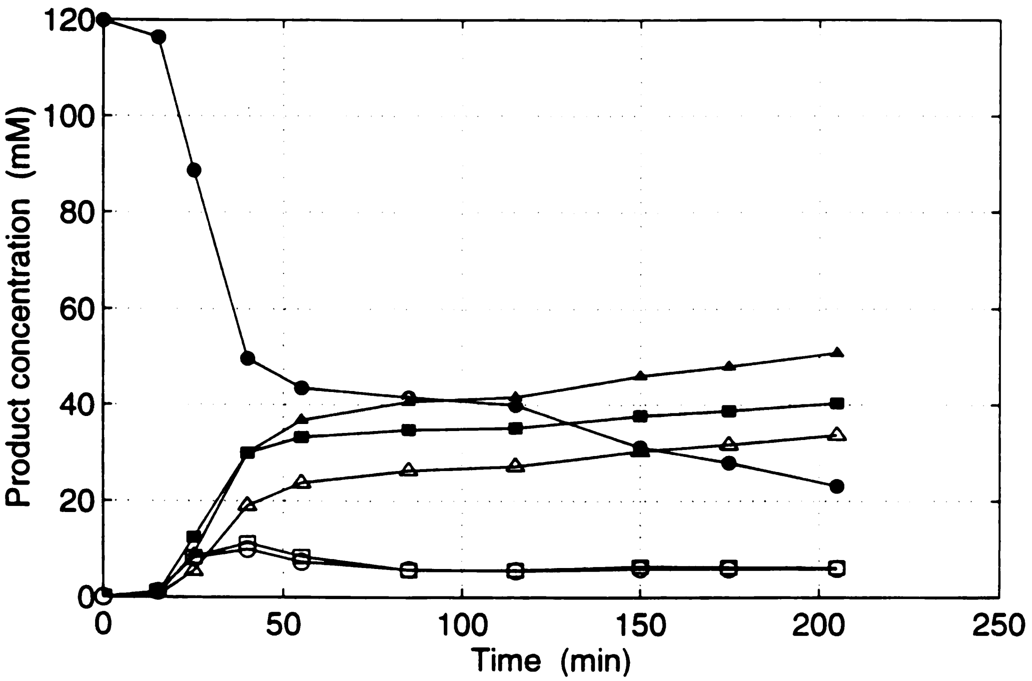


Figure 5-3 Product v.s Reaction Time Profiles. Experimental Conditions: 220 °C, 5.0 MPa H_2 pressure, 0.1 g Ni/kieselguhr catalyst, 0.4 *ml* 1 N NaOH and 40 *ml* water solvent. Symbols: ● 2,4-PD; ■ EtOH; ○ acetone; ▲ i-PrOH; □ 2-pentanone; △ 2-pentanol.

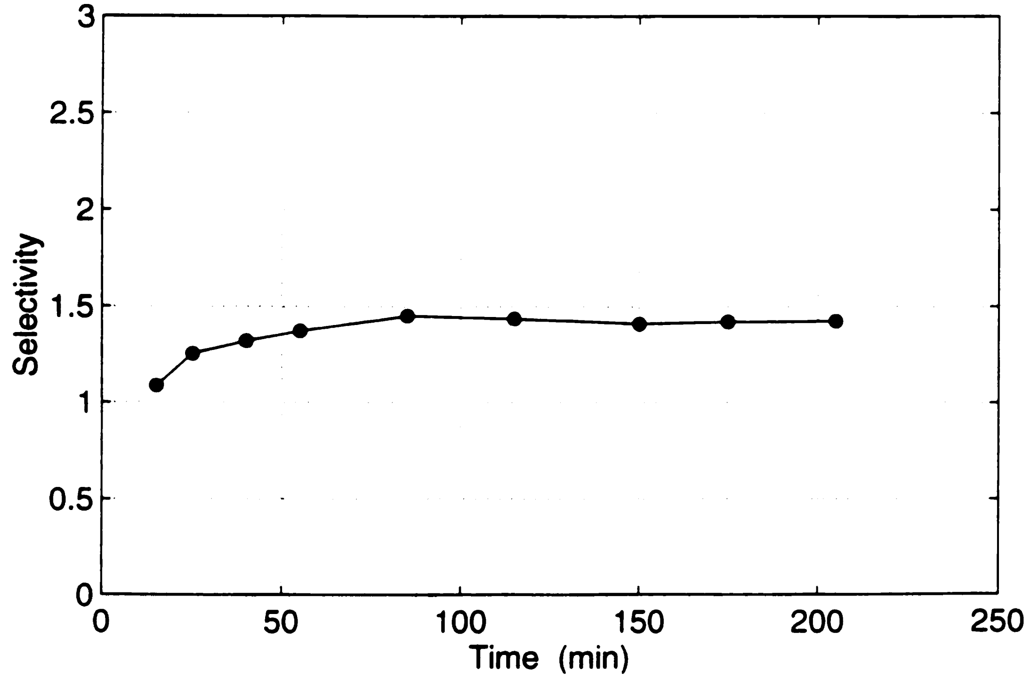


Figure 5-4 Selectivity v.s. Reaction Time Profile Derived from Figure 5-3

Table 5-1 Effect of Temperature on Selectivity

Experiment Series # 1 [a]		Experiment Series # 2 [b]	
Temperature (°C)	Selectivity	Temperature (C)	Selectivity
180	1.38	—	—
200	1.42	200	1.06
220	1.42	220	1.02
240	1.45	240	1.10

a. Reaction Conditions: 5 MPa H_2 pressure, 0.1 g Ni/kieselguhr, 0.4 ml 1 N NaOH, 0.5 starting 2,4-PD and 40 ml water. *b.* Reaction Conditions: 5.0 MPa H_2 pressure, 0.25 g Raney Cu, 0.2 ml 1 N NaOH, 0.5 g starting 2,4-PD and 40 ml water.

Table 5-2 Effect of Base Concentration on Selectivity [a]

Experiment Series # 1 [b]		Experiment Series # 2 [c]	
NaOH Added (μl)	Selectivity	NaOH Added (μl)	Selectivity
0	0.46	0	0.26
400	1.42	200	1.02
1000	1.56	500	1.73

a. In all cases, base is added as 1 N aqueous NaOH solution. *b.* Reaction Conditions: 200 °C, 5.0 MPa H_2 pressure, 0.1 g Ni/kieselguhr, 0.5 starting 2,4-PD and 40 ml water. *c.* Reaction Conditions: 220 °C, 5.0 MPa H_2 pressure, 0.25 g Raney Cu, 0.5 g starting 2,4-PD and 40 ml water.

Table 5-3 Effect of Hydrogen Pressure on Selectivity

Experiment Series # 1 [a]		Experiment Series # 2 [b]	
Pressure (MPa)	Selectivity	Pressure (MPa)	Selectivity
3.0	1.50	3.0	0.80
5.0	1.42	5.0	1.02
7.0	1.49	7.0	1.15

a. Reaction Conditions: 200 °C, 0.1 g Ni/kieselguhr, 0.4 ml 1 N NaOH, 0.5 starting 2,4-PD and 40 ml water. *b*. Reaction Conditions: 220 °C, 0.25 g Raney Cu, 0.2 ml 1 N NaOH, 0.5 g starting 2,4-PD and 40 ml water.

Table 5-4 Effect of Catalyst Amount on Selectivity

Experiment Series # 1 [a]		Experiment Series # 2 [b]	
Catalyst (g)	Selectivity	Catalyst (g)	Selectivity
0.1	1.42	0.1	1.22
0.2	1.49	0.25	1.02
0.5	0.90	0.5	0.75

a. Reaction Conditions: 220 °C, 5.0 MPa H_2 pressure, Ni/kieselguhr, 0.4 ml 1 N NaOH, 0.5 starting 2,4-PD and 40 ml water. *b*. Reaction Conditions: 220 °C, 5.0 MPa H_2 pressure, Raney Cu, 0.2 ml 1 N NaOH, 0.5 g starting 2,4-PD and 40 ml water.

t

in

the

incre

hydro

condit

obs*erva*

consiste

Effe

catalysts.

effect on *th*

Effect of Temperature To investigate the effect of temperature, 2,4-PD is hydrogenolyzed under two sets of base conditions with varying temperature. The selectivity, as Table 5-1 shows, is found to barely change with the temperature, although increasing temperature greatly enhances the reaction rate.

Effect of Base Concentration The base concentration, as Table 5-2 shows, has a profound effect on the selectivity, as well as on the reaction rate. Increase in the amount of base added to the reaction solution increases the reaction rate, and favors the cleavage of C-C bonds. This effect on the selectivity is most easily seen when the data from reactions with base addition are compared with those from reactions without base addition. One thing that needs to be pointed out is that the base concentration, as indicated by the PH of the reaction solution, is generally found to be lower than the initial concentration after the initial period of reaction.

Effect of Hydrogen Pressure The effect of hydrogen pressure seems to vary with the catalyst used. With Raney Cu as the catalyst, an increase in the hydrogen pressure increases the selectivity; while with Ni on kieselghur as the catalyst, the increase in the hydrogen pressure causes little change in the selectivity within the experimental conditions explored in this work. In the case of Raney Cu, hydrogen pressure is also observed to have an inhibiting effect on the rate of 2,4-PD hydrogenolysis. This effect is consistent with the observation made by Chang *et al.* (1985) in hydrogenolysis of sobitol.

Effect of Catalyst Amount The effect of catalyst amount again varies with the catalysts. However, the general trend is that high catalyst concentration has an adverse effect on the selectivity. With Raney Cu as the catalyst, the selectivity steadily decreases

with the catalyst amount. With Ni on kieselghur as the catalyst, the effect of catalyst amount only becomes significant at high level.

Effect of Catalyst Type A good catalyst is considered to be the key to achieve the control over the C-O cleavage in sugar hydrogenolysis. In this current work, seven different types of catalysts have been investigated. The results are presented in Table 5-5. As can be seen from this table, the selectivity varies widely with the type of catalyst used. The best selectivity is furnished by barium-promoted copper chromite, and is as high as 2.5, which is yet to be optimized against other reaction conditions. In contrast to the barium-promoted copper chromite, the plain copper chromite catalyst only provides a selectivity of 1.21 in our experiments. It is interesting to see the difference made by the presence of barium oxide. The effect of the amount of barium oxide used in preparation of the catalyst may be another factor deserving study in the context of selectivity improvement.

Table 5-5 Effect of Catalyst Type on Selectivity [a]

Catalyst Type	Selectivity
nickel on silica-alumina	1.12
nickel kieselguhr	1.18
copper chromite	1.21
ruthenium on carbon	1.36
Raney nickel	1.46
Raney copper	1.73
barium-promoted copper chromite	2.50

a. All reaction are run at 210 °C, 3.5 MPa H_2 pressure, with 0.05 g metal catalyst, 0.2 ml 1 N NaOH, 0.5 g starting 2,4-PD and 40 ml water.

t

p

inv

reas

from

5-5 a

I

Theref

unsatur

hydride

result of

be re-used

5.3 Simulation Study

In order to rationalize the experimental results just presented, a simulation study has been carried out on the hydrogenolysis of 2,4-PD. In this study, the effect of base concentration, hydrogen pressure, catalyst amount and catalyst type are simulated and compared against the experimental results. The effect of temperature is not studied in this initial simulation effort, because first it is more difficult to do and second this effect is not as profound as other factors. Therefore, all the simulated reactions are assumed to be isothermal and take place at an arbitrarily chosen temperature of 220 °C.

5.3.1 Model Development

At this time, the reaction pathway of 2,4-PD hydrogenolysis is clear to us. However, the pathway alone is not sufficient to allow us to develop the process model. It does not provide enough reaction details on how the H_2 and the metal and base catalysts are involved in the reaction, which are necessary for process model development. For this reason, a more detailed reaction scheme of 2,4-pentanediol hydrogenolysis is developed from the reaction pathway in Figure 5-1. This detailed reaction scheme is shown in Figure 5-5 and is used as the basis to develop the process model.

In the absence of transitional metal catalysts, molecular hydrogen is not reactive. Therefore, it must be activated by the metal catalyst before it can be used to reduce any unsaturated compounds. The result of the reaction of H_2 with the metal catalyst is a metal hydride species, which has the ability to hydrogenate C=C and C=O double bonds. As a result of this hydrogenation reaction, the metal catalyst must be regenerated, so that it can be re-used in the next cycle of catalysis. The above mechanism has been used by many res

hyd

PD h

the ma

with *th*

is furthe

reaction

works as

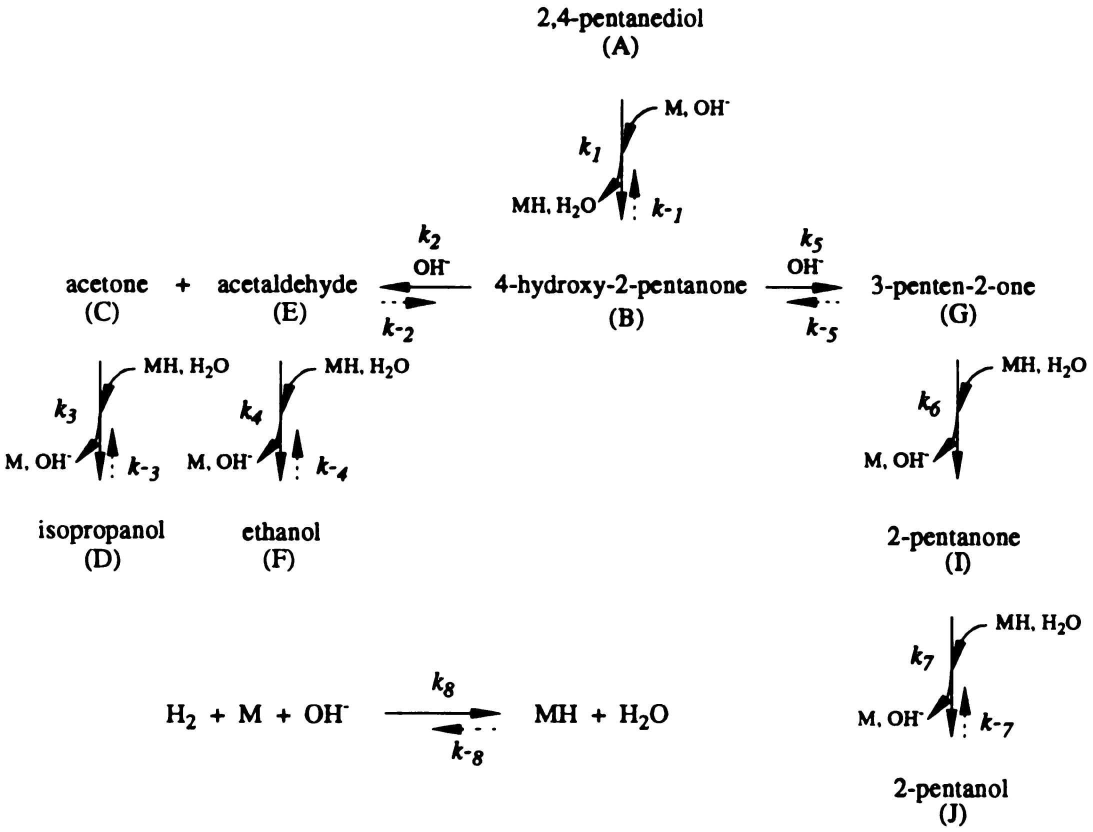


Figure 5-5. Detailed Reaction Scheme of 2,4-PD Hydrogenolysis

researchers to explain the hydrogenation process of C=C and C=O bonds with molecular hydrogen, and is adopted in the current work to help develop the reaction scheme of 2,4-PD hydrogenolysis.

The hydrogenation of carbonyl compounds by the metal hydride yields alcohol and the metal catalyst. Since this reaction is reversible, alcohols must be also able to react with the metal catalyst to get dehydrogenated and to release a metal hydride. Therefore, it is further pictured in Figure 5-5 that the hydrogenolysis of 2,4-PD is initiated by the reaction of this starting compound with the metal catalyst, and that the metal hydride works as a hydrogen carrier to transport hydrogen from 2,4-PD and molecular H_2 to those h

Ra

of

but f

equil

carrie

time on

and thus

the reacti

with the g

unsaturated intermediate products.

For the convenience of later mathematical model development, the reactions shown in Figure 5-5 are all numbered (the reaction number corresponds to the subscript of the rate constants shown in Figure 5-5), and the products are also designated by single letters. From Figure 5-5, it may be noticed that the base catalyst (hydroxide ion in this case) is not only involved in the retro-aldol and dehydration reactions as a real catalyst, but also participates directly in the dehydrogenation of 2,4-PD and activation of H_2. Participation of bases in H_2 activation and alcohol dehydrogenation has been well documented in literature. As the dehydrogenation step is most likely to be the rate limiting step in 2,4-PD hydrogenolysis, the above postulation is in consistence with the fact that 2,4-PD hydrogenolysis rate is enhanced by the addtion of bases.

It may also be noticed from Figure 5-5 that all the reaction step in 2,4-PD hydrogenolysis, except the hydrogenation of 3-penten-2-one, are assumed to be reversible. Retro-aldolization and dehydration are well-known reversible reactions. Hydrogenation of ketones and aldehydes and dehydrogenation of alcohols are also known to be reversible, but hydrogenation of alkene is generally considered to be irreversible, because the reaction equilibrium lies far to the product end.

To derive the mathematical model from Figure 5-5, we assume that the reaction is carried out in a batch reactor, and thus the product concentrations are functions of reaction time only. We also assume that the reaction is carried out under isothermal conditions, and thus the reaction rate constants do not change with time. The concentration of H_2 in the reaction solution may also be assumed to be time-independent and be in equilibrium with the gaseous phase, as the reaction is assumed to take place under a constant H_2

In th

conce

ethan

concen

and [O

pressure and the solution is under constant violent stirring during the reaction. A mass balance on each of the species present in Figure 5-5 except H_2 leads to:

$$\frac{d}{dt}[A] = -X_1 \tag{1}$$

$$\frac{d}{dt}[B] = X_1 - X_2 - X_5 \tag{2}$$

$$\frac{d}{dt}[C] = X_2 - X_3 \tag{3}$$

$$\frac{d}{dt}[D] = X_3 \tag{4}$$

$$\frac{d}{dt}[E] = X_2 - X_4 \tag{5}$$

$$\frac{d}{dt}[F] = X_4 \tag{6}$$

$$\frac{d}{dt}[G] = X_5 - X_6 \tag{7}$$

$$\frac{d}{dt}[I] = X_6 - X_7 \tag{8}$$

$$\frac{d}{dt}[J] = X_7 \tag{9}$$

$$\frac{d}{dt}[M] = \frac{d}{dt}[OH] = -\frac{d}{dt}[MH] = -X_1 + X_3 + X_4 + X_6 + X_7 - X_8 \tag{10}$$

In the above equations, [A], [B], [C], [D], [E], [F], [G], [I] and [J] are the molar concentration of 2,4-PD, 4-hydroxy-2-pentanone, acetone, isopropanol, acetaldehyde, ethanol, 3-penten-2-one, 2-pentanone and 2-pentanol, respectively. [M] is the molar concentration of the metal catalyst, [MH] is the molar concentration of the metal hydride, and [OH] is the molar concentration of hydroxide ion in the reaction solution. X_1 to X_8

are the reaction fluxes of Reactions No.1 to No.8 in Figure 5-5, respectively. Assuming all these reactions are first order in the substrates and catalysts, we further have

$$X_1 = k_1 [A]\,[M]\,[OH] - k_{-1} [B]\,[MH] \tag{11}$$

$$X_2 = k_2 [B]\,[OH] - k_{-2} [C]\,[E]\,[OH] \tag{12}$$

$$X_3 = k_3 [C]\,[MH] - k_{-3} [D]\,[M]\,[OH] \tag{13}$$

$$X_4 = k_4 [E]\,[MH] - k_{-4} [F]\,[M]\,[OH] \tag{14}$$

$$X_5 = k_5 [B]\,[OH] - k_{-5} [G]\,[OH] \tag{15}$$

$$X_6 = k_6 [G]\,[MH] \tag{16}$$

$$X_7 = k_7 [I]\,[MH] - k_{-7} [J]\,[M]\,[OH] \tag{17}$$

$$X_8 = k_8 [H]\,[M]\,[OH] - k_{-8} [MH] \tag{18}$$

In the last equation, [H] is the molar concentration of H_2 dissolved in the reaction solution.

At the beginning of the reaction, we may assume that all the products, but the substrate (2,4-PD) and the metal and base catalysts, have a zero concentration. Therefore,

$$[A] = [A]_o, [M] = [M]_o, [OH] = [OH]_o$$

and

$$[B] = [C] = [D] = [E] = [F] = [G] = [I] = [J] = [MH] = 0$$

for $t = 0$.

The above equations and initial conditions constitute a closed problem. If all the relevant reaction rate constants are obtained, the above equations can be solved to give product concentrations as functions of reaction time.

5.3.2 Determination of Kinetic Parameters

As mentioned previously, the simulation study is to be carried out at a constant temperature to simulate the effects of reaction conditions other than temperature on the selectivity. Therefore, we need only to determine the reaction rate constants for one temperature at which we choose to run the simulation. This temperature is chosen here to be 220 °C. This way, we could use the experimental data presented in Figure 5-3 to help determine these rate constants. The data in Figure 5-3 are obtained at 220 °C.

Among the eight reactions shown in Figure 5-5, reactions No. 2 (retro-aldo) and No. 5 (dehydration) are, though at low temperature, well-studied. From the kinetic data published by Jensen and Hassan (1976), it is derived that k_2=752 $M^{-1}min^{-1}$, k_{-2}=4480 $M^{-2}min^{-1}$, k_5=14100 $M^{-1}min^{-1}$ and k_{-5}=6590 $M^{-1}min^{-1}$ at 220 °C (see Appendix D). The rate constants (eleven in total) for the rest of the reactions shown in Figure 5-5 vary with the metal catalyst involved, and are not available from literature. Therefore, they are determined below, indirectly, from our 2,4-PD hydrogenolysis data.

The eleven rate constants to be determined are not all independent. They are bound together by thermodynamic relations. Of these relations, an obvious one is that, for any reversible reaction, the ratio of the forward reaction rate constant to the backward reaction rate constant is equal to the reaction equilibrium constant. Thus,

$$\frac{k_i}{k_{-i}} = K_i \tag{19}$$

for i=1, 3, 4, 7 and 8. In the above equation, K_i is the equilibrium constant of reaction No. i. The reaction is assumed to take place under dilute conditions.

The relations which are not so obvious are that the above equilibrium constants are also interdependent. These relations become apparent when the following two chemical equations are examined:

$$R_1CHOHR_2 + M + OH^- \xrightleftharpoons{\Delta G^o, K} R_1COR_2 + MH + H_2O$$

$$R_1CHOHR_2 \ - \ H_2(l) \xrightleftharpoons{\Delta \underline{G}^o, \underline{K}} R_1COR_2$$

The first equation in the above is a general representation of the dehydrogenation/ hydrogenation reactions shown in Figure 5-5. This first equation is also the result of the second equation above added to Reaction No.8 in Figure 5-5. Therefore, we have

$$\Delta G^o = \Delta \underline{G}^o + \Delta G_8{}^o \tag{20}$$

where ΔG^o and $\Delta \underline{G}^o$ are the free energy changes of the first and second reactions above, respectively. From Eq.(20), we further have

$$K = \underline{K} K_8 \tag{21}$$

where K and $\underline{K}$ are the equilibrium constants for the first and second reactions, respectively.

Unlike ΔG and K, $\Delta \underline{G}^o$ and $\underline{K}$ are well defined and are not dependent on the catalyst involved. Values of $\underline{K}$'s relevant to 2,4-PD hydrogenolysis have been estimated in this study from the free energy data documented in Guthrie (1977) for ketones and aldehydes and in Young (1981) for hydrogen dissolved in aqueous phase, and are listed in Table 5-6. Due to lack of free energy data at high temperature, these equilibrium constants have been calculated using free energies at 25 °C. Also because of lack of data, $\Delta \underline{G}^o$'s for Reactions No.1 and No.7 are assumed to be the same as Reaction No.3. The rationale is that these reactions are all about dehydrogenation of a secondary alcohol to a ketone.

Table 5-6 Equilibrium Constants of Relevant Dehydrogenation Reactions

No.	Alcohol	Ketone/Aldehyde	$\Delta \underline{G}^o$ (*kcal*)	$\underline{K}$
1	2,4-PD	4-hydroxy-2-pentanol	12.54	2.81×10^{-6}
3	isopropanol	acetone	12.54	2.81×10^{-6}
4	ethanol	acetaldehyde	16.59	4.52×10^{-8}
7	2-pentanol	2-pentanone	12.54	2.81×10^{-6}

Substituting Eq.(21) into Eqs.(19) for each *i* and rearranging gives

$$k_1 = \underline{K}_1 K_8 k_{-1} \tag{22}$$

$$k_{-3} = \underline{K}_3 K_8 k_3 \tag{23}$$

$$k_{-4} = \underline{K}_4 K_8 k_4 \tag{24}$$

$$k_{-7} = \underline{K}_7 K_8 k_7 \tag{25}$$

$$k_8 = K_8 k_{-8} \tag{26}$$

Elimination of K_8 from the above equations leaves four relations relating the rate constants. Therefore, of the eleven rate constants to be determined, only seven are independent. The remaining four have to be determined from the seven independent rate constants chosen, in order to assure thermodynamical consistency.

Besides the thermodynamic consistency, it is also important for the determined rate constants to fall within a reasonable range, so that the simulated processes are as close as possible to those actually occurring in our experiments. To achieve this, the best approach would be to accommodate as much experimental information as possible into the rate constant determination process. Therefore, data from the experiments presented previously in Figure 5-3 are used in the following to help determine the rate constants. That experiment was carried out at 220 °C.

Figure 5-3 shows how the concentration of 2,4-PD (A), acetone (C), isopropanol (D), ethanol (F), 2-pentanone (I) and 2-pentanol (J) changes with reaction time in the above experiment. Concentration of 4-hydroxy-2-pentanone (B), acetaldehyde (E) and 3-penten-2-one (G) are low (estimated to be less than 1 *mM*) and are not determined in the experiment. The concentration of metal catalyst (M), metal hydride (MH) and hydroxide ion (OH) are also undetermined, but at beginning of the reaction they are calculated as 28, 0 and 10 mM, respectively, from the amounts of regents used in the experiment. The initial concentration of 2,4-PD (A) is 120 mM. The H_2 concentration in the reaction solution is found to be about 0.1 M in equilibrium with 5 MPa hydrogen pressure at 220 °C (Young, 1981).

From Figure 5-3, it is seen that, after t=100 min, [C] and [I] are quite steady. Considering also that [B], [E], [G] and [OH] are low, we may assume that the reaction is at a pseudo-steady state after the initial period. Thus from Eqs.(2), (3), (5), (7), (8) and (10), it is derived that

$$X_2 = X_3 = X_4 \tag{27}$$

$$X_5 = X_6 = X_7 \tag{28}$$

and

$$X_1 = X_8 = X_2 + X_5 \tag{29}$$

From Figure 5-3, X_3 and X_7 can be determined to be 8.85 x 10^{-5} $M\ min^{-1}$ and 6.07 x 10^{-5} M

min^{-1}, respectively, at t=175 *min*. All the other reaction fluxes at t=175 *min* are calculated with Eqs.(27) to (29) from X_3 and X_7, and are listed in Table 5-7, together with the product concentrations at t=175 *min* and t=0 *min*. Concentrations of ethanol (F) and 2,4-PD (A) in Table 5-7 have been re-calculated to make the mass perfectly balanced. These data are used below in conjunction with Eqs.(11) through (18) to determine the reaction rate constants.

From Eq.(11), we have

$$\begin{aligned} X_1 &= k_1[A]\,[M]\,[OH] - k_{-1}[B]\,[MH] \\ &= k_{-1}[MH]\left(\frac{k_1}{k_{-1}}\frac{[M]\,[OH]}{[MH]}[A] - [B]\right) \\ &= k_{-1}[MH]\left(\underline{K}_1 K_8 \frac{[M]\,[OH]}{[MH]}[A] - [B]\right) \end{aligned}$$

Let

$$K_0 = K_8 \frac{[M]\,[OH]}{[MH]} \tag{30}$$

and substitute it into the above equation. We get

$$X_1 = k_{-1}[MH]\,(\underline{K}_1 K_0[A] - [B]) \tag{31}$$

Similarly, from Eqs.(13), (14), (17) and (18) we may get

$$X_3 = k_3[MH]\,(\,[C] - \underline{K}_3 K_0[D]\,) \tag{32}$$

$$X_4 = k_4[MH]\,(\,[E] - \underline{K}_4 K_0[F]\,) \tag{33}$$

$$X_7 = k_7[MH]\,(\,[I] - \underline{K}_7 K_0[J]\,) \tag{34}$$

and

$$X_8 = k_{-8}[MH]\,(K_0[H] - 1) \tag{35}$$

Table 5-7 Summary of Product Concentrations and Reaction Fluxes

	t = 0 *min*	*t* = 175 *min*	Unit
[A]	120	28.0	mM
[B]	0	less than 1 *mM*	mM
[C]	0	5.89	mM
[D]	0	48.0	mM
[E]	0	less than 1 *mM*	mM
[F]	0	53.9	mM
[G]	0	less than 1 *mM*	mM
[I]	0	6.26	mM
[J]	0	31.7	mM
[H]	100	100	mM
[OH]	10	unknown	mM
[M]	28	unknown	mM
[MH]	0	unknown	mM
X_1	–	1.49×10^{-4}	M min^{-1}
X_2	–	8.85×10^{-5}	M min^{-1}
X_3	–	8.85×10^{-5}	M min^{-1}
X_4	–	8.85×10^{-5}	M min^{-1}
X_5	–	6.07×10^{-5}	M min^{-1}
X_6	–	6.07×10^{-5}	M min^{-1}
X_7	–	6.07×10^{-5}	M min^{-1}
X_8	–	1.49×10^{-5}	M min^{-1}

Combining Eqs.(31) through (35) with Eqs.(12), (15) and (16), there are now eight equations available in total for eleven unknowns. These unknowns include six rate constants (k_{-1}, k_3, k_4, k_6, k_7 and k_8), four concentrations ([B], [E], [G] and [OH]) and a new variable K_0. [M] and [MH] are related to [OH] through the following equation:

$$[MH] = [M]_o - [M] = [OH]_o - [OH] \tag{36}$$

which is obtained by integration of Eq.(10). As the available equations are not enough for unknowns, three of them have to be assumed before others can be solved. In the following, this liberty is taken to make sure that the determined [B], [E], [G] and [OH] conform with our experimental observations and that the relative magnitudes of the determined rate constants are consistent with our knowledge of hydrogenation reactions.

If the dehydration (Reaction No.5) were irreversible during hydrogenolysis, the maximum selectivity of 2,4-PD hydrogenolysis would be $k_2/k_5 = 0.053$, or the C-O bond cleavage would be tremendously favored over the C-C bond cleavage. The experiment shows otherwise. Therefore, the dehydration reaction must be reversible in reality in 2,4-PD hydrogenolysis. The retro-aldol reaction (Reaction No.2) may also be reversible in 2,4-PD hydrogenolysis, depending on the reaction conditions. In order to describe the degree that the above reactions are reversed, a reversibility parameter may be defined for each of these reactions, as the ratio of the forward reaction rate to the reverse reaction rate, or

$$R_2 = \frac{k_{-2}[C]\,[E]\,[OH]}{k_2[B]\,[OH]} = \frac{k_{-2}[C]\,[E]}{k_2[B]} \tag{37}$$

and

$$R_5 = \frac{k_{-5}[G]\,[OH]}{k_5[B]\,[OH]} = \frac{k_{-5}[G]}{k_5[B]} \tag{38}$$

As later we will see, the reaction selectivity is closely related to these two parameters.

With the newly defined reversibility parameters, we may rewrite Eqs.(2) and (5) as

$$X_2 = k_2[B]\,[OH]\,(1-R_2) \tag{39}$$

and

$$X_5 = k_5[B]\,[OH]\,(1-R_5) \tag{40}$$

Dividing Eq.(39) by Eq.(40) and solving for R_5 yields:

$$R_5 = 1 - \frac{k_2X_5}{k_5X_2}(1-R_2) = 0.97 + 0.03R_2 \tag{41}$$

By definition, $0 < R_2 < 1$. Hence, $0.97 < R_5 < 1$, which implies that the dehydration reaction is highly reversible in the 2,4-PD hydrogenolysis process.

Also derivable from the above equations are:

$$[B] = \frac{X_2}{k_2(1-R_2)\,[OH]} \tag{42}$$

$$[E] = \frac{R_2X_5}{k_{-2}(1-R_2)\,[C]\,[OH]} \tag{43}$$

and

$$[G] = \frac{k_5X_2}{k_2k_{-5}(1-R_2)\,[OH]} - \frac{X_5}{k_{-5}[OH]} \tag{44}$$

Thus, [B], [E] and [G] can be determined if [OH] and R_2 are assumed. The pH of the reaction solution has been checked during the experiment to be around 11. The retro-aldol reaction is speculated to be reversible but to a much less degree than the dehydration reaction. Let $[OH] = 1\ mM$ and $R_2 = 0.2$. It is obtained that $[B] = 0.147\ mM$, $[E] = 0.838\ mM$ and $[G] = 0.305\ mM$, all less than 1 mM. From Eqs.(36) and (41), it is also obtained that $[M] = 19\ mM$, $[MH] = 9\ mM$ and $R_5 = 0.976$.

Now that all the product concentrations and reaction fluxes are known, all the concerned reaction rate constants are ready to be determined, providing that an appropriate value is assigned to K_0. The equations needed are derived from Eqs.(31) to (35) and Eq.(16), and are given as follows:

$$k_{-1} = \frac{X_1}{[MH]\ (\underline{K}_1 K_0 [A] - [B])} \tag{45}$$

$$k_3 = \frac{X_3}{[MH]\ ([C] - \underline{K}_3 K_0 [D])} \tag{46}$$

$$k_4 = \frac{X_4}{[MH]\ ([E] - \underline{K}_4 K_0 [F])} \tag{47}$$

$$k_6 = \frac{X_6}{[MH]\ [G]} \tag{48}$$

$$k_7 = \frac{X_7}{[MH]\ ([I] - \underline{K}_7 K_0 [J])} \tag{49}$$

and

$$k_{-8} = \frac{X_8}{[MH]\ (K_0 [H] - 1)} \tag{50}$$

Let $K_o = 5000$. k_{-1}, k_3, k_4, k_6, k_7 and k_{-8} are calculated as 67.1, 1.89, 11.9, 22.1, 1.16 and $3.22\times10^{-5}\ M^{-1}\ min^{-1}$, respectively. These rate constants satisfy that $k_{-1} > k_7$ and that

$k_6 > k_4 > k_3 > k_7$, and thus are consistent with our knowledge of hydrogenation reactions. With the above just determined rate constants, k_1, k_{-3}, k_{-4}, k_{-7} and k_8 can be further calculated from Eqs.(22) through (26). Table 5-8 below summarizes all the rate constants obtained from the above procedure.

Table 5-8 Summary of Determined Reaction Rate Constants

k_1 ($M^{-2}min^{-1}$)	k_2 ($M^{-2}min^{-1}$)	k_3 ($M^{-2}min^{-1}$)	k_4 ($M^{-2}min^{-1}$)	k_5 ($M^{-2}min^{-1}$)	k_6 ($M^{-2}min^{-1}$)	k_7 ($M^{-2}min^{-1}$)	k_8 ($M^{-2}min^{-1}$)
435	752	1.89	11.9	14100	22.1	1.16	76.2
k_{-1} ($M^{-2}min^{-1}$)	k_{-2} ($M^{-2}min^{-1}$)	k_{-3} ($M^{-2}min^{-1}$)	k_{-4} ($M^{-2}min^{-1}$)	k_{-5} ($M^{-2}min^{-1}$)	k_{-6} ($M^{-2}min^{-1}$)	k_{-7} ($M^{-2}min^{-1}$)	k_{-8} (min^{-1})
67.4	4480	12.2	1.24	6590	0	7.48	3.32×10^{-5}

Although some arbitrary measure has been used in the above rate constant determination process to assign values to R_2 and K_0, the determined rate constants remain sensible in the sense that:

a) they are thermodynamically consistent;

b) they are within a reasonable range of absolute and relative magnitude; and

c) most importantly, the simulation results obtained with these rate constants are comparable to those obtained experimentally, as will be seen in next section, which is the ultimate test for the determined rate constants.

These reaction rate constants may not represent Ni on kieselguhr or any other catalysts that have actually been used in our experiments, but they may represent a hypothetical catalyst which is not very different from them. If this is the case, the effects of reaction conditions on the selectivity should be similarly reflected on the actual and the hypothetical catalysts. Thus, the simulation study based on these rate constants would be useful at least qualitatively in interpretation of the experimental results, which is our goal in this study.

5.3.3 Simulation Results and Discussion

Figures 5-6 to 5-9 present the results of a simulated run of 2,4-PD hydrogenolysis. The assumed reaction conditions for this simulated run are the same as those for the experimental run shown in Figures 5-3 and 5-4, except that the experimental run has undergone a temperature rise from ambient temperature to 220 °C during the initial period of reaction, while the simulated run is computed under isothermal condition. Because of this difference in temperature history, the concentration and selectivity profiles in Figures 5-6 and 5-7 do not match those in Figures 5-3 and 5-4 exactly. Nevertheless, they still bear the major features of the later profiles. For example, the selectivity profile in Figure 5-7 also becomes time-independent after the initial period of reaction. The concentration of acetone (C) and 2-pentanone (I) in the simulated run also undergo an up-and-down behavior during the reaction, as in the experimental run. In addition to the information on major hydrogenolysis products, the simulation study also reveals how the concentration of minor products and the concentration of the base catalyst (hydroxide ion) change during the reaction (Figures 5-8 and 5-9). All the minor products shown in Figure 5-8 seem at a higher level than that observed in the experimental run, which, however, may result from

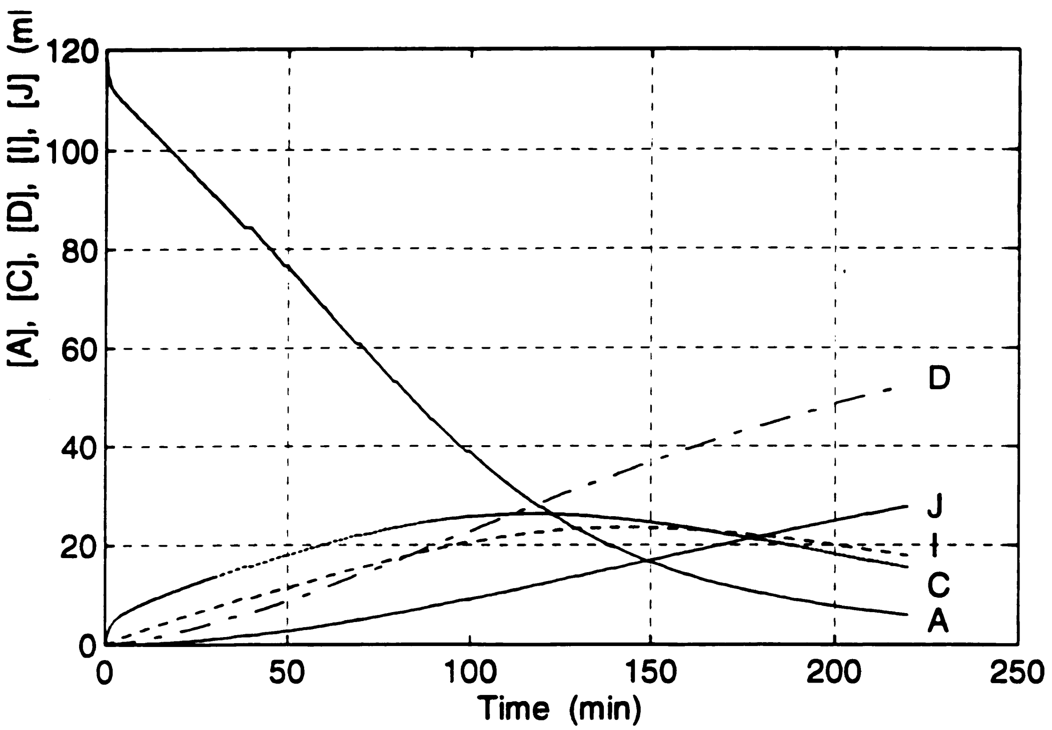


Figure 5-6 Simulated Concentration Profiles of Major Products. Simulation conditions: 220 °C, [H]=100 *mM*, $[M]_0$=28 *mM*, $[OH]_0$=10 *mM*, $[A]_0$=120 *mM*.

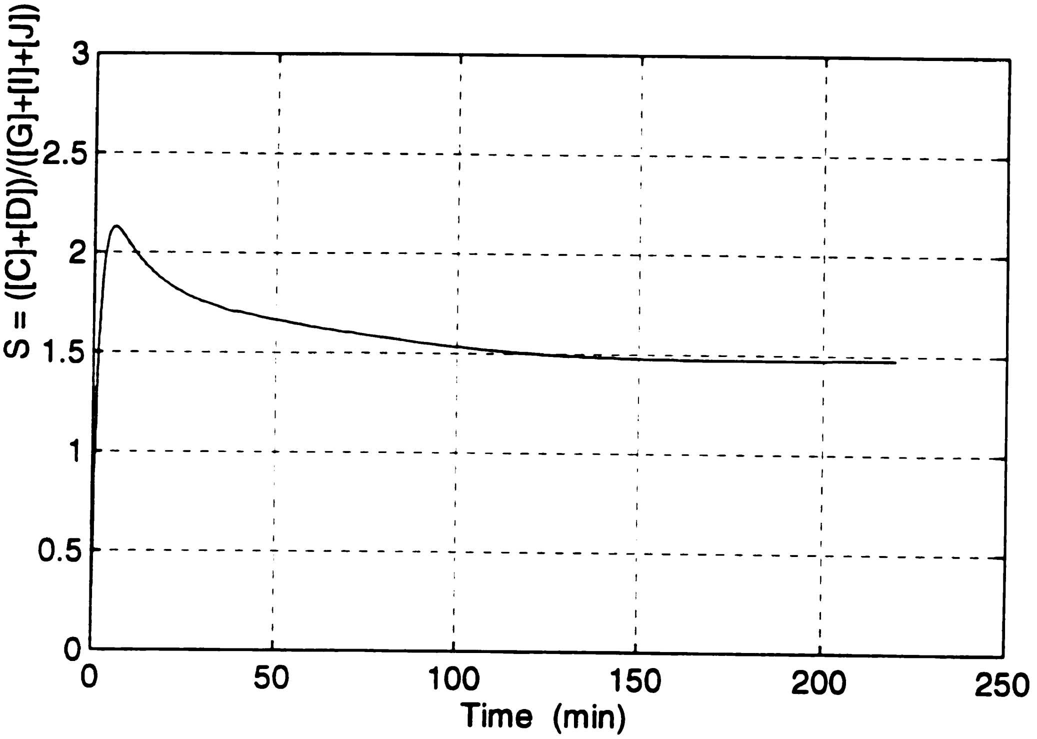


Figure 5-7 Simulated Selectivity Profile. S is calculated as ratio of the sum of [C] and [D] to the sum of [G], [I] and [J].

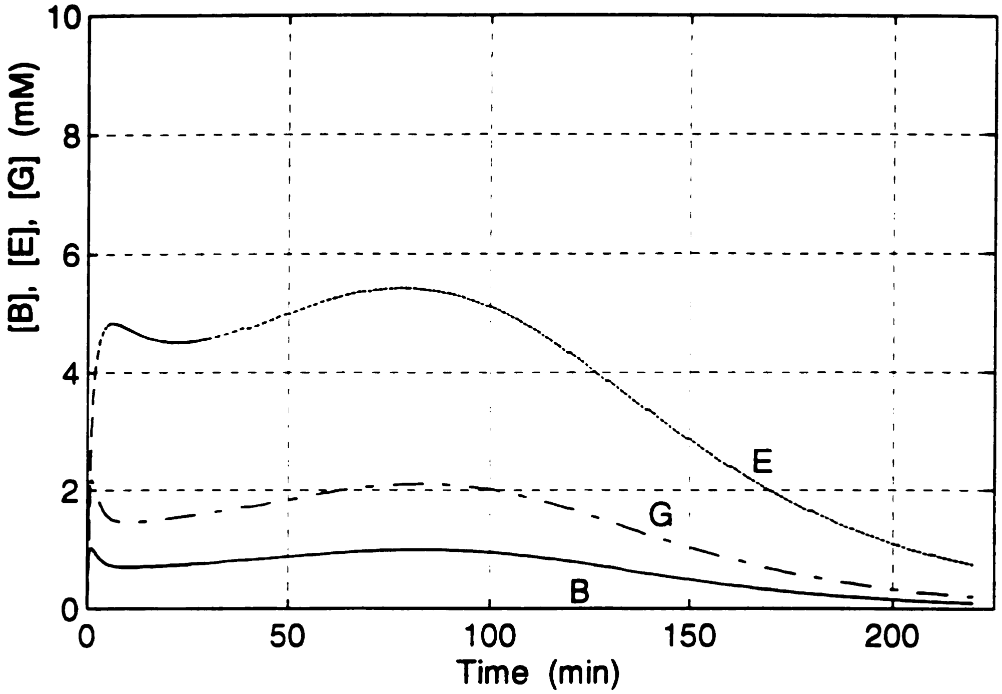


Figure 5-8 Simulated Concentration Profiles of Minor Products

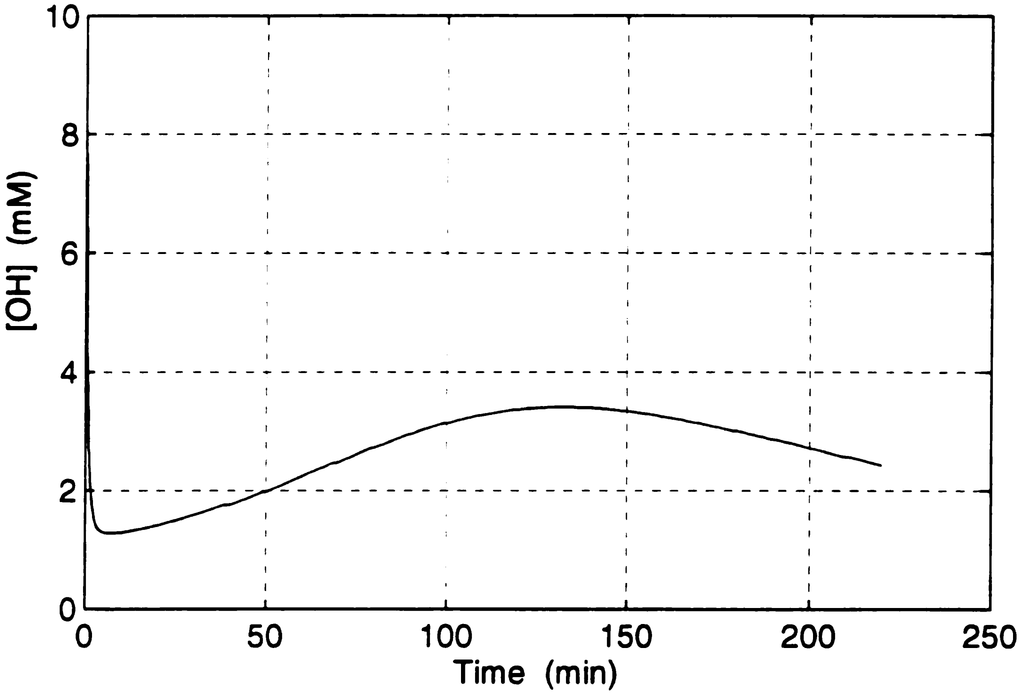


Figure 5-9 Simulated Base Concentration Profile

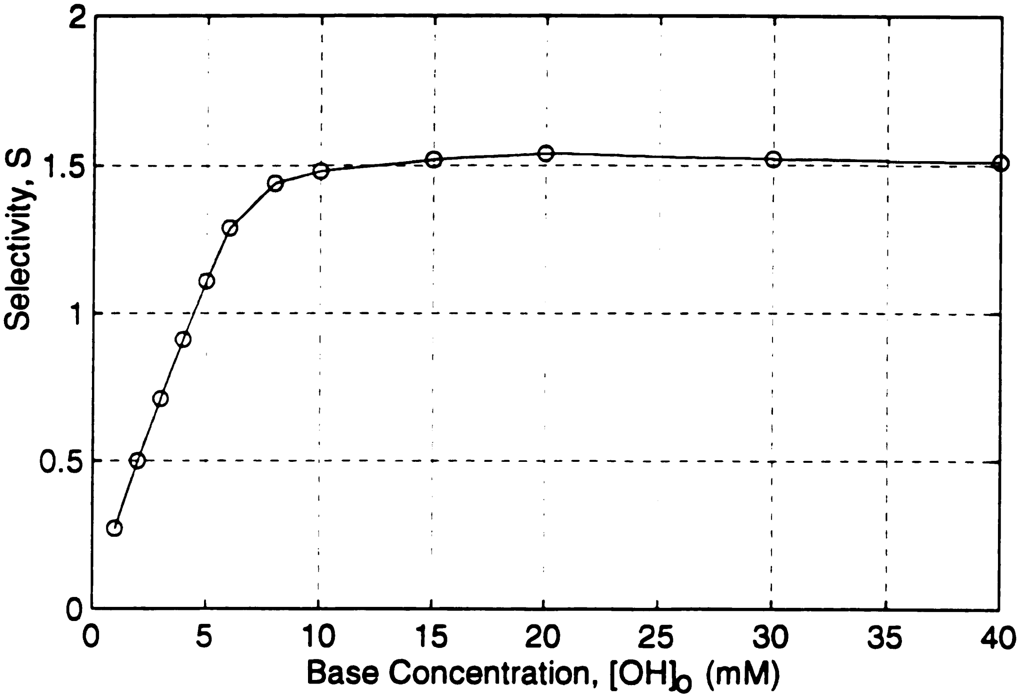


Figure 5-10 Simulated Effect of Base Concentration on Selectivity. Simulation Conditions: 220 °C, [H]=100 *mM*, $[M]_0$=28 *mM*, $[A]_0$=120 *mM*, varying $[OH]_0$.

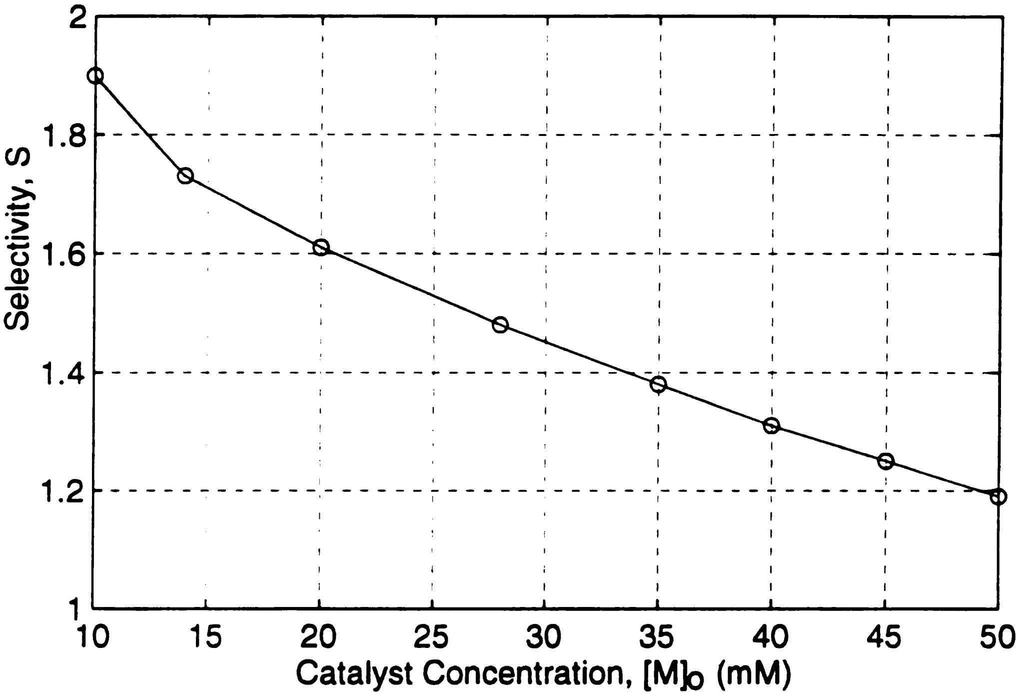


Figure 5-11 Simulated Effect of Catalyst Concentration on Selectivity Simulation Conditions: 220 °C, [H]=100 *mM*, $[OH]_0$=10 *mM*, $[A]_0$=120 *mM*, varying $[M]_0$.

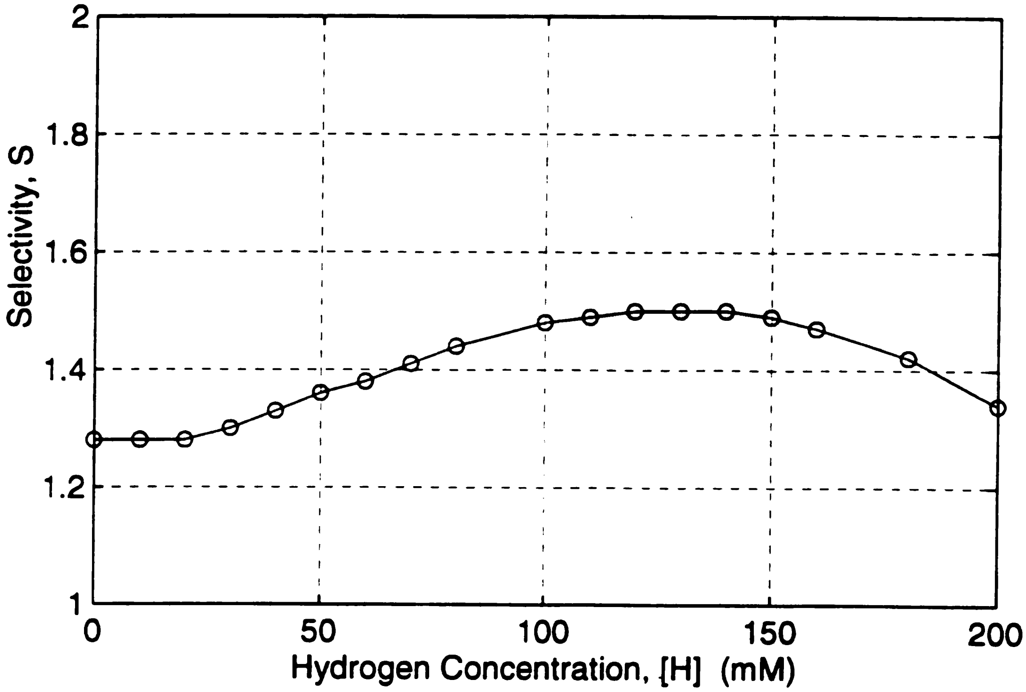


Figure 5-12 Simulated Effect of Hydrogen Concentration on Selectivity Simulation Conditions: 220 °C, $[M]_0$=28 *mM*, $[OH]_0$=10 *mM*, $[A]_0$=120 *mM*, varying [H].

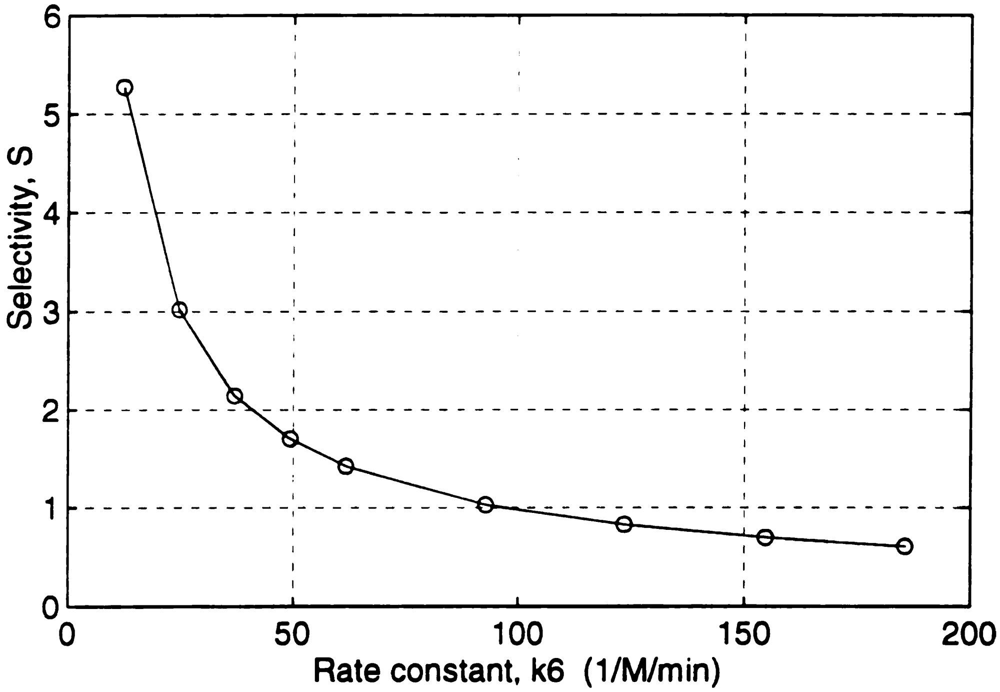


Figure 5-13 Simulated Effect of k_6 on Selectivity. Simulation Conditions: 220 °C, [H]=180 *mM*, $[M]_0$=28 *mM*, $[OH]_0$=10 *mM*, $[A]_0$=120 *mM*, but varying k_6.

the temperature history difference that exists between the experimental and simulated runs.

As in the experimental study, the effects of reaction conditions on the selectivity are also investigated in the simulation study. Figure 5-10 shows how the selectivity is affected by the change in base concentration. As observed in our experiments, the simulation study also indicates that the selectivity increases with the base concentration. This effect is most profound at low base concentration, but diminishes as the base concentration gets high. Because of the limited range of base concentration explored, the independence of the selectivity on base concentration at high base concentration is not revealed by the experiment.

Figure 5-11 shows how the selectivity is affected by the change in the amount of catalyst used in the reaction. Again as in our experiment, the selectivity is found to decrease with the catalyst amount. This effect remains over the whole range of catalyst concentration that has been explored. Lower catalyst concentration makes the reaction more selective, but it also makes the reaction slower.

As for the effect of hydrogen pressure on the selectivity, one set of experimental data (with Raney Cu as catalyst) show that it increases with the hydrogen pressure, while the other set of data (with Ni on Kieselguhr as catalyst) show that it is basically independent of the hydrogen pressure. The simulation study reveals a more complete picture and provides a good explanation to the above apparently different behaviors of the selectivity. It shows that, for a given catalyst, the selectivity increases with the hydrogen pressure at low pressure, is indifferent to the change in hydrogen pressure within the medium pressure range, and decreases with the hydrogen pressure at high pressure (Figure 5-12). These low, medium and high pressures are relative, and are catalyst-dependent. For Raney Cu, 7 MPa must be still in its low pressure range, while for Ni on kieselguhr, 3 to 7 MPa must happen to be its medium range. This explains why with different catalysts the selectivity behaves differently within the same hydrogen pressure range.

The effects of reaction conditions on the selectivity may be understood at a deeper level with the help of some mathematical equations relating the selectivity to base concentration, metal hydride concentration and the reversibility parameter for the retro-aldol reaction. These equations are derived as follows.

To start, we have

$$S = \frac{X_2}{X_5} = \frac{k_2(1-R_2)\,[OH]\,[B]}{k_5(1-R_5)\,[OH]\,[B]} = \frac{k_2(1-R_2)}{k_5(1-R_5)} \tag{51}$$

Assuming [G] is at a pseudo-steady state, we have

$$\frac{d}{dt}[G] = k_5[B]\,[OH] - k_{-5}[G]\,[OH] - k_6[G]\,[MH] \equiv 0 \tag{52}$$

which leads to

$$\frac{[G]}{[B]} = \frac{k_5[OH]}{k_{-5}[OH] + k_6[MH]} \tag{53}$$

Substituting the above equation into Eq.(38) and rearranging yields

$$R_5 = \left(1 + \frac{k_6[MH]}{k_{-5}[OH]}\right)^{-1} \tag{54}$$

Further substituting Eq.(54) into Eq.(51), we obtain

$$S = \frac{k_2}{k_5}(1-R_2)\left(1 + \frac{k_{-5}[OH]}{k_6[MH]}\right) \tag{55}$$

or

$$S = \frac{k_2}{k_5}(1-R_2)\left[1+\frac{k_{-5}}{k_6}\left(\frac{[OH]_0}{[MH]}-1\right)\right] \tag{56}$$

Replace the rate constants in Eq.(56) with numbers. We get

$$S = 0.053\,(1-R_2)\left[1+298\left(\frac{[OH]_0}{[MH]}-1\right)\right] \tag{57}$$

which provides additionally some quantitative ideas.

Eqs.(56) and (57) clearly show that the selectivity will increase as $[OH]_0$ increases, if other variables are kept unchanged. However, increase in $[OH]_0$ will inevitably lead to increase in [MH]. Increase in [MH], as well as increase in R_2 , leads the selectivity to decrease. The level of R_2 depends on levels of [OH] and [MH], as well as other factors. The simulation study reveals that, at low base concentration, R_2 decreases as the $[OH]_0$ is increased. The combination of the effects of $[OH]_0$and R_2 overrides the effect of [MH]. As a result, the selectivity shows an overall increase as the base concentration is increased. However, at high base concentration, R_2 increases with $[OH]_0$. The effect of $[OH]_0$ is offset by the combination of the effects of [MH] and R_2. The overall result is a selectivity independent of base concentration.

Increase in the amount of catalysts used simply increases the metal hydride level in the solution. Change in R_2 is minor. Therefore, the selectivity decreases with the catalyst amount. Increase in hydrogen pressure decreases both [MH] and R_2. At low hydrogen pressure, R_2 is very sensitive to the change in hydrogen pressure. As the pressure increases, it becomes less and less sensitive, which explains why the selectivity responds to the change in hydrogen pressure differently in different pressure range.

From Eq.(56), it is also seen that the selectivity should increase as the rate constant k_6

decreases. This deduction is confirmed by the simulation results as shown in Figure 5-13. Since different catalysts feature different k_6 values, the dependence of the selectivity on k_6 explains why it varies widely with the type of catalysts used. To improve the reaction selectivity, catalysts with small k_6 value should be used. Figure 5-13 suggests that the effect of k_6 on the selectivity is very profound. Therefore, the selectivity may be well improved by use of a good catalyst. A good catalyst implies that this catalyst possesses only a moderate capability to hydrogenate the α,β-unsaturated ketone while still keeping a reasonable capability to hydrogenate saturated ketones and aldehydes.

Lowering the reaction temperature may also lead to a reduced k_6. However, it will also change other rate constants, including k_2, k_5 and k_{-5} in Eq.(56). As a result, the selectivity may not be improved by reduction of the reaction temperature. As a matter of fact, our experiments indicate that the selectivity is not sensitive to the change in temperature, at least within the temperature range we have explored.

PART II

SELECTIVE DEHYDROXYLATION OF GLYCEROL

CHAPTER 6

INTRODUCTION: GLYCEROL DEHYDROXYLATION

6.1 On-going Research on Glycerol Dehydroxylation

The purpose of glycerol dehydroxylation is to convert glycerol to 1,3-propanediol (1,3-PD) by removing the second hydroxyl group of glycerol. Research on this process has been motivated mainly by two considerations. First, the current commercial processes to produce 1,3-PD from acrolein and ethylene oxide are not efficient, as has been discussed in Chapter 1. Second, glycerol is a biomass-derivable chemical. It can not only be potentially produced from sugars through fermentation and hydrogenolysis, but also be obtained from processing of animal fats and vegetable oils. Considering the promise of 1,3-PD in polyester fibers, films and coatings, it is significant being able to derive this chemical from biomass sources.

The glycerol dehydroxylation processes reported so far are mostly fermentation processes (Gunzel *et al.*, 1991; Boenigk *et al.*, 1993; Zeng *et al.*, 1993; Biebl, 1995; Barbirato, 1996; Cameron, 1998; Reimann, 1998). Nevertheless, Che (1987) has invented an one-step catalytic process to convert glycerol to 1,3- and 1,2-PD's. This process uses a synthesis gas co-feed, and is typically carried out under a temperature of 100-200 °C and a pressure of 100-10,000 psi, in the presence of tungsten and a Group VIII component. Like the current 1,3-PD production processes, however, this process furnishes only a low yield of 1,3-PD. The main products of this process are propanol and propylene glycol. 1,3-PD accounts for only a small portion of the reaction product (generally less than 20%).

The fermentation processes are based on the observation that, under appropriate conditions, certain bacteria, such as *Colostrium*, *K. pneumoniae* and *Citrobacter freundii*, can convert glycerol to 1,3-PD. This conversion is generally accompanied with formation of by-product ethanol, acetic acid, butyric acid, lactic acid, hydrogen and carbon dioxide, but by careful control of the fermentation conditions the yield of 1,3-PD can be maximized. Research on glycerol fermentation has been started since the 1960's. At the current time, this process is able to furnish a 1,3-PD yield as high as 0.66 mole per mole glycerol or 55% on weight basis (Zeng *et al.*, 1993), which, unfortunately, is about the highest yield that one can obtain from the glycerol fermentation process.

Having a low theoretical yield is one of the major disadvantages of the fermentation process. The reason for this low theoretical yield can be understood by examination of the reaction pathway of glycerol fermentation. Figure 6-1 shows a simplified reaction pathway of glycerol fermentation, which is derived from a more complex one in Zeng *et al.* (1993). From Figure 6-1, it is seen that the conversion of glycerol to 1,3-PD is completed through dehydration of glycerol followed by hydrogenation of the resulting 3-hydropropionaldehyde (HPA). Hydrogenation of HPA consumes $NADH_2$, which is regenerated in the oxidation of glycerol to pyruvate, the precursor to by-product ethanol, acetate, lactate, butyrate, H_2 and CO_2 (the latter species are not shown in Figure 6-1). In other words, the conversion of glycerol to 1,3-PD is sustained by the formation of by-products, which inevitably reduces the theoretical yield of 1,3-PD. The theoretical yield that a fermentation process can provide varies with the by-product it produces. In the ideal case, only acetate would be produced as the by-product. As conversion of pyruvate to

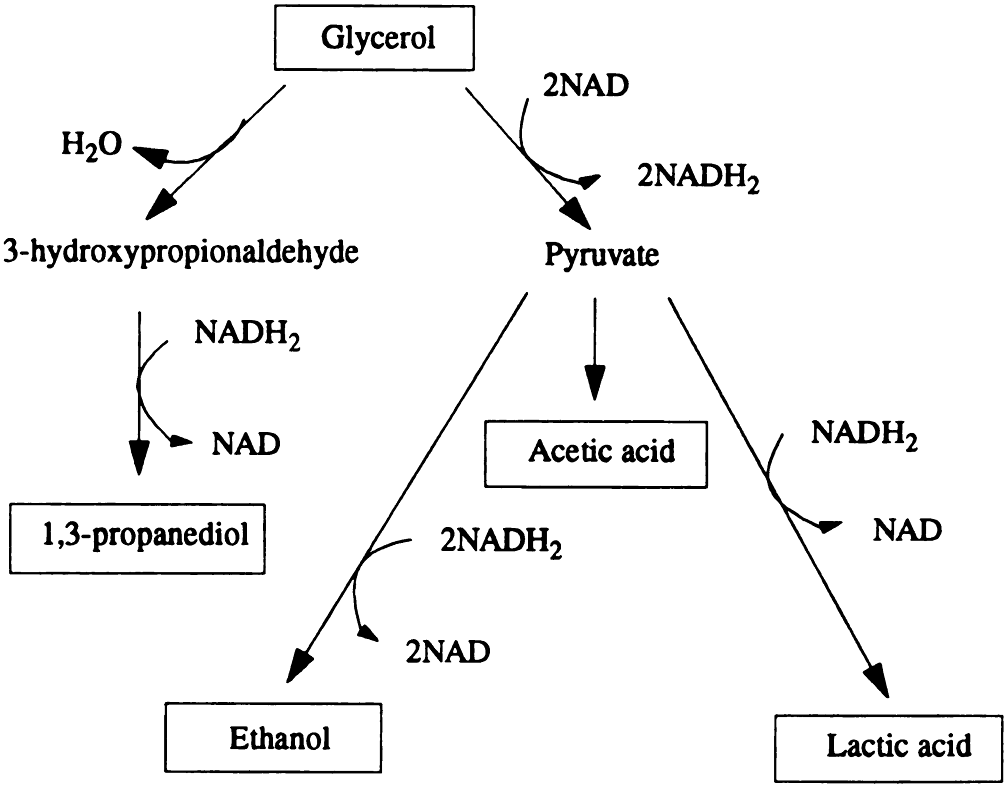


Figure 6-1. A Simplified Reaction Pathway of Glycerol Fermentation

acetate does not consume $NADH_2$, the theoretical yield of 1,3-PD would be 67% in this case. When other by-products are produced, the theoretical yield is expected to be lower than 67%.

Another major disadvantage of the fermentation process is that this process is substrate-inhibited. The bacteria used in the fermentation are generally not able to stand a glycerol concentration above 17%. As a result, both the product concentration and the productivity are low. In a continuous process, Zeng *et al.* (1993) have obtained a 1,3-propanediol concentration of 30 g l^{-1} with a productivity of 8.1 g l^{-1} h^{-1}, which are the best results reported so far in literature.

6.2 The New Conversion Concept and Supportive Work

In the current research, we propose a new glycerol dehydroxylation concept to selectively remove the second hydroxy group of glycerol and thus to convert it to 1,3-PD. This new conversion concept has potential to provide a high 1,3-PD yield and does not have the disadvantages of the current glycerol dehydroxylation processes.

The new glycerol dehydroxylation concept is presented in Figure 6-2. It consists of three steps, namely acetalization, tosylation and detosyloxylation. The idea is to selectively transform the second hydroxyl group of glycerol into a tosyloxy group (tosylation) and then remove it by catalytic hydrogenolysis (detosyloxylation). Compared to the hydroxyl group, the tosyloxy group is a better leaving group and is easier to replace with a hydride ion. In the following, a detailed discussion is made on each of the conversion steps.

Step 1: Acetalization. In order to selectively tosylate the second hydroxyl group of glycerol, the first and third hydroxyl groups of glycerol need to be protected. According to the proposed conversion concept, this is completed by acetalizing glycerol with benzaldehyde. Acetalization is an equilibrium reaction, but can be driven to completion by removing the water formed in the reaction. The difficulty with this step is that, besides the desired 1,3-product (5-hydroxyl-2-phenyl-1,3-dioxane, or HPD), the undesired 1,2-product (4-hydroxylmethy-2-phenyl-1,3-dioxolane, or HMPD) may also be formed. Nevertheless, these products can be separated, and the separated 1,2-product can be returned to the acetalization reactor, where either it itself can be converted to the 1,3-product or it can help shift the reaction toward the 1,3-product.

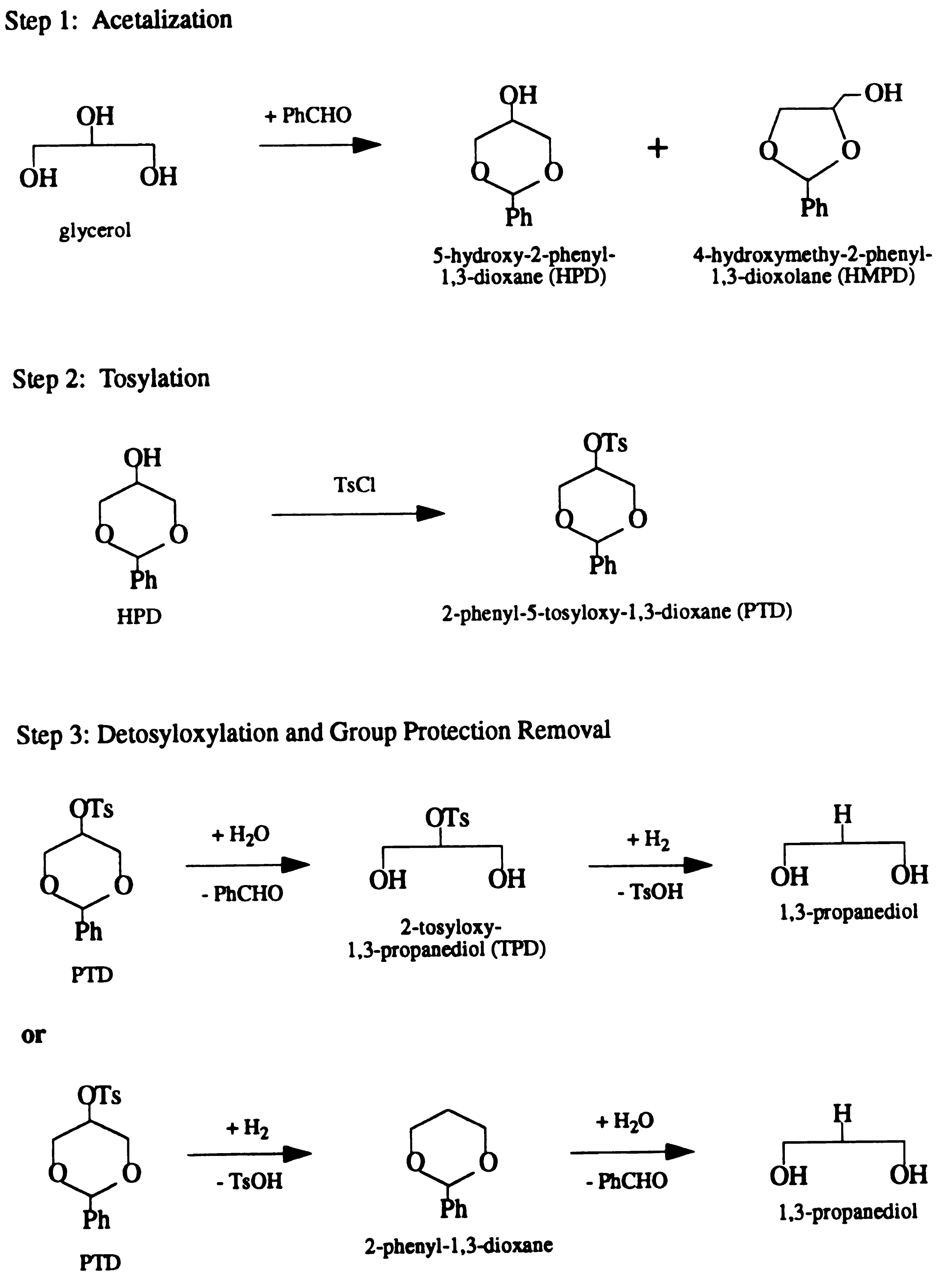


Figure 6-2. Illustration of the New Concept of Glycerol Dehydroxylation

Besides benzaldehyde, many other carbonyl compounds could also be used as the hydroxyl group protection regent. The condensation between glycerol and various aldehydes and ketones has been extensively reviewed by Showler and Darley (1967). Generally, the reaction between glycerol and aldehydes gives more 1,3-product than the reaction between glycerol and ketones (Trosr, 1991). For our purpose, it is obvious that aldehydes are preferred to ketones.

Besides the product yield, the ease of separating the 1,3- from the 1,2-product is another important factor that needs to be considered in selection of the group protection regent. In terms of the later aspect, benzaldehyde is superior to aliphatic aldehydes. The products from aliphatic aldehydes are generally high-boiling-point oils (Piasecki and Burczyk, 1980; Hilbbert and Carter, 1928), and the differences between the boiling points of the 1,2 and 1,3 products are usually small. For example, the condensation between glycerol and acetaldehyde gives four products: the *cis*- and *trans*- 5-hydroxyl-2-methyl-1,3-dioxanes (1,3-product) and the *cis*- and *trans*- 4-hydroxylmethyl-2-methyl-1,3-dioxolanes (1,2-product). As documented in *Beilstein*, the boiling points of these products are 73, 100, 86, and 94 °C, respectively, under 18 torr.

The 1,2- and 1,3- products from benzaldehyde have considerably different solubilities in benzene-ligroin mixture. The 1,3-product can be readily crystallized from the benzene-ligroin solution (Hill *et al.*, 1928; Baggett *et al.*, 1960).

The reaction between glycerol and benzaldehyde has been carried out previously, in several ways. The early methods (Irvine *et al.*, 1915; Baggett *et al.*, 1960) allowed direct contact of glycerol with benzaldehyde. In some cases, acids, such as H_2SO_4, were added as catalysts. The late methods (Baggett *et al.*, 1965; Szeja, 1983) are featured by use of a benzene solvent. The advantage of doing the reaction in benzene is that the water formed in the reaction can be removed azeotropically, and thus the reaction can be driven to completion. This advantage can be further enhanced by using a Dean-Stark trap (Casey, *et al.,* 1990), as Szeja (1983) has done. Acid catalysts were generally used in the late methods.

The condensation between glycerol and benzaldehyde gives four products: the *cis* and *trans*- HPD's and the *cis*- and *trans*- HMPD's. As mentioned above, separation of the 1,3-product HPD from the 1,2-product HMPD has been achieved by Hill *et al.* (1928) and Baggett *et al.* (1960), through crystallization from benzene-ligroin solution. Although the *trans*-HPD (b.p. 63.5 °C) can also be potentially crystallized, this procedure yields mainly *cis*-HPD (b.p. 83.5 °C) . *Cis*- HPD is the more stable diastereomer of HPD (Showler and Darley, 1967).

The equilibrium between the 1,2- and 1,3- products under the acetalization conditions has been studied. Hill *et al.* (1928) showed that the 1,2- product is favored over the 1,3-product by a ratio of 5.7: 1 in the absence of solvent. As stated by the authors, this result was more qualitative than quantitative, because only the fractionated part of the products was assumed as the 1,3-product in their study. The data from Baggett *et al.* (1965) also favor the 1,2-product, but only by a ratio of 1.9:1. The data documented in Jochims and Kobayshi (1974) show the contrast to the previous work: the 1,3-product is favored over the 1,2-product (by a ratio of 1.5:1). Both the data of Baggett *et al.* and of Jochims and Kobayshi were obtained by integration of the characteristic H^1 NMR signals of the products, but the former was done in dioxane and the latter was done in chloroform. The solvents used may have effect on the position of the reaction equilibrium. Another example that favors the 1,3-product is given by Juaristi and Antiunez (1992). They obtained a 47:30:23 mixture of HMPD, *cis*- HPD and *trans*- HPD from the reaction between glycerol and benzaldehyde. Upon continued exposure to acid, this ratio changed to 22:34:44. Therefore, they concluded that the reaction thermodynamics favors the 1,3-products. No solvent was mentioned in their work.

Clearly, more research is needed to accurately determine the equilibrium ratio of the 1,2- and 1,3- products. However, the previous work should have cleared any doubts about the feasibility to quantitatively produce the 1,3-product (mainly *cis*-HPD) from condensation of glycerol with benzaldehyde, and about the ready interconversion between the 1,2- and 1,3- products under acidic conditions.

Step 2: Tosylation. In this step, the unprotected hydroxy group of glycerol is transformed into a tosyloxy group, so that it can be removed in the subsequent detosyloxylation reaction. This group transformation is completed by treating HPD, the 1,3-product from the first-step reaction, with tosyl chloride. Tosylation of alcohols is a well-known reaction and is generally carried out under basic conditions. Bases are needed to neutralize the hydrogen chloride formed in this reaction. If not neutralized, the chlorine ion can potentially attack the newly formed tosyl group (Tipson, 1953).

A general procedure exists for tosylation of alcohols in pyridine (Fieser and Fieser, 1967). Pyridine functions both as a solvent and as a base in this reaction. The hydrogen chloride produced in tosylation may form a complex with pyridine, which crystallizes from pyridine at 0 °C. Based on this procedure, Juaristi and Antiunez (1992) have tosylated both the *cis*- and *trans*- HPD's in 98% yields. In another example, Hessel *et al.* (1954), by using a similar procedure, was able to obtain 2-phenyl-5-tosyl-1,3-dioxane

(PTD) in 94% yield in the tosylation of HPD. Besides the organic base, inorganic bases, such as sodium hydroxide and sodium carbonate, can also be used in alcohol tosylation, which has been reported in several incidents to tosylate other alcohols (Tipson, 1953; Flowers, 1971).

Step 3: Detosyloxylation and Group Protection Removal. In order to finally convert the selectively tosylated glycerol to 1,3-PD, the tosyloxy group, as well as the group protection, needs to be removed from PTD. As shown in Figure 6-2, there are two potential pathways to go from PTD to 1,3-PD. Either the hydroxy group protection can be removed, followed by removal of the tosyloxy group; or alternately the tosyloxy group can be removed, followed by removal of the hydroxy group protection. In either approach, removal of the group protection can be done with a hydrolysis reaction, and removal of the tosyloxy group is to be done with a hydrogenolysis reaction. The hydrolysis reaction regenerates benzaldehyde, which can be reused in the acetalization reaction.

If the hydrolysis reaction is carried out first, 2-phenyl-1,3-dioxane results as an intermediate. Hydrolysis of this compound is expect to be easy, because no additional functional groups other than the ether linkages may be affected. If the hydrolysis reaction is carried out first, however, caution needs to be exercised to prevent the potential attack of solvents on the tosyloxy group of PTD and/or TPD. Although according to Flowers (1971) tosylates are exceedingly stable under the acid hydrogenolysis conditions, and many successful examples of tosylate hydrolysis have been documented by Tipson (1953), our experiments show that the tosyloxy group is subject to the attack of protic solvents at temperatures above 60 °C.

Hydrolysis of PTD yields TPD. Although this reaction has never been reportedly done, TPD has been synthesized by Chong and Sokoll (1993) through a different route, which makes both the H^1 and C^{13} NMR data available for characterization of this compound.

Removal of the tosyloxy group is expected to be the most difficult step of the proposed glycerol conversion concept. According to Figure 6-2, detosyloxylation is to be done through a hydrogenolysis reaction with molecular hydrogen as the reducing regent. In the literature, hydrogenolysis of tosylates is generally effected with a lithium hydride, such as lithium aluminum hydride ($LiAlH_4$) or lithium triethylborohydride ($LiHBEt_3$). This reaction has never been reportedly done using molecular hydrogen as the reducing regent. Although $LiAlH_4$ and $LiHBEt_3$ are effective as detosyloxylation regents, however, they are too expensive to use on industrial scale. Therefore, it is up to us to develop a catalytic tosylate hydrogenolysis process with molecular hydrogen as the hydrogen source.

In summary, the new glycerol dehydroxylation concept presented in Figure 6-2 has provided us with an alternate and promising route to convert glycerol to 1,3-propanediol. The first and second step reactions of the new concept have been successfully performed by previous researchers, although for different purposes. The third step reaction, detosyloxylation with molecular hydrogen as reducing regent, is the key to the success of this new conversion concept, which has never been reportly done in literature.

6.3 Objective and Scope of Current Research

The objective of the current research is to explore the technical feasibility of the new glycerol dehydroxylation concept presented in Figure 6-2. As discussed above, removal of the tosyloxy group from the selectively tosylated glycerol is expected to be the most difficult step of the new conversion concept. Therefore, our primary task in this work is to develop a catalytic hydrogenolysis process to remove the tosyloxy group from ether PTD or TPD. In this capacity, the two potential pathways shown in Figure 6-2 to carry out the conversion from PTD to 1,3-PD has been tested and compared.

The reactions involved in the acetalization and tosylation steps have been performed by previous investigators for different purposes. The results from their work are promising. In this work, these reactions are re-performed to verify the published procedures and to provide the PTD needed in studying the detosyloxylation and protection removal reactions.

CHAPTER 7

EXPERIMENTAL PROCEDURES

7.1 Acetalization

The acetalization between glycerol and benzaldehyde is an equilibrium reaction. To drive this reaction to completion, the water formed in this reaction needs to be constantly removed from the reaction flask. In this experiment, water removal is done by performing the reaction in benzene solvent and removing the water as an azeotrope with benzene.

Figure 7-1 shows the experimental set-up used in this experiment. This set-up includes a round-bottomed reaction flask, a condenser and a Dean-Stark trap. The function of the Dean-Stark trap is to trap the water formed in the reaction. The reaction takes place in the flask. The water formed in the reaction is boiled off from the reaction flask as an azeotrope with benzene (boiling point: 65 °C). The vaporized water and benzene flow condense in the condenser and flow down into the Dean-Stark trap. As water and benzene are immiscible and have different densities, they separate in the Dean-Stark trap with water forming the bottom layer. The Dean-Stark trap is pre-filled with benzene. The condensed benzene is returned to the flask by overflow.

In a typical experiment, 100 g glycerol, 120 g benzaldehyde (c.a. 6% excess) and 300 *mL* benzene, together with 1 g *p*-toluene sulfonic acid catalyst are placed in a 500 mL round-bottom flask, equipped with a magnetic stirring bar. The reaction is initiated by bringing the reaction solution to a boiling state. Thereupon, vaporization and

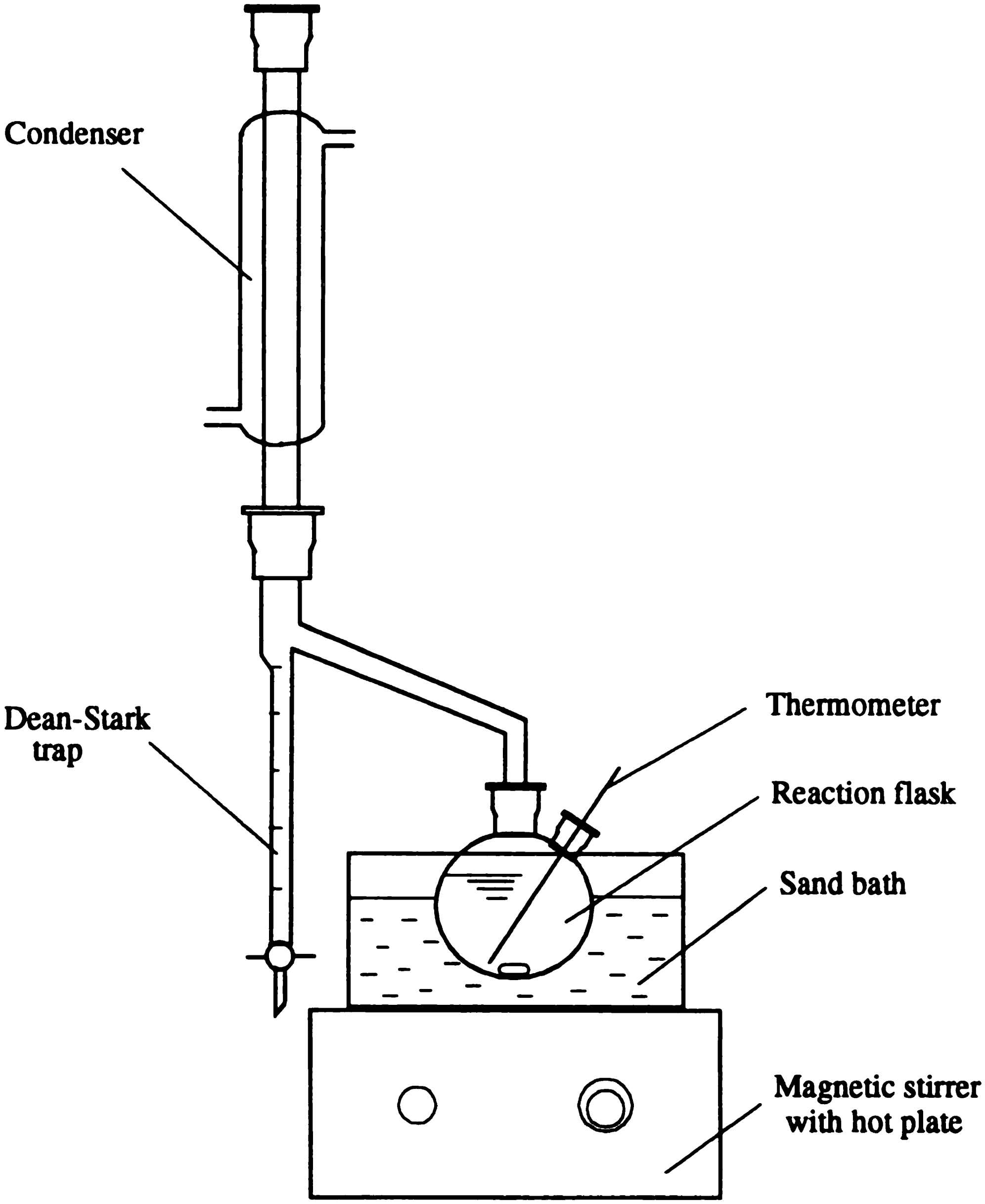


Figure 7-1. Experimental Set-up for Acetalization of Glycerol with Benzaldehyde

condensation commences in the reaction flask and the condenser, respectively, and the water is seen to accumulate at the bottom of the Dean-Stark trap. The Dean-Stark trap is graduated. Therefore, progress of the reaction can be monitored by the volume of the water accumulated in the Dean-Stark trap. When the water in the Dean-Stark trap reaches a steady level, the reaction is completed. Completion of the reaction is also indicated by the temperature change of the reaction solution. Before completion, the temperature stays constant at about 80 °C. When the reaction is close to completion, the temperature starts to climb, until a new level (about 160 °C) is reached. After the reaction is completed, the valve with the Dean-Start trap is turned open, and the benzene is boiled off, leaving only the product in the reaction flask.

The reaction product is a mixture of *cis*- and *trans*- 5-hydroxy-2-phenyl-1,3-dioxane (HPD, the 1,3-product) and *cis*- and *tran*- 4-hydroxy-methyl-2-phenyl-1,3-dioxolane (HMPD, the 1,2-product). A small amount of benzaldehyde may also exist in the product, because the excess benzaldehyde used in the reaction. To isolated HPD from this mixture, it is crystallized from a benzene-ligroin solution. The procedure is taken from Hill *et al.* (1928) and is documented in the following:

1) Dissolve the reaction product in a benzene-ligroin mixture. Typically, for an amount of 60 g of reaction mixture, about 90 mL of benzene and 150 mL of ligroin are needed.

2) Leave the above solution in a freezer for about one hour. At this time, crystals may not form from the solution.

3) Slowly add benzene while shaking, until the oil layer disappear. Crystals may or may not form at this time. Place the solution in the freezer, for about another hour. Crystals should form at this point.

4) Filter the solution with a Buckner filter under vacuum, and wash the crystals with a 50% benzene-ligroin solvent. Continue washing until the yellow color disappears. The yellow color indicates the presence of benzaldehyde in the crystals.

At the end of this procedure, a white, wax-like crystal product yields, which is *cis*-HDP. The *trans*-HDP has a better solubility in the benzene-ligroin solvent and is more difficult to crystallize than the *cis-HPD*. The above procedure can be repeated to further purify the HDP product obtained.

Analysis of the raw reaction product is performed with GC. Characterization of the purified HPD is done with ^{1}H and ^{13}C nmr. The GC column used is a DB-5 column from J&W. The carrier gas is hydrogen (at a flow rate of 1 *ml/min*). The oven temperature is programmed so that it stays at 150 °C for one minutes, then increases at a rate of 40 °C/ min and then stays at 320 °C for 3 minutes. The retention times for the relevant compounds are documented in Table 7-1.

Table 7-1. GC Retention Times for Acetalization Products

Compounds	Retention time (min)
benzene	1.30
benzaldehyde	1.42
cis-HPD	3.36
cis- and *trans*- HMPD	3.48
trans-HPD	3.83

7.2 Tosylation

Tosylation of 5-hydroxy-2-phenyl-1,3-dioxane (HPD) is carried out in pyridine. To start the experiment, HPD and TsCl are placed in an Erlenmeyer flask. Then to the flask is added cold dry pyridine. The flask is shaken until both HPD and TsCl dissolve in pyridine. Then the flask is placed in a refrigerator (*c.a.* 5 °C) to allow the reaction to continue for about 12 hours. Typically, 5-10% excess TsCl is used in this reaction, and for each gram of HPD, about 20 mL pyridine is needed.

Progress of this reaction can be monitored by formation of needle crystals. These crystals are pyridine-hydrochloride complex. When no more crystals are forming, the reaction is complete. At this time, the flask is removed from the refrigerator. The content of the flask is poured with stirring into a beaker containing about 6 g ice for each milliliter pyridine. The tosylate product (2-phenyl-5-tosyl-1,3-dioxane, or PTD) precipitates immediately.

Stirring is continued until all the ice melts. Then the solution is filtered with a Buckner funnel under vacuum, and the crystals is washed with water for three times. Finally, the crystals are dried in a desiccator under vacuum. After this procedure, PTD is obtained as white dry wax-like crystals. Characterization of PTD is accomplished using ^{1}H and ^{13}C nmr.

7.3 Hydrolysis

Hydrolysis of PTD has been performed in both water and methanol. To carried out the reaction in water, PTD from the previous reaction is placed in a glass vial equipped with a magnetic stirring bar. Then to the glass vial is added a small amount of *p*-toluene sulfonic acid (TsOH) and a large amount of water. PTD is not soluble in water. Therefore, it floats on the water at beginning of the reaction.

The glass vial is heated in a water or sand bath. The reaction solution is constantly stirred. After 4 to 6 hours' heating and stirring, the PTD floating on the water disappears, and yellow oil droplets are seen at the bottom of the glass vial. These yellow droplets are the benzaldehyde formed in the reaction. Upon cooling and sitting, benzaldehyde separates from the aqueous phase. The benzaldehyde phase is removed from the glass vial. The aqueous phase is neutralized with NaOH, and is transferred to the hydrogenolysis reactor for further reaction. Possibly because of the two hydroxyl groups present in 2-tosyl-1,3-propanediol (TPD), most of the TPD produced in the hydrolysis reaction stays in the aqueous phase.

To carry out the hydrolysis reaction in methanol, PTD is again placed in a glass vial. Then to this glass vial, the methanol solution of TsOH is added. The glass vial is simply placed in an oven at 40 °C. After 2 hours, the reaction is completed. The benzaldehyde formed in the reaction does not separate from the methanol phase. To isolate PTD, the reaction product is first extracted with hexane to remove benzaldehyde, and then it is dried at a temperature below 40 °C to remove the methanol solvent. Thus obtained PTD is re-dissolved in dioxane and then transfer to the hydrogenolysis reactor.

Comparing the above two procedures, the later one is more successful than the former. The hydrolysis reaction in water is usually carried out at a temperature above 80 °C. At this temperature, tosylates are subject to the attack of protic solvents, as is discovered in this work. The hydrolysis reaction in methanol is carried out at a temperature of 40 °C. At this temperature, the solvent attack on the tosyloxy group is insignificant.

7.4 Hydrogenolysis

In this work, hydrogenolysis of tosylates is carried out under hydrogen pressure with either Ni on kieselguhr or Ru on carbon as the catalyst. The same experimental system and the same experimental procedure as described in Chapter 3 are used, but the reactor used in this experiment has a smaller capacity (10 mL). The 1,3-PD produced in TPD hydrogenolysis is quantified using GC.

CHAPTER 8

RESULTS AND DISCUSSION

8.1 Acetalization

Acetalization with benzaldehyde protects the first and third hydroxyl groups of glycerol from being tosylated and removed in the subsequent reactions. This reaction has two important features: a) it is an equilibrium reaction, but can be driven to completion; and b) it is non-selective: besides the desired 1,3-product HPD, the undesired 1,2-product HMPD is also produced, which has to be separated from HDP and returned to the acetalization reactor. Because of the later feature, the percentage of HDP in the acetalization products and the ease to separate HPD from HMPD are our primary concern in this research.

Three acetalization experiments have been performed. Two are done in benzene, and one is done in a 1:1 benzene-ligroin mixture. In the first experiment, 50 g glycerol and 60 g benzaldehyde (c.a. % excess) are condensed in 300 ml benzene. The reaction takes about 3 hours to complete. GC analysis of the raw reaction product shows three product peaks. Of these three peaks, two are determined to result from HPD (*cis*- and *tran*- HPD), and one from HMPD. The two diastereomers of HMPD can not be separated with the GC column we were using.

To separate HPD from the product mixture, it is crystallized from a benzene-ligroin mixture with the procedure described in Chapter 7. The crystallized product is characterized with ^{1}H and ^{13}C nmr. The obtained spectra are found to be consistent with the structure of HPD and with those documented for this compound in the literature. Measurement of the melting point of this crystallized product (75-80 °C) further identifies it as the *cis* diastereomer of HDP. The previously reported melting points are 37 °C for HMDP, 65 °C for *trans*-HDP and 83 °C for *cis*-HDP. The crystallized *cis*-HPD is not 100% pure. It contains a small amount of *trans*-HPD, but very little HMPD. HMPD is believed to not crystallize with *cis*-HPD, and therefore can be removed in the process of filtration and washing. *Trans*-HPD may crystallize with *cis*-HPD, although to a much less extent. Both *cis*-HPD and *trans*-HPD are desired in the acetalization reaction.

From the first experiment, about 10 g *cis*-HPD is obtained after purification. The yield is calculated as 25%. Before purification, the yield of *cis*-HPD is estimated to be about 42%, based on the sizes of GC peaks. The ratio of *cis*-HPD to *trans*-HPD to HMPD is 42:33:25. In the second experiment, 100 g glycerol is condensed with 120 g benzaldehyde in 300 ml benzene. The (*cis*-) HPD yield from this experiment is similar to that of the first experiment.

From these results, it is seen that the yield of HPD from the acetalization reaction is in high percentage. The procedure to separate HPD from the product mixture is fairly simple and easy to carry out. It is also seen, however, that the undesired HMDP and unrecovered HDP in combination still account for about 75% of the reaction product. They need to be recycled back to the acetalization reactor, if an industrial process is to be designed.

After crystallization, the undesired HMDP and unrecovered HDP are left in the benzene-ligroin mixture. If the acetalization is carried out in the same solvent, recycle of this residue will be straightforward. It is motivated by this consideration that the third experiment is run in a 1:1 benzene-ligroin mixture to explore the feasibility to carry out the acetalization in such a solvent. This experiment turned out to be a success and furnished an HPD yield of 23%.

8.2 Tosylation

The purpose of tosylation is to transform the unprotected hydroxy group of HPD into a good leaving group, so that it can be removed in the subsequent reactions. In the current research, this group transformation is accomplished by treating HPD with tosyl chloride (TsCl) in pyridine.

Two experiments have been performed. In one experiment, 2 g HPD is treated with 2.4 g TsCl (c.a. 12% excess), which gives 3.1 g PTD. The yield is calculated as 83%. In the other experiment, 5 g HPD is treated with 6 g TsCl (c.a. 12% excess), which furnishes 8.1 g PTD. The yield is 87%. In the literature, a yield as high as 98% has been reported in tosylation of HPD (Juaristi and Antiunez, 1992). The lower yield in our experiments may result from the unpurified TsCl and the undried pyridine used in this experiment, which are believed to affect the yield. However, no additional effort has been made in the current research to maximize the product yield. We are convinced that higher yield is achievable if more care is exercised in performing the reaction.

The obtained PTD is characterized with ^{1}H and ^{13}C nmr. These spectra are consistent with the structure of PTD and with the data documented in the literature (Juaristi and Antiunez, 1992).

8.3 Detosyloxylation

Detosyloxylation, or removal of the tosyloxy group, is the focus of this work. This reaction has never been done with molecular hydrogen as the reducing regent. In this work, we attempt to develop such a hydrogenolysis process to remove the tosyloxy group from either TPD or PTD, and to create a pathway from PTD to 1,3-PD.

As discussed previously, the conversion of PTD to 1,3-PD can potentially be approached in two different ways. One approach is to first remove the hydroxy group protection and then remove the tosyloxy group. The other is to first remove the tosyloxy group and then remove the hydroxy group protection. Both approaches have been explored in this work.

The second approach proves to be unsuccessful. PTD is found to be inactive under hydrogenolysis conditions. The experiment has been carried out in dioxane with Ni on kieselguhr as the catalyst. The reaction is run under 3 MPa H_2 pressure. The temperature has been kept at 120 °C for two hours, at 130 °C for two hours, at 140 °C for 10 hours and then at 150 °C for another 10 hours. No product is found at the end of the experiment.

The initial attempt to convert PTD to 1,3-PD via the first approach did furnish 1,3-PD. However, the yield was low (less than 15%). To start this experiment, PTD is hydrolyzed at 80 °C in 0.01 N aqueous *p*-toluene sulfonic acid solution. This reaction normally takes about 4 to 5 hours. After the reaction, the benzaldehyde released from the reaction, which separates itself from the aqueous phase, is removed. The aqueous phase, which contains most of the TPD resulting from the hydrolysis, is neutralized with NaOH and transferred to the hydrogenolysis reactor to remove the tosyloxy group. Three catalysts, including Ni on kieselguhr, Raney Ni and Ru on carbon, have been used in the hydrogenolysis, and none of them has provided a 1,3-PD yield higher than 27%. A more detailed account of the about results may be found in DeAthos (1995), who has assisted this author in performing the above experiments.

In spite of the low 1,3-PD yield delivered by this experiment, it shows that TPD, in contrast to PTD, is reactive under the hydrogenolysis condition. Comparing the structures of PTD and TPD, the tosyloxy group of PTD is isolated, while the tosyloxy group of TPD is next to a hydroxy group. Possession of this adjacent hydroxy group must have somehow facilitated the removal of the tosyloxy group in hydrogenolysis of TPD.

To confirm the above speculation, experiments are carried out to hydrogenolyze 6-tosyloxy-hexanol (TH) and 2-tosyloxy-cyclohexanol (TCH). Like PTD, TH has an isolated tosyloxy group; while like TPD, the tosyloxy group of TCH is next to a hydroxy group. As expected, TH is found to be inactive under the hydrogenolysis conditions. TCH, on the hand, is hydrogenolyzed at a temperature above 140 °C. Below 140 °C, the reaction is slow. Both the hydrogenolysis of TH and of TCH have been conducted in dioxane. Hydrogenolysis of TCH has been conducted with both Ni on kieselguhr and Ru on carbon. Hydrogenolysis of TH, however, has been conducted only with Ni on kieselguhr. The results of these experiments confirm our speculation that the presence of a hydroxy group next to the tosyloxy group facilitates its removal in hydrogenolysis.

Hydrogenolysis of TCH yields two products. One is cyclohexanol and the other is cyclohexanone, as found in our GC-MS analysis. With Ni on kieselguhr as the catalyst, the ratio of cyclohexanol to cyclohexenone in the product is about 1:1; with Ru on carbon as the catalyst, the ratio is about 3:1. No other products are found. Based on the observed reaction products, the hydrogenolysis of TCH may occur as shown in Figure 8-1, with

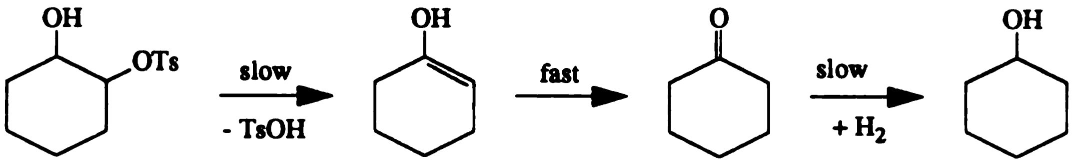


Figure 8-1. Reaction Pathway of TCH Hydrogenolysis

cyclohexanone as the precursor to cyclohexanol. The function of transition metal catalysts in this reaction is not limited to catalyzing the hydrogenation of cyclohexanone to cyclohexanol in the last step. They must be involved in the initial detosyloxylation step as well, because, in the absence of transition metal catalysts, TCH is found to be inactive at 140 °C. .

The assistance of the adjacent hydroxy group to detosyloxylation can be understood on the assumption that the initial detosyloxylation step in the above reaction scheme is thermodynamically unfavorable. Presence of the adjacent hydroxy group stabilize the initial detosyloxylation product through a subsequent tautomerization reaction. In the absence of such a hydroxy group, as in the cases of PTD and TH, the subsequent tautomerization is impossible and thus the initial detosyloxylation product is not stabilized. This explains the inactivity of PTD and TH under hydrogenolysis conditions.

To find out the reason for the low 1,3-PD yield in our initial attempt to convert PTD to 1,3-PD, further experiments are done to hydrogenolyze TCH in 90% aqueous methanol. To our surprise, this reaction yields neither cyclohexanol nor cyclohexanone. The reaction does provide two products, but these products are from the reactions of TCH with water and with methanol, respectively. Further experiments show that the reactions of TCH with water and methanol can both be effected simply by heating TCH in these solvents over 60 °C. At 80 °C, these reactions becomes fairly fast. It has been suggested in the literature that tosylate is stable under hydrolysis conditions (Flower, 1971). This statement appears not true to TCH, and is probably not true to PTD and TPD either. In hydrolysis of PTD, it has been observed that the reaction solution becomes substantially more acidic at the end of the reaction than at the beginning of the reaction. Increase in the acidity of the reaction solution is a strong sign that the attack of water on the tosylate has occurred. The reaction of water (and methanol) with tosylates releases TsOH, which increases the acidity of the reaction solution.

Based on the above study on TCH hydrogenolysis, a new procedure is developed to convert PTD to 1,3-PD. This procedure starts with a hydrolysis reaction in methanol. PTD has a much better solubility in methanol than in water. Therefore, the reaction can be carried out at a temperature as low as 40 °C, while still giving a reasonable reaction rate (normally complete in two hours). No acidity increase of the reaction solution is observed at the end of the reaction, which implies that the solvent attack on the tosyloxy group is insignificant at 40 °C.

Hydrolysis of PTD yields TPD and benzaldehyde (in the form of acetal with methanol). To separate benzaldehyde from TPD, the raw product is extracted with hexane. Then the reaction solution is dried at the room temperature to remove methanol. The dried product is mostly TPD. To hydrogenolyze TPD, it is dissolved in dioxane, and then heated up to 140 °C in the presence of Ni on kieselguhr. Dioxane is an aprotic solvent, and it does not attack tosylate.

The first experiment performed with the new procedure starts with 213 *mg* PTD. At the end of hydrogenolysis, 27 mg 1,3-PD is obtained in the product. The yield is calculated as 56%. In addition to 1,3-PD, hydrogenolysis of TPD also gives *n*-propanol (24%). This is understandable, because hydrogenolysis of TPD has 3-hydropropionaldehyde (HPA) as an intermediate, which may also undergo a dehydration pathway to give *n*-propanol, as shown in Figure 8-2.

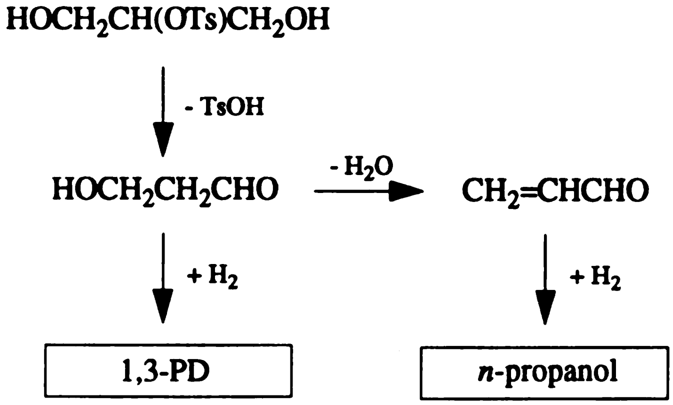


Figure 8-2. Reaction Pathway of TPD Hydrogenolysis

From Figure 8-2, the selectivity of TPD hydrogenolysis is controlled by the relative hydrogenation and dehydration rates of HPA. Increasing the amount of the metal catalyst increases the hydrogenation rate. Therefore, the selectivity to 1,3-PD should increase as more catalyst is used. This proves to be true. When the mole ratio of Ni catalyst to substrate is increased from 1:1 in the first experiment to 2:1 in the second experiment we carried out, it is observed that the mole ratio of 1,3-PD to *n*-propanol in the product increases from 2.3:1 in the first experiment to 4:1 in the second experiment. In the second experiment, 34 *mg* 1,3-PD has been obtained from 210 *mg* PTD. The 1,3-PD yield is 72%. The *n*-propanol yield is calculated as 18%. No further experiments are conducted to maximize the 1,3-PD yield. Nevertheless, the above experimental results show that the new procedure is promising in carrying out the conversion of PTD to 1,3-PD.

In addition to the 1,3-PD yield, the catalytic nature of TPD hydrogenolysis consists of another major concern of the current research. The stoichiometrical reaction between transition metal and tosylate has been previously reported, in spite of the fact that in the reported reaction it is the O-S bond, instead of the C-O bond as in TPD hydrogenolysis, that is broken. Therefore, in the current work, the Ni on kieselguhr catalyst used in the second TPD hydrogenolysis experiment is collected after the reaction, and is reused in hydrogenolysis of TCH. It is found that the catalyst is still active and a turnover number of about 50 has been achieved in 24 hours, at 160 °C and 3 MPa H_2 pressure. At this point, there should be no doubt that the hydrogenolysis of TPD in the presence of Ni on kieselguhr is a catalytic reaction in its nature.

8.4 Design Concept of Industrial Conversion Process

As the goal of this research, the technical feasibility of the new glycerol dehydroxylation concept presented in Figure 6-2 is verified on the laboratory scale by the experiments just discussed. On the industrial scale, processes as shown in Figures 8-3 to 8-6 may be designed to produce 1,3-propanediol from glycerol.

The acetalization process shown in Figure 8-3 features a continuous acetalization reactor, a continuous forced-circulation HPD crystallizer and a continuous vacuum filter. The reactor is equipped with a water trap of the same principle as the Dean-Stark trap used in our bench-top experiments. The purpose is to remove the water formed in the reaction. The design of this process has incorporated the following observations made in our

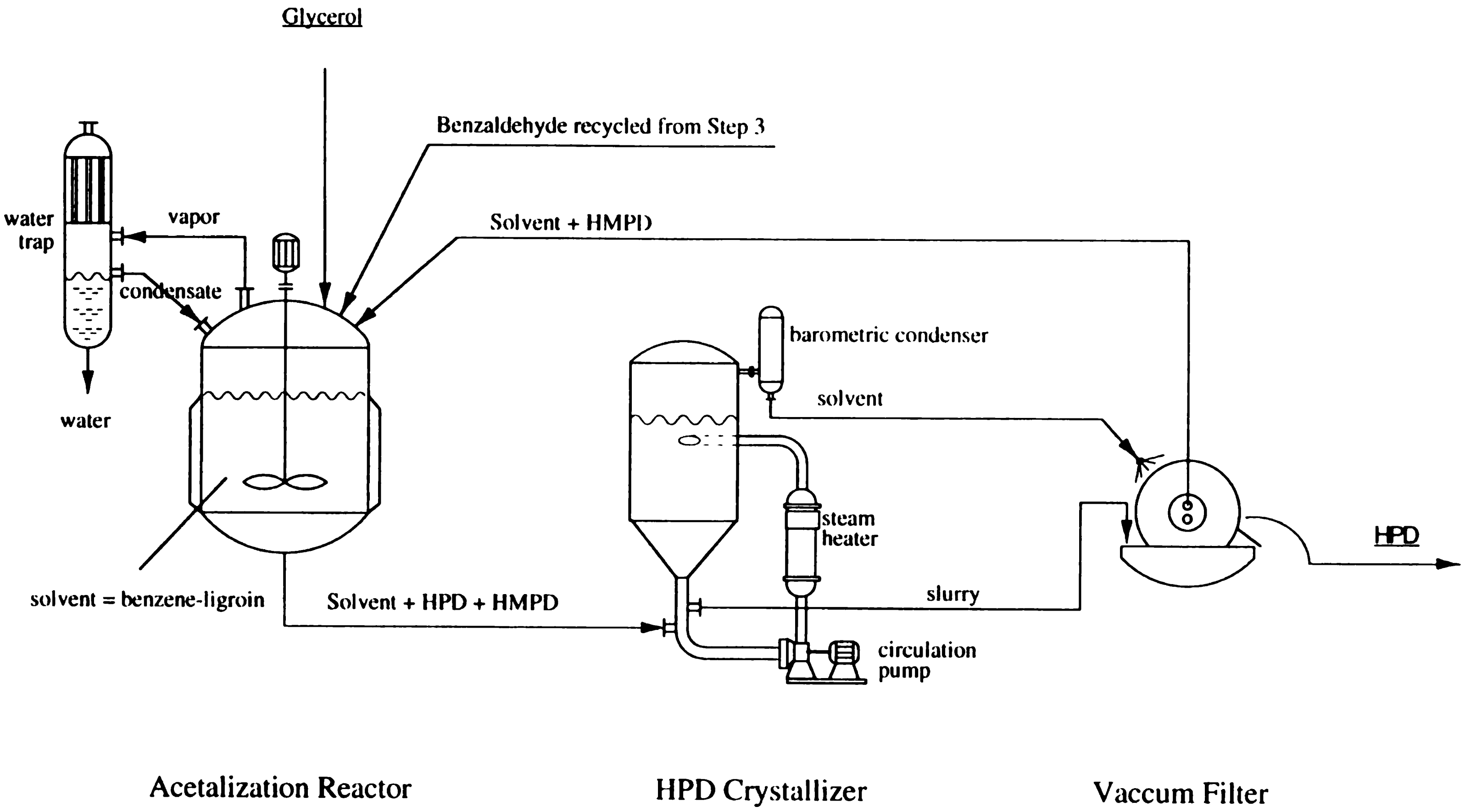


Figure 8-3. Glycerol Dehydration Process - Step 1: Acetalization

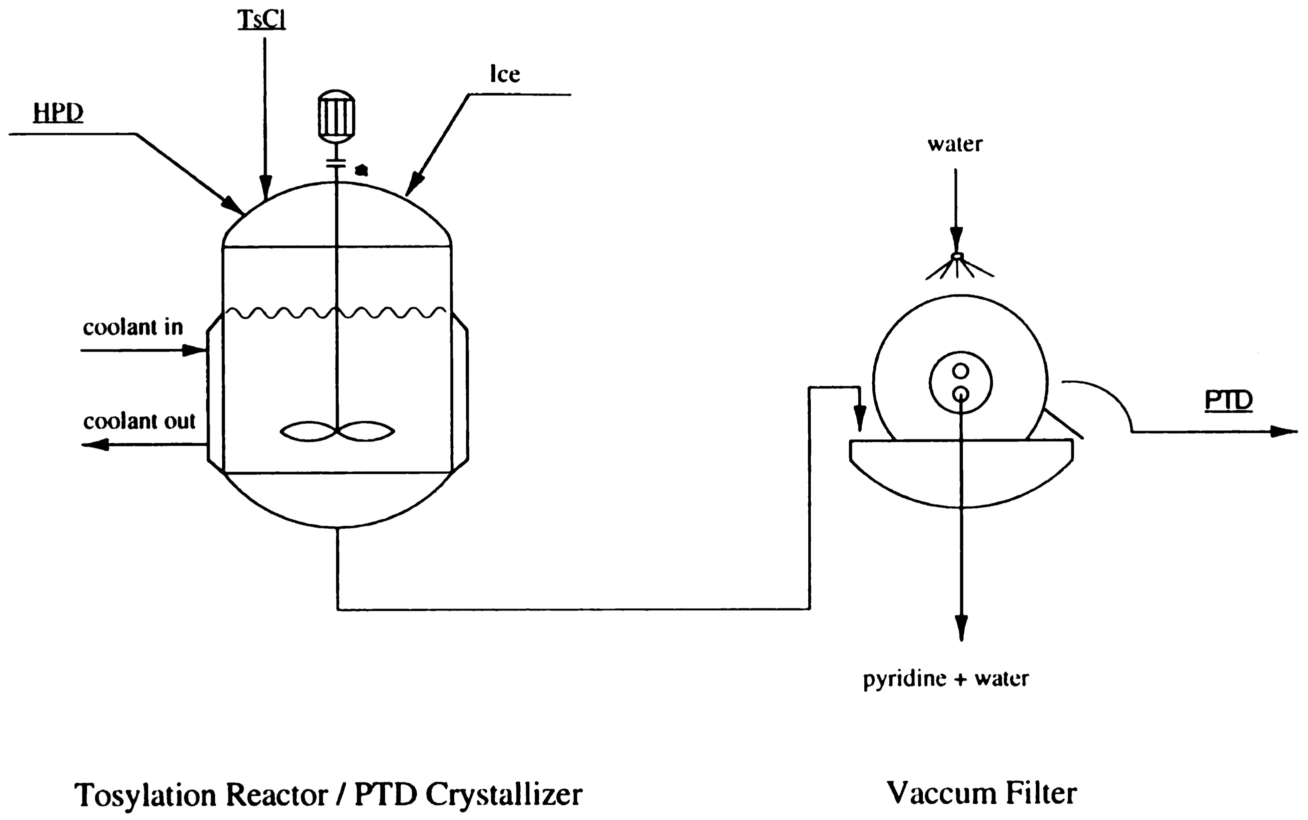


Figure 8-4. Glycerol Dehydration Process - Step 2: Tosylation (Design #1)

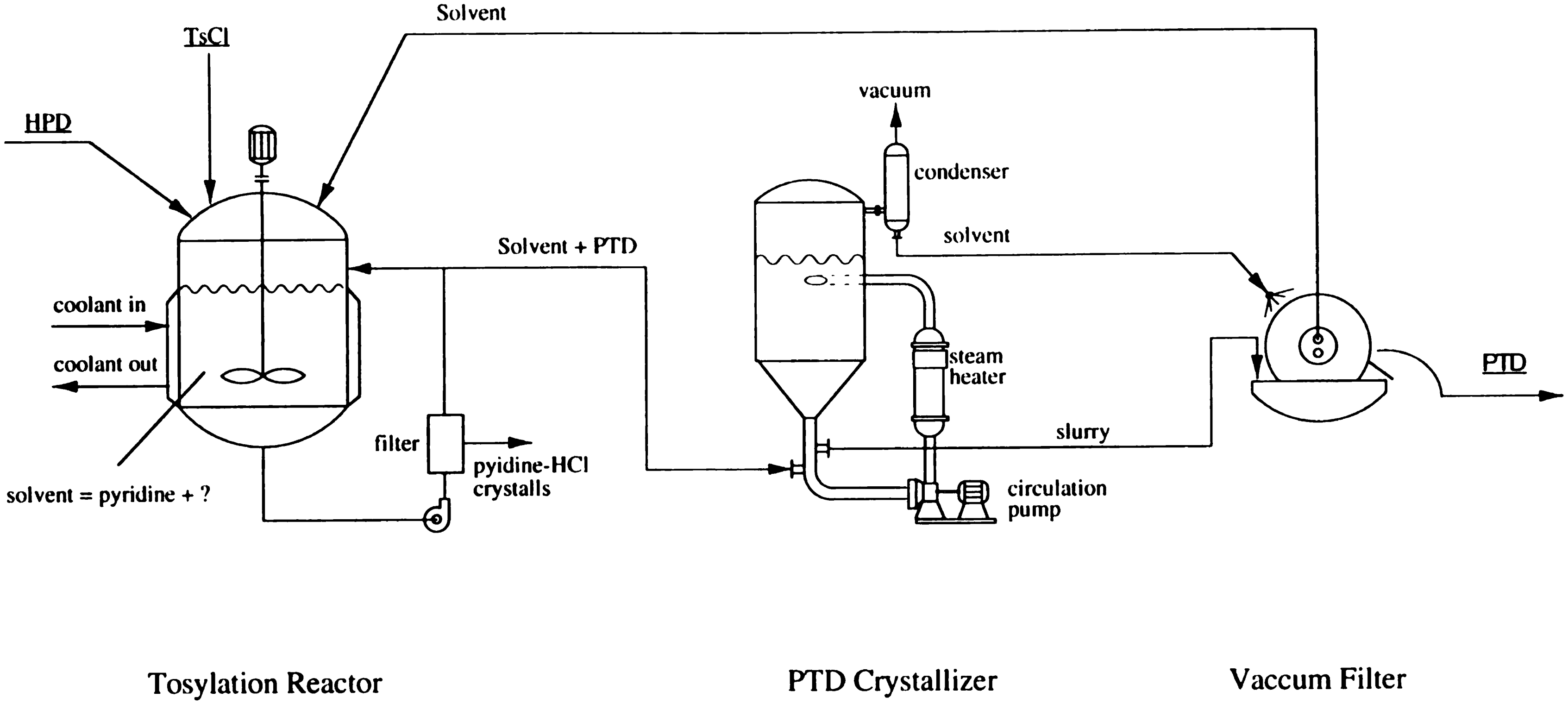


Figure 8-5. Glycerol Dehydration Process - Step 2: Tosylation (Design #2)

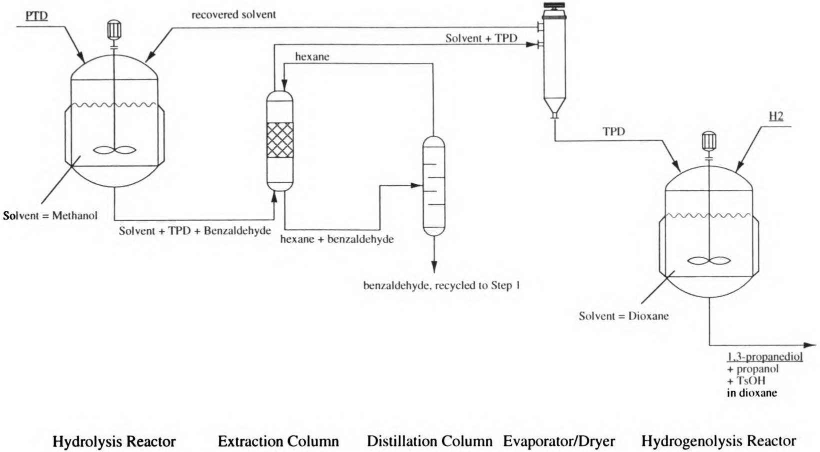


Figure 8-6. Glycerol Dehydration Process - Step 3: Detosyloxylation

acetalization experiments:

a) acetalization of glycerol with benzaldehyde occurs readily in the presence of acid catalyst, and can be driven to completion by using a Dean-Stark trap to remove the water formed in the reaction.

b) the desired 1,2-product HPD can be readily purified from the product mixture by crystallizing it from benzene-ligroin mix. The unreacted glycerol and benzaldehyde and the undesired 1,3-product HMPD will stay in the solution.

c) acetalization of glycerol with benzaldehyde can be carried out in benzene-ligroin mix, as well as benzene only, thus allowing direct crystallization of HPD from the reaction solution and direct recycling of the unreacted glycerol and benzaldehyde and the undesired HMPD back to the reactor, if benzene-ligroin is used as the solvent.

According to the design, the HPD rich product will be directly fed into the crystallizer from the reactor. The desired HPD is crystallized from the solution and then separated from it by the filter. Owing to the nature of the selected crystallizer, some solvent will be vaporized in the crystallizer and then condensed in the condenser equipped with the crystallizer. This solvent will be collected and used to wash the HPD cake formed on the filter surface. The filter cake discharged from the filter may need further drying. The filtrate, composed of the solvent and the undesired HMPD and the unreacted glycerol and benzaldehyde dissolved in it, is lean in HPD and is recycled back to the reactor. The benzaldehyde used in acetalization will also be recycled, but from Step 3, the detosyloxylation process.

Because of the recycling of HMPD, the process shown in Figure 8-3 produces no by-product. Under acetalization condition, HMPD and HPD are readily inter-convertible. As a result, the HMPD formed in the reaction can only accumulate to a certain level in the reactor, in equilibrium with the HPD present. Once that level is reached, no HMPD will be further produced in the reactor. HPD will be the only product of the reaction of glycerol and benzaldehyde, as it is continuously removed from the reactor and process. Therefore, with the process shown in Figure 8-3, one mole HPD will be expected from each mole glycerol fed into the reactor, or the HPD yield will be 100% (or close to 100% if possible loss in filter is considered), under stable conditions. High HPD yield is a major advantage of the continuous process shown in Figure 8-3.

The tosylation process shown in Figure 8-4 is designed strictly based on our lab tosylation procedure described in Chapter 7. It involves three major steps:

a) allowing HPD to reactor with TsCl in pyridine at low temperature, so that the hydrochloride formed in the reaction can precipitate from the reaction solution as pyridine-hydrochloride complex.

b) mixing the reaction product with large quantity of ice following Step a). The purpose is to further lower the temperature and to force the tosylation product PTD to crystallize from the product solution. and

c) separating PTD crystals by filtration

High PTD yield has been obtained with this procedure in lab experiments. As an industrial process, however, this procedure has a major disadvantage: mixing reaction product with ice in Step b) creates a difficulty to the recycling of pyridine.

At industrial scale, the pyridine solvent has to be recycled, to minimize the process cost and waste discharge. After PTD removal, the pyridine is in a mixture with water in Figure 8-4. To reuse pyridine in tosylation, it has to be first separated from water and then thoroughly dried. Tosyl chloride is attacked by very small quantity of water present in pyridine.

To overcome the above difficulty, an alternate process as shown in Figure 8-5 is considered. This design eliminates ice from the process and attempts to crystallize PTD directly from the reaction medium, thus allowing direct recycling of the medium, together with the unreacted starting material in it. The reaction medium for this process may be pure pyridine or a mixture of pyridine with another solvent, ligroin for example, which helps lower the solubility of PTD in the reaction medium. Pyridine, as a base, is needed in the reaction medium to neutralize the hydrochloride released from the reaction. To remove the pyridine-hydrochloride complex precipitated from the reaction medium, the tosylation reactor in Figure 8-5 is incorporated with a circulation loop, which contains a continuous in-line filter. The reaction product sent to the crystallizer is designed to be free of hydrochloride. The crystallizer in Figure 8-5 is of evaporative type, so that the solvent can be partially removed to give a PTD saturated solution in the crystallizer. The solvent removed from the solution may be used to wash the PTD crystal in filtration step.

At the time being, the solubility data of PTD in pyridine or other relevant solvents are not available yet. It is also left for speculation wether the tosylation reaction can be carried out in a mix of pyridine with another solvent as smoothly as in pyridine alone. It is clear that further experiments are needed to verify the feasibility of this process. However, if successful, this process has great advantages over the one shown in Figure 8-4, in terms of both processing cost and waste discharge. Like the acetalization process in Figure 8-3, this process can potentially furnish a product yield of 100%, under ideal condition.

The detosyloxylation process as shown in Figure 8-6 is designed based on the discovery made in this research: the detosyloxylation of PTD can be accomplished by a hydrolysis (or methnolysis more accurately) reaction carried out in methanol at moderate temperature, followed by a catalytic hydrogenolysis reaction carried out in dioxane. It features a hydrolysis reactor, an extraction column to remove benzaldehyde from the hydrolysis product solution, a distillation column to separate the extracted benzaldehyde from the hexane extractant, a thin-film evaporator/dryer to remove the methanol solvent from the hydrolysis product TPD, and a hydrogenolysis reactor to finally convert TPD to 1,3-PD. Separation of 1,3-PD from the solvent dioxane and other hydrogenolysis products, including TsOH and propanol, is yet to be added to this process.

According to the design, both the methanol and the hexane solvents used in this process are recycled. The benzaldehyde reclaimed in this process is also recycled, but back to the Step 1 acetalization process.

Figure 8-7, obtained from combining and simplifying the processes in Figures 8-3, 8-5 and 8-6, illustrates the material flow in glycerol dehydroxylation. It is seen from this diagram that the acetalization process, if designed as in Figure 8-3, produces no other product but HPD, at 100% yield. Similarly, the tosylation process, if designed as in Figure 8-5, gives only PTD, at 100% yield. Therefore, the overall yield of the glycerol dehydroxylation process is solely determined by the yield of the detosyloxylation process. In our experiment, a 1,3-PD yield as high as 72% has been achieved in PTD detosyloxylation, under un-optimized conditions. This yield can be taken as the overall yield of the new glycerol dehydroxylation process. For comparison, the theoretical yield of glycerol fermentation is 67%.

From Figure 8-7, it is also seen that production of 1,3-PD is at the expense of tosyl

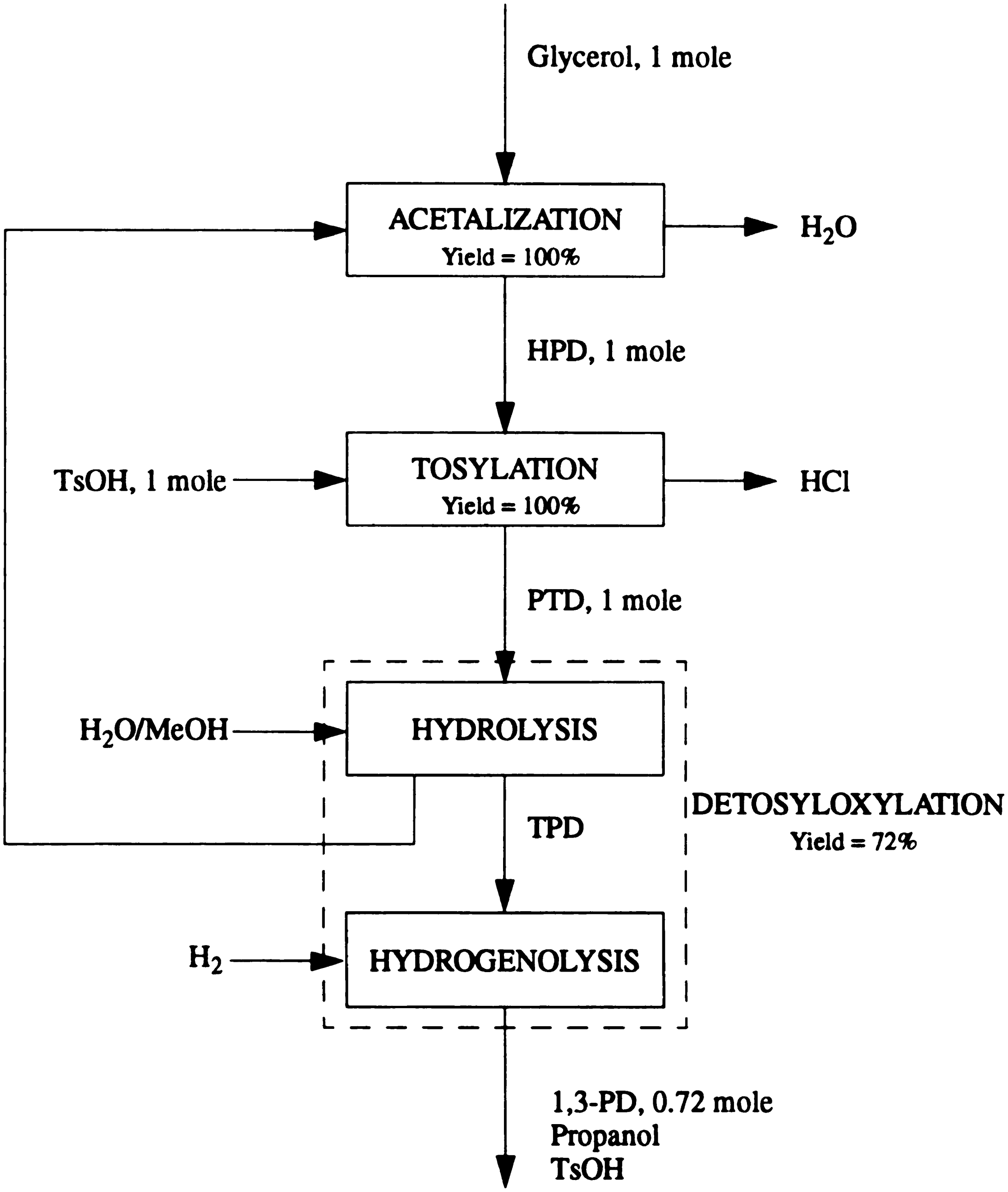


Figure 8-7. Material flow in glycerol dehydroxylation

chloride, gaseous hydrogen, as well as glycerol. Benzaldehyde is not consumed in the process because of recycling. Assuming the overall yield of the process is 72%, production of each pound of 1,3-PD will consume 1.68 lb glycerol, 3.61 lb tosyl chloride and 4.12 mole hydrogen, which cost about $1.68, $5.60 and $0.12, respectively. The total raw material cost will be $7.40 per pound of 1,3-PD, of which 76% results from tosyl chloride. The above costs are calculated based on a unit price of $1.00 per pound for glycerol, $1.55 per pound for tosyl chloride, and $0.03 per mole for hydrogen gas. These prices are from the Chemical Market Report, Aceto Corp and AGA Gas, respectively.

It is seen from the above that the majority of the raw material cost of 1,3-PD production results from tosyl chloride. The price of this chemical is fairly high on the market, as a result of the small demand and thus small production of this chemical. As a solution to reduce the raw material cost, on-site synthesis of tosyl chloride may be considered. On-site synthesis of tosyl chloride may require a large scale glycerol conversion process to justify it. The glycerol conversion processes shown in Figures 8-3, 8-5 and 8-6 are mostly continuous, and are therefore suitable for large scale production.

Another way to improve the economics of the glycerol dehydroxylation process is to recover and sell the *t*-toluene sulfuric acid (TsOH) produced in this process. As can be seen from Figure 8-7, the glycerol dehydroxylation process produces two by-products: propanol and TsOH. Propanol competes the raw materials with 1,3-PD and is to be minimized from the process; while TsOH is produced at the same time as TsCl is consumed in the process, on the mole to mole basis. Spectrum Chemical MFG has quoted a price of $5.87 per pound on TsOH. Selling of TsOH could basicly compensate the cost of tosyl chloride. Then the net raw material cost for production of 1,3-propanediol from glycerol would be only $1.80 per pound of 1,3-propanediol, which is extremely favorable.

PART III

VAPOR-PHASE HF SACCHARIFICATION

CHAPTER 9

MODELING THE HF ADSORTION PROCESS IN A PACKED-BED REACTOR

HF vapor is a potent and selective regent for saccharification of lignocellulose. The vapor-phase HF saccharification consists of two sequential operations: HF adsorption and solvolysis (or simply HF adsorption as it is more commonly called) followed by HF desorption. The current research focuses on the first operation, that is, HF adsorption.

Research on vapor-phase HF saccharification can be traced back to the early experiments by German scientists (Fredenhagen and Cadenbach, 1933; Luers, 1938). More recently, this process has been studied by Bentsen (1982), Ostrovski *et al.* (1984 and 1985), and Franz *et al.* (1982 and 1987) on pilot-scales. These research was aimed to demonstrate the technical and economic promise of vapor-phase HF saccharification. Because of its empirical and proprietary nature, however, these research provided very limited data for process design and development.

The research at Michigan State University (MSU) was started in the late 1980's, aiming to provide the necessary fundamental chemical engineering data for process development and design. Specifically, Mohring and Hawley (1989) studied the intrinsic adsorption of HF on wood chips. Rorrer *et al.* (1988) and Rorrer (1989) studied the intrinsic reaction of HF with lignocellulose. Reath (1989) observed the behavior of HF adsorption on wood chips in a bench-scale, packed-bed reactor. These studies have yielded a great deal of useful results, but are not yet complete; as is especially true to the research on HF adsorption in a packed-bed reactor. Questions of primary importance to design and operation of the HF adsorption process in a packed-bed reactor but not yet explored before the current work include: a) under given operating conditions, how long does the adsorption need to be carried out to achieve a certain overall HF loading level? and b) how is the adsorbed HF distributed through the reactor?

The current work is a continuation of the research initiated by Hawley, Mohring, Rorrer and Reath, and has focused on modeling the HF adsorption process on wood chips in a packed-bed reactor. A predictive model relating HF loading to the adsorption time and conditions is considered to be the best solution to the two questions raised above.

Several breakthroughs have been made in this work. Experimentally, the HF adsorption behavior in the bench-scale, packed-bed reactor has been studied in a broader temperature and HF supply rate ranges than in the previous work, which leads to the finding that the rate of HF adsorption is controlled by two factors: the intrinsic adsorption rate and the HF supply rate. These two rate-limiting mechanisms take control at different phases of the adsorption process and leads to different behavior of HF adsorption. Based on this finding, a conceptual model has been developed, which explains all the observed behavior of HF adsorption in the bench-scale, packed-bed reactor. Based on this conceptual model, a mathematical model has also been developed, which can be used to calculate the overall HF loading as a function of the adsorption time. However, the significance of this model is undermined, by its inability to provide information on the HF loading distribution in the reactor.

Further work has led to a more advanced model of the HF adsorption process in the packed-bed reactor. This model is developed based on a detailed analysis of the HF flow, the intrinsic HF adsorption and the heat transfer processes occurring in the reactor during HF adsorption. This advanced model provides a great deal of insight into the HF adsorption process in the packed-bed reactor, and can be used to predict the HF loading distribution, as well as the overall HF loading, as a function of the adsorption time and operating conditions. This model has been validated by the experimental data from the bench-scale, packed-bed reactor under study.

Based on this work, two papers have been written and been published in *Chemical Engineering Science* (Wang *et al.*, 1994; Wang *et al.*, 1995a). These papers basically document all the work that has been done in the current research on HF adsorption. To avoid rewriting, only abstracts of these papers are included in this dissertation.

The first paper is entitled "Adsorption model of HF on Wood Chips in a Bench-Scale, Packed-Bed Reactor", representing the experimental work and the work on the more primitive lumped HF adsorption model. the abstract of this paper is quoted below:

> ***Abstract:*** *The adsorption process of HF on wood chips in a packed-bed reactor was studied. Two adsorption rate limiting mechanisms exist for this process, namely HF supply control and intrinsic adsorption control. In the initial period of this process, the adsorption rate is determined by the HF supply rate; after the initial period, the adsorption rate is determined by the intrinsic adsorption rate. Consequently, the HF loading profile for this adsorption process includes two distinct parts: an initial linear part and following non-linear part, corresponding to the two different rate limiting mechanism. This conceptual model of HF adsorption in the packed-bed reactor was supported by experimental observations from a bench-scale. packed-bed reactor. Based on this conceptual model, a mathematical model was developed to predict the HF loading for a given adsorption time under given operating conditions. To demonstrate its application, the mathematical model was used to analyze the effect of the heat dissipation rate of the reactor on the adsorption process.*

The second paper is entitled "Modeling the HF Adsorption Process on Wood Chips in a Packed-Bed Reactor", representing the work on the more advanced detailed HF adsorption model. The abstract of this paper is also quoted below:

Abstract: *In this work, a detailed model, along with the numerical procedure to solve this model, was developed for the HF adsorption process on wood chips in a packed-bed reactor. This model is aimed to predict the HF loading distribution, as well as the overall HF loading, with respect to the adsorption time. However, the temperature field in the HF reactor may also be obtained using this model, as a function of time. To validate the developed model, the computed overall HF loading profiles were compared with the experimental data acquired previously from a bench-scale, packed-bed reactor filled with big-tooth aspen wood chips, and a good agreement was obtained. By taking advantage of the newly developed adsorption model, the HF loading distribution and temperature field in the bench-scale, packed-bed reactor was examined. It was found that a uniform HF loading distribution and temperature field is always obtained at the end of the adsorption, provided that the adsorption is carried out sufficiently long. This finding is significant, since a uniform HF loading distribution is always desired in operation of the HF adsorption process.*

The above modeling work carried out in the current research provides a theoretical foundation to design and control of the HF adsorption process in the packed-bed reactor.

CHAPTER 10

SUMMARY AND CONCLUSIONS

In the current research. three biomass conversion processes have been investigated, namely sugar hydrogenolysis, glycerol dehydroxylation and HF saccharification, all aiming to produce value-added, useful chemicals from the biomass resources. Results from these investigations are summarized as follows.

10.1 Sugar Hydrogenolysis

The research on the sugar hydrogenolysis process has focused on understanding of the reaction mechanism and improvement of the reaction selectivity. In the mechanism study, a series of 1,3-diol model compounds have been hydrogenolyzed, to establish the mechanism of C-C and C-O bond cleavage in sugar hydrogenolysis. The experimental work confirmed our theoretical conception that the C-C bond breaks via the retro-aldol reaction of a β-hydroxyl carbonyl precusor and the C-O bond breaks via the dehydration of the same carbonyl precusor. Establishment of the above mechanism makes it possible for one to adopt a more rational approach than the current practice in control of the selectivity of sugar hydrogenolysis.

The selectivity study in the current research is also carried out with a 1,3-diol model compound, namely 2,4-pentanediol(2,4-PD). Focus of this selectivity study has been placed on understanding of the factors controlling the C-C v.s C-O selectivity. In this capacity, the effects of temperature, base concentration, hydrogen pressure, catalyst amount and catalyst type on the selectivity are experimentally investigated. Additionally, a mathematical model is also developed and the 2,4-PD hydrogenolysis process is simulated with the developed model, to rationalize the experimental results and to look into ways to improve the selectivity. It is found out that the temperature has little effect on the selectivity; increasing the base concentration can increase the selectivity to certain extent; increase in the amount of catalysts used has an adverse effect on the selectivity; and the selectivity varies widely with the type of catalysts used. The effect of hydrogen pressure on the selectivity is the most interesting. At low pressure, the selectivity increases with the pressure; at medium pressure, the selectivity is not sensitive to the change in the pressure; while at high pressure, the selectivity decreases as the pressure is increased. Of the seven different types of catalysts that has been studied in our experiments, the best one is barium-promoted copper chromite, which has furnished a C-C vs. C-O selectivity of 2.5 in hydrogenolysis of 2,4-PD. Our simulation study additionally points out that, to improved the selectivity, a catalyst with a reasonable capability to hydrogenate ketones and aldehydes but only moderate ability to hydrogenate α,β-unsaturated ketones should be sought.

10.2 Glycerol Dehydroxylation

The purpose of glycerol dehydroxylation is to convert glycerol to 1,3-propanediol, a very-high-valued chemical. In this research, a new concept has been presented to selectively transform the second hydroxyl group of glycerol into a tosyloxy group with the help of a group protection technique, and then to remove it by hydrogenolysis. To verify the technical feasibility of this new concept, experiments are carried out in this work to investigate each of the steps involved in the new conversion concept. The results are promising: an overall yield of 72% or higher is found to be achievable with this new conversion concept.

Another major accomplishment of this research is that, for the first time, tosylates are hydrogenolyzed catalytically with molecular hydrogen. The standard method to hydrogenolyze tosylates at the current time is to use base metal hydrides, such as lithium aluminum hydride ($LiAlH_4$) and lithium triethylborohydride ($LiHBEt_3$). It is discovered in the current research that the tosyloxy group of a tosylate, when assisted by a hydroxy group next to it, can be removed with molecular hydrogen, in the presence of a nickel or ruthenium catalyst. This discovery is vital to the new concept of glycerol conversion. It makes it possible to detosyloxylate TPD economically with gaseous hydrogen. Otherwise, hydrogenolysis of TPD has to be carried out with lithium aluminum hydride or lithium triethylborohydride. Both are too expensive to use at industrial scale.

10.3 HF Saccharification

The work on HF saccharification has focused on modeling of the HF adsorption process in a packed-bed reactor. Two models have been developed. The first one is phenomenological in nature, and is developed based on experimental observations of the HF adsorption behavior in a bench-scale, packed-bed reactor. The second model is more advanced than the first one. It is developed based on a detailed analysis of the HF flow, the intrinsic HF adsorption and the heat transfer processes occurring in the reactor during

HF adsorption. This model provides a great deal of insight into the HF adsorption process in a packed-bed reactor, and it can be used to predict the HF loading distribution, as well as the overall HF loading, as functions of the adsorption time and operating conditions. The above modeling work accomplished in this research provides a theoretical foundation to design and operation of the HF adsorption process in a packed-bed reactor.

CHAPTER 11

RECOMMENDATIONS ON FUTURE WORK

11.1 Future Work On Sugar Hydrogenolysis

Future work on sugar hydrogenolysis should continue focusing on control of the C-O bond cleavage. The selectivity study may continue being carried out with the 2,4-pentanediol model (2,4-PD) compound (ideally 2,3,4-pentanetriol though, because of its closer analogy to sugars). Analysis of both the products and data are simple with this model compound, and the study may also be assisted by computer simulation, since a process model is now available for this purpose and has proven to be useful.

In our simulation study, the process model has predicted some phenomena that have not been observed in the experiment, possibly because the limited range of reaction conditions within which our experiments have been conducted. Included in these predictions are that the selectivity will become independent of the base concentration when the concentration gets too high, and that the selectivity will decrease with hydrogen pressure when the pressure gets too high. In further work, experiments may be performed in a larger base concentration and hydrogen pressure ranges to verify the above predictions.

Changing the catalyst is the most effective way to change the selectivity. The simulation study suggests that catalysts with strong ability to hydrogenate saturated ketones and aldehydes but only moderate ability to hydrogenate α,β-unsaturated carbonyls have potential to deliver high selectivity. Some homogeneous rhodium catalysts with the above properties have been reported by Mestroni *et al.* (1978). These catalysts may be tested in 2,4-PD hydrogenolysis experiments, to see if they can provide improved selectivity.

The most promising catalyst found so far in our experiments is barium-promoted copper chromite. It provides a much better selectivity than other catalysts tested, including the plain copper chromite catalyst. These results clearly indicate that the selectivity of copper chromite is enhanced by the presence of barium. Therefore, future work may also be carried out to study the effect of addition of barium, as well as other elements, in preparation of the catalyst on the selectivity of 2,4-PD hydrogenolysis.

Finally and most importantly, the results from studying the model compound 2,4-propanediol (2,4-PD) should be applied to sugars in the future, so as to improve the selectivity of sugar hydrogenolysis. The optimal conditions for sugar hydrogenolysis may be different from those for 2,4-PD hydrogenolysis. However, the effects of operating conditions on the former process should parallel to those on the later. This is yet to be verified in the future research.

11.2 Future Work on Glycerol Dehydroxylation

Future work on glycerol dehydroxylation has two immediate goals: a) to modify the procedure of tosylation, so as to facilitate the recycling of solvent; and b) to optimize the detosyloxylation condition, so as to increase the yield of 1,3-PD.

The standard lab procedure used in this research furnishes high PTD yield. However, introduction of ice following the reaction makes it difficult to recycle the solvent, as the solvent has to be separated from water and thoroughly dried before it can be returned back to the reactor. Solvent recycling is extremely important at industrial scale. A better process would allow both the reaction and crystallization to be carried out in the same solvent, so that the solvent can be directly recycled as in Figure 8-5. Therefore, future work should check the feasibility to directly crystallize PTD from pyridine. If direct crystallization of PTD from pyridine proves to be difficult, a co-solvent may be found, to help the precipitation of PTD from pyridine. If a co-solvent is needed to facilitate the crystallization, it ought to be verified that the tosylation can proceed in a mixture of this co-solvent with pyridine as smoothly as in pyridine alone. In both experiments, it may become necessary to proceed the crystallization with a pre-evaporation step to remove a portion of the solvent from the PTD solution.

As discussed in Chapter 8, the overall yield of the glycerol dehydroxylation process is determined by the yield of the detosyloxylation step. Although a 1,3-PD yield as high as 72% has been obtained in the current work, it is not optimized against the reaction conditions. Therefore, future work is needed to study the effect of reaction conditions, including temperature, medium acidity, and catalyst, on the product yield.

The 1,3-PD yield of the detosyloxylation step is mainly affected by the formation of by-product propanol in TPD hydrogenolysis. Propanol competes with 1,3-PD for starting TPD. The ratio of 1,3-PD to propanol produced in this reaction is determined by the rate of 3-hydropropionaldehyde hydrogenation relative to the 3-hydropropionaldehyde dehydration (Figure 8-2). Any factors affecting this rate has potential to be optimized to improve the yield of 1,3-PD.

As a general rule, hydrogenation has a higher activation energy than dehydration.

improve the yield of 1,3-PD.

As a general rule, hydrogenation has a higher activation energy than dehydration. Therefore, increase in temperature should increase the rate of hydrogenation relative to dehydration, and thus increase the yield of 1,3-PD in TPD hydrogenolysis. In the current work, TPD hydrogenolysis is carried out at a relatively low temperature (140 °C), due to the concern that the 1,3-PD formed in this reaction might be further hydrogenolyzed. In retrospection, this concern may not be well founded, as our experiments on 1,3-diol hydrogenolysis has shown that hydrogenolysis of 1,3-PD is slow even at 210 °C. Hence, the effect of temperature on TPD hydrogenolysis should be investigated in future research, so that the reaction can be carried out at an optimal temperature to maximize the yield of 1,3-PD.

In addtion to 1,3-PD and *n*-propanol, TPD hydrogenolysis also generates *p*-toluene sulfonic acid (TsOH). In the current work, the TsOH generated during TPD hydrogenolysis is not neutralized. Since dehydration of HPA is catalyzed by acids, neutralization of the reaction medium during the reaction may be helpful to control the formation of by-product *n*-propanol. This measure to improve 1,3-PD yield should also be investigated in the future research.

Future research should also investigate the effect of catalyst on TPD hydrogenolysis. A good catalyst enhances the hydrogenation of 3-hydropropionaldehyde, and thus may improve the yield of 1,3-PD.

In addition to the 1,3-PD yield, the possibility of catalyst poisoning by the sulfur containing compounds in TPD hydrogenolysis also needs to be addressed. Although it has been found in our experiments that the Ni catalyst used in TPD hydrogenolysis is still was stopped only after the catalyst completed a turnover number of about 50, to demonstrate the catalytic nature of the reaction. Further work should furnish, and improve if necessary, the overall turnover number that a catalyst can achieve in its lifetime.

Theoretically, mesyl chloride may work just as well as tosyl chloride in the new concept of glycerol conversion. Future work may look into the feasibility of using this alternative compound. Because of its smaller molecular weight, mesyl chloride is about 40% cheaper than tosyl chloride per mole, although the prices of these two compounds are similar on per pound basis. This prices difference provides a material cost advantage.

11.3 Future Work on HF Saccharification

Focus of the future work on HF saccharification should shift from the HF adsorption process to the HF desorption process. Due to the low price of sugars and the relatively high price of hydrogen fluoride, recovery and reuse of this regent is crucial to the economical viability of the HF saccharification process.

Although not reported here, some work has been done on HF desorption in the current research. It was found that, under some conditions, the desorption process was extremely slow, and it took more than 30 hours for the process to complete. Under these conditions, the HF residue level was normally observed to be high and it ranged from 5 to 10% of the HF loaded onto the wood chip substrate. However, some desorption runs were also completed in a time less than one hour, with an HF residue level less than 0.5%. Further work is needed to investigate the reason causing the above difference. It may possibly be linked to the temperature history experienced by the substrate in the HF adsorption process.

APPENDIXES

APPENDIX A

COMPUTER PROGRAMS FOR SIMULATION STUDY

APPENDIX A

COMPUTER PROGRAMS FOR SIMULATION STUDY

This appendix documents the computer programs used to solve the process model of 2,4-PD hydrogenolysis. These programs are written in Matlab language, and must be run in Matlab environment. The function of each program in solving the problem are explained in the comments included in the program.

Main Program:

```
% Program  SIMU.M  (Script M file)
% Version 4.0,  June 1, 1997
% This program is used to simulate the hydrogenolysis reaction of 2,4-pentanediol.
% It solves the differential equation system as defined in function M file CPRIME.M,
% and displays and saves the results.

% t == time (not used); c == concentrations; y == rates of concentration change
% Units: time = min; concentration = mol/l; flux and rate = mol/l/min

% Table of reactant and products:

   % 1. A, 2,4-pentanediol
   % 2. B, 4-hydroxyl-2-pentanone
   % 3. C, acetone
   % 4. D, 2-propanol
   % 5. E, acetaldehyde
   % 6. F, ethanol
   % 7. G, 3-pentene-2-one
   % 8. I, 2-pentanone
   % 9. J, 2-pentanol
   % 10. M, metal catalyst
   % 11. MH, metal hydride
   % 12. OH, hydroxide ion
   % Additional species: H, molecular hydrogen; H2O, water.
```

```
%%% Main Body of Program

 % Load Parameter (Including initial conditions)
  clear; clear global       %clean work space
  para                          %sub-program containing rate constants and initial conditions

 % Initial Concentrations:
  c0 = [A, B, C, D, E, F, G, I, J, M, MH, OH]’;  % A, B ... provided by Program PARA.M

 % Reaction time
  ti = 0;
  tf = 210;                     % tf-ti == duration of reaction
 % Solve the Differential Equation System
  [t, c] = ode45(‘cprime’, ti, tf, c0, 1e-6, 1);

 % Save the Solution in file: rsl2\sol and “Reaction Conditions” in rsl\condi, if n=2.
  l = length(t); sol = [sol; [c(1:10:l,:),t(1:10:l,:)]];
  dir = [‘rsl’ int2str(n)];
  eval([‘!mkdir ‘ dir])
  eval([‘!copy para.m ‘ dir ‘/condi’])
  eval([‘save ‘ dir ‘/sol sol -ascii’])

 % Display Results

  % Data preparation
   A=sol(:,1); B=sol(:,2); C=sol(:,3); D=sol(:,4); E=sol(:,5); F=sol(:,6);
   G=sol(:,7); I=sol(:,8); J=sol(:,9); M=sol(:,10); MH=sol(:,11); OH=sol(:,12);
   t=sol(:,13); l = length(t);

  % Main products
   figure(1)
   plot(t,A*1000, t,C*1000,’--’, t,D*1000,’-.’, t,I*1000,’:’, t,J*1000)
   axis([0 250 0 120])
   title(‘Major Products’)
   xlabel(‘Time (min)’)
   ylabel(‘[A],  [C],  [D],  [I],  [J]   (mM)’)
   grid

  % Minor products
   figure(2)
   plot(t,B*1000, t,E*1000,’--’, t,G*1000,’-.’)
   axis([0 250 0 5]);
   title(‘Minor Products’)
   xlabel(‘Time (min)’)
   ylabel(‘[B],  [E],  [G]   (mM)’)
   grid
```

```
    % Selectivity
     figure(3)
     S = (C+D) ./ (G+I+J);
     plot(t, S, ‘-’)
     axis([0 250 0 5])
     title(‘Selectivity’)
     xlabel(‘Time (min)’)
     ylabel(‘ s = ( [C]+[D] ) / ( [G]+[I]+[J] )’)
     grid

    %Base concentration
     figure(4)
     plot(t, OH*1000)
     title(‘Base Concentration’)
     xlabel(‘Time (min)’)
     ylabel(‘[OH]  (mM)’)
     grid
     eval([‘print -deps ‘ dir ‘/base.eps’])   % save the figure

%%% End End End End End
```

Sub-Program #1:

```
% Program PARA.M  (Scrip M file)
% Version 4.0, June 1, 1997
% This program is used to simulate the hydrogenolysis reaction of 2,4-pentanediol.
% It defines the rate constants and initial conditions

% t == time (not used); c == concentrations; y == rates of concentration change
% Units: time = min; concentration = mol/l; flux and rate = mol/l/min

% Table of reactant and products:

    %  1. A, 2,4-pentanediol
    %  2. B, 4-hydroxyl-2-pentanone
    %  3. C, acetone
    %  4. D, 2-propanol
    %  5. E, acetaldehyde
    %  6. F, ethanol
    %  7. G, 3-pentene-2-one
    %  8. I, 2-pentanone
    %  9. J, 2-pentanol
    % 10. M, metal catalyst
    % 11. MH, metal hydride
    % 12. OH, hydroxide ion
    % Additional species: H, molecular hydrogen; H2O, water.
```

```
% Kinetic Parameters

  k1f = 435; k1b = 67.4;
  k2f = 752; k2b = 4480;
  k3f = 1.89; k3b = 12.2;
  k4f = 11.9; k4b = 1.24;
  k5f = 14100; k5b = 6590;
  k6f = 22.1;
  k7f = 1.16; k7b = 7.48;
  k8f = 76.2; k8b = 3.32e-5;

% Reaction Conditions:

 % Water Concentration
  H2O = 46.5; % M  (not used)

 % Hydrogen pressure (base: 5 MPa)
  H = 0.1;    % M, expressed as the concentration of molecular hydrogen
              % dissolved in the reaction solution.

 % Initial Base Concentration (0.4 ml 1 N NaOH)
  OH0 = 0.010;  % M

 % Initial catalyst concentration  (base: 0.1 g Ni/K)
  M0 = 0.028;  % M

 % Initial 2,4-Pentanediol Concentration (base 0.5 g diol in 40 ml water)
  A0 = 0.12;  % M

% Pass data to CPRIME.M
 global k1f k1b k2f k2b k3f k3b k4f k4b
 global k5f k5b k6f    k7f k7b k8f k8b
 global H2O H OH0 M0

% Conditions to start  “START.M”
 A=A0; B=0; C=0; D=0; E=0; F=0; G=0; I=0; J=0; OH=OH0; M=M0; MH=0;


% Define the number of the directory to save the results
 n = 1;
%%% End End End End End
```

Sub-Program#2:

```
function  y = cprime(t, c)

% Program CPRIME.M  (function M file)
% Version 4.0, June 1, 1997
% This program defines the problem of 2,4-pentanediol hydrogenolysis
% It is to be used with program SIMU.

% t == time (not used); c == concentrations; y == rates of concentration change
% X's == reaction fluxes
% Units: time = min; concentration = mol/l; flux and rate = mol/l/min

% Table of reactant and products:

   %  1. A, 2,4-pentanediol
   %  2. B, 4-hydroxyl-2-pentanone
   %  3. C, acetone
   %  4. D, 2-propanol
   %  5. E, acetaldehyde
   %  6. F, ethanol
   %  7. G, 3-pentene-2-one
   %  8. I, 2-pentanone
   %  9. J, 2-pentanol
   % 10. M, metal catalyst
   % 11. MH, metal hydride
   % 12. OH, hydroxide ion
   % Additional species: H, molecular hydrogen; H2O, water.

%Get Data from PARA.M

 global k1f k1b k2f k2b k3f k3b k4f k4b\
 global k5f k5b k6f     k7f k7b k8f k8b
 global H H2O

% Flux Expressions
 X1 = k1f*c(1)*c(10)*c(12) - k1b*c(2)*c(11);
 X2 = k2f*c(2)*c(12) - k2b*c(3)*c(5)*c(12);
 X3 = k3f*c(3)*c(11) - k3b*c(4)*c(10)*c(12);
 X4 = k4f*c(5)*c(11) - k4b*c(5)*c(10)*c(12);
 X5 = k5f*c(2)*c(12) - k5b*c(7)*c(12);
 X6 = k6f*c(7)*c(11);
 X7 = k7f*c(8)*c(11) - k7b*c(9)*c(10)*c(12);
 X8 = k8f*H*c(10)*c(12) - k8b*c(11);
```

```
% Differential Equations

 y(1) = -X1;                 % A
 y(2) = X1 - X2 - X5;        % B
 y(3) = X2 - X3;             % C
 y(4) = X3;                  % D
 y(5) = X2 - X4;             % E
 y(6) = X4;                  % F
 y(7) = X5 - X6;             % G
 y(8) = X6 - X7;             % I
 y(9) = X7;                  % J
 y(10) = -X1 + X3 + X4 + X6 + X7 - X8;   % M
 y(11) = -y(10);   %MH
 y(12) =  y(10);   % OH

% End End End End End
```

APPENDIX B

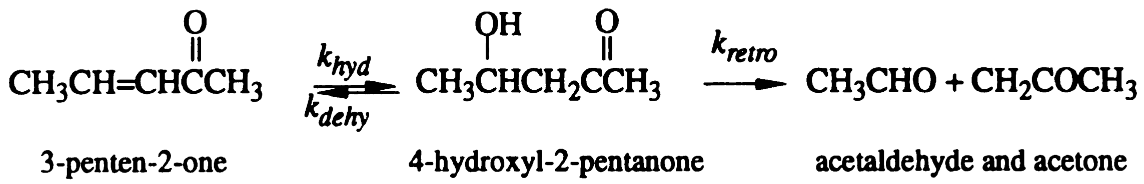
RETRO-ALDOL AND DEHYDRATION RATE CONSTANT DERIVATION PROCEDURE

APPENDIX B

RETRO-ALDOL AND DEHYDRATION RATE CONSTANT DERIVATION PROCEDURE

This appendix documents the procedure used to derive the rate constants for the retro-aldol and dehydration reactions of 4-hydroxy-2-pentanone, or the Reactions No.2 and No.5 in Figure 5-5. The basis of this derivation is the kinetic data obtained by Jenson and Hassan (1976) on the hydration of 3-penten-2-one.

In Jenson and Carre's experiments, 3-penten-2-one was allowed to undergo the following reactions at 40 and 50 °C in 0.1 N NaOH aqueous solution:



$$CH_3CH{=}CH\overset{O}{\overset{\|}{C}}CH_3 \underset{k_{dehy}}{\overset{k_{hyd}}{\rightleftharpoons}} CH_3\overset{OH}{\overset{|}{C}}HCH_2\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{k_{retro}} CH_3CHO + CH_2COCH_3$$

The hydration rate constant k_{hyd} was determined at 40 and 50 °C, and was presented along with an observed rate constant k_{obs}. This observed rate constant is related to k_{hyd}, k_{dehy} and k_{retro} as follows:

$$k_{obs} = \frac{k_{hyd}k_{retro}}{k_{dehyd} + k_{retro}} \tag{D-1}$$

Thus, if the reaction equilibrium constant for the hydration/dehydration reaction pair, or the ratio of k_{hyd} to k_{dehy}, is obtained, the dehydration rate constant k_{dehy} may be calculated from k_{hyd}, and the retro-aldol rate constant k_{retro} can then be solved from Eq.(D-1), which is exactly what has been in this work. The relevant data and results are all given in Table D-1. The equilibrium constants in Table D-1 are from Jenson and Carre (1974), and are measured in 2.57 M $HClO_4$ solution.

Table D-1 Rate Constants Directly from Jenson and Hassan (1976) [a]

	$k_{obs}\times10^4$ [b]	$k_{hyd}\times10^4$ [b]	k_{hyd}/k_{dehy} [c]	$k_{dehy}\times10^4$ [d]	$k_{retro}\times10^4$ [d]
40 °C	.50	9.5	3.14	3.03	0.168
50 °C	1.1	21	2.67	7.87	0.435

a. unit for all rate constants: s^{-1}; *b.* from Jenson and Hassan (1976); *c.* from Jenson and Carre (1974); *d.* calculated in this work.

The rate constants listed in Table D-1 are the products of those in Figure 5-3 for the same reactions with the concentration of hydroxide ion in the solution. As the hydroxide ion concentration at which the above rate constants are obtained are known (0.1 M), the rate constants k_5, k_{-5} and k_2 in Figure 5-3 can be determined from the rate constants in Table D-2, and then from these rate constants at low temperatures, the rate constants for 220 °C can be extrapolated with the help of the Arrhenius equation. To obtain the rate constant k_{-2}, the equilibrium constant for the retro-aldol and aldol reaction pair is needed. In the current work, it is estimated from the free energy data at 25 °C (again data at other temperature are unavailable) in Cuthrie (1977) to be 0.168. With this equilibrium constant, k_{-2} is calculated, and is documented in Table D-2, together with other determined rate constants.

Table D-2 Determined Rate Constants

	k_5 ($M^{-1}min^{-1}$)	k_{-5} ($M^{-1}min^{-1}$)	k_2 ($M^{-1}min^{-1}$)	k_{-2} ($M^{-2}min^{-1}$)
40 °C	0.182	0.570	0.0101	
50 °C	0.472	1.260	0.0261	
220 °C	14100	6590	752	4480

APPENDIX C

EXPERIMENTAL DATA OF 2,4-PD HYDROGENOLYSIS

APPENDIX C

EXPERIMENTAL DATA OF 2,4-PD HYDROGENOLYSIS

This appendix documents the experimental data of 2,4-pentanediol (2,4-PD) hydrogenolysis, collected in the selectivity of sugar hydrogenolysis. In this study, 2,4-PD is used as a model compound to facilitate the rersearch.

Experiment #1-3[a]

Temp.: 220 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.5 g); Base: 1N NaOH (none); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	119.30
25	2.55	12.85	1.27	36.22	2.23	66.74
40	2.88	16.59	4.17	68.38	10.71	19.44
55	2.17	13.42	4.94	57.93	13.55	29.47
85	2.19	9.93	6.25	43.37	18.25	41.51
115	2.37	8,87	8.10	40.29	24.59	37.45
150	2.29	7.27	9.73	33.56	30.21	38.54
175	2.74	6.35	10.48	29.80	33.00	39.67

a. Hydrogen applied after preheating. Preheating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-4[a]

Temp.: 220 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.5 g); Base: 1N NaOH (none); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.02
13	0.00	0.00	0.00	0.27	0.00	119.75
21	0.07	4.01	0.00	4.23	0.53	111.25
23	0.20	4.25	0.78	7.61	1.75	105.64
33	0.61	7.27	3.55	13.59	9.88	85.73
53	0.74	6.77	6.00	27.52	17.74	61.99
68	0.82	6.46	7.12	28.56	22.07	55.81
88	0.86	5.54	8.20	25.11	26.21	54.95
113	0.90	4.97	9.54	23.16	31.57	50.78
153	0.98	4.14	11.30	19.64	37.92	47.01
178	0.95	3.33	11.23	15.50	38.33	51.63
203	1.01	3.45	12.48	17.32	43.61	43.16

a. Hydrogen applied after preheating. Preheating took 23 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-5[a]

Temp.: 220 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.5 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.04
15	0.51	1.31	0.00	1.19	0.16	117.39
25	12.90	15.16	7.53	17.79	5.74	73.83
40	12.96	18.23	17.63	13.34	8.23	62.61
58	12.14	18.85	23.89	28.14	21.79	27.36
73	11.55	17.51	25.29	26.97	23.50	26.78
85	10.40	14.83	24.80	22.84	23.45	34.12
115	9.49	10.64	24.91	15.17	23.74	45.59
145	11.41	11.67	32.10	17.67	31.30	27.30
175	11.69	10.46	33.65	15.57	32.97	27.39
205	11.14	8.18	33.22	12.73	33.50	32.41

a. Hydrogen applied after preheating. Preheating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-6[a]

Temp.: 220 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.2 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.60
15	0.00	0.57	0.20	0.46	0.30	119.06
25	7.26	4.02	5.94	4.14	3.95	102.53
40	20.50	16.97	18.45	14.90	11.96	58.31
55	26.90	14.36	28.60	9.56	19.69	48.39
85	22.42	13.74	25.98	6.73	18.31	55.83
115	27.96	13.14	34.10	6.74	23.03	43.59
145	27.76	14.61	34.73	9.23	24.42	37.60
175	29.25	14.99	37.16	9.23	25.82	33.39

a. Hydrogen applied after preheating. Preheating took 25 mins. *b*. unit is min. *c*. unit is mM.

Experiment #1-7[a]

Temp: 220 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	119.80
15	0.86	1.21	0.58	1.19	0.46	116.37
25	12.47	8.25	9.08	8.32	5.51	88.63
40	29.95	9.94	19.99	11.27	18.98	49.62
55	33.26	7.35	36.79	8.46	23.73	43.48
80	33.91	5.52	39.05	5.93	25.30	44.00
85	34.81	5.75	40.63	5.53	26.35	41.54
115	35.16	5.52	41.57	5.62	27.20	39.89
150	37.69	5.92	45.98	6.34	30.39	31.16
175	38.72	5.89	48.01	6.26	31.70	27.95
205	40.31	5.96	50.85	6.18	33.73	23.09

a. Hydrogen applied after preheating. Preheating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-8[a]

Temp: 220 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.00
15	0.00	0.48	0.00	0.37	0.07	119.07
25	2.09	1.38	1.87	1.36	1.34	114.04
40	10.57	2.81	10.78	3.10	7.31	95.99
55	14.66	2.31	16.58	2.12	12.10	86.87
70	19.87	2.49	23.14	1.98	16.79	75.60
115	26.66	1.31	19.61	0.84	20.82	67.41
145	34.03	1.92	37.67	1.31	26.39	52.71
180	36.65	1.66	40.46	1.37	28.44	48.08
205	34.53	1.71	38.18	1.34	26.67	52.09
265	40.62	2.05	45.34	1.71	31.54	39.35

a. Hydrogen applied after preheating. Preheating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-9[a]

Temp: 180 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	119.54
12	0.00	0.52	0.40	0.39	0.14	118.09
15	0.00	0.85	0.20	1.14	0.30	117.05
30	2.74	1.19	2.71	1.71	2.02	111.91
45	5.31	1.04	5.80	1.70	4.37	106.63
80	9.44	0.79	10.81	1.17	8.08	98.68
105	10.55	0.66	12.25	0.64	9.39	96.60
135	11.90	0.00	13.99	0.00	10.30	95.25
170	12.82	0.00	14.77	0.00	11.02	93.75
195	14.84	0.38	17.11	0.13	12.74	89.17
255	17.46	0.50	19.85	0.32	14.78	84.09
315	18.60	0.76	21.24	0.36	15.90	81.28
375	23.20	0.81	25.12	0.36	18.38	74.87
435	27.15	0.76	29.16	1.98	21.26	66.38

a. Hydrogen applied after preheating. Preheating took 15 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-10[a]

Temp: 240 C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanal[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.07
15	0.69	1.17	0.71	1.27	0.37	116.55
28	20.26	15.99	15.33	14.32	8.45	65.98
43	29.80	17.14	30.60	16.12	17.21	38.99
58	30.32	15.52	35.68	14.53	21.07	33.26
73	31.73	15.69	40.16	14.13	23.75	26.34
90	28.72	14.52	38.79	13.21	23.40	30.15
118	27.86	14.83	41.93	13.20	25.81	24.30
148	24.86	14.36	41.29	13.29	25.19	25.93
178	25.18	14.62	44.19	10.90	25.90	24.46

a. Hydrogen applied after preheating. Preheating took 28 mins. *b*. unit is min. *c*. unit is mM.

Experiment #1-11[a]

Temp.: 200 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (1 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	119.90
10	0.00	1.04	0.00	0.56	1.08	117.23
20	1.59	2.19	1.27	1.82	0.66	113.96
35	12.29	4.14	12.44	4.67	7.13	91.53
52	20.56	3.49	24.14	3.90	14.84	73.54
65	23.75	2.87	27.73	2.36	17.51	69.43
80	28.52	3.13	32.82	2.37	20.90	60.68
110	32.01	2.90	36.61	2.00	23.53	54.86
140	33.79	3.04	38.37	1.94	24.97	51.58
170	35.98	3.33	40.69	1.98	26.25	47.65
200	36.51	5.11	41.32	2.51	26.88	44.07

a. Hydrogen applied after preheating. Preheating took 20 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-12[a]

Temp.: 200 °C; Pressure: 5.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (none); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	119.90
20	0.00	1.64	0.92	0.91	0.49	115.94
50	1.76	1.73	1.64	3.86	2.78	109.90
80	2.21	1.66	2.37	4.10	4.57	107.20
110	2.80	1.57	3.02	3.76	6.12	105.43
140	3.45	1.55	3.70	3.43	7.76	103.46
200	4.37	1.52	4.72	2.69	10.63	100.34
265	5.52	1.52	5.89	3.04	13.15	96.30
320	6.52	1.48	6.94	2.84	15.27	93.36

a. Hydrogen applied after preheating. Preheating took 20 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-13[a]

Temp.: 200 °C; Pressure: 3.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	119.97
20	1.37	2..71	1.04	2.40	0.82	113.01
50	15.47	6.32	14.03	6.70	8.96	83.96
80	21.10	10.50	21.76	7.67	13.64	66.40
110	18.72	9.05	18.88	5.48	11.09	75.48
140	25.37	11.29	27.03	6.67	15.57	59.41
200	35.00	2.43	40.23	2.89	26.57	47.85

a. Hydrogen applied after preheating. Preheating took 20 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-14[a]

Temp: 210 °C; Pressure: 3.5 MPa; Catalyst: 65% Ni on Kieselguhr (0.05 g); Base: 1N NaOH (0.2 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.07
28	3.66	4.61	2.59	3.27	2.53	107.07
43	11.04	10.24	11.44	6.28	8.83	83.28
58	13.10	12.00	16.09	7.39	12.07	72.51
88	16.11	14.49	25.30	10.52	18.18	51.57
118	16.64	15.59	32.27	12.24	22.93	37.03
148	14.29	13.98	33.79	11.73	23.50	37.06
208	9.67	14.12	35.91	13.61	24.50	31.93

a. Hydrogen applied after preheating. Preheating took 28 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-15[a]

Temp.: 210 °C; Pressure: 3.5 MPa; Catalyst: 65% Ni on Kieselguhr (0.05); Base: 1N NaOH (0.2 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.07
30	0.98	1.90	0.82	0.71	0.58	116.06
60	3.39	4.30	1.61	1.43	1.01	111.71
95	5.83	5.49	3.11	1.87	1.67	107.93
120	7.09	5.56	4.13	1.92	2.30	106.16
180	10.45	6.99	6.91	2.56	3.02	100.59
240	12.94	7.32	9.60	2.82	3.92	96.41

a. Hydrogen applied after preheating. Preheating took 30 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-16[a]

Temp.: 210 °C; Pressure: 3.5 MPa; Catalyst: 65% Ni on Kieselguhr (0.05 g); Base: 1N NaOH (0.2 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.09
30	0.84	0.31	1.71	1.27	1.03	115.78
60	6.42	1.17	3.17	4.47	2.60	108.69
90	11.34	1.54	6.97	5.87	4.73	100.98
120	17.89	2.00	13.15	7.47	8.20	89.27
180	18.15	1.55	15.95	5.96	9.99	86.65
240	28.11	2.02	26.77	8.20	15.66	67.45

a. Hydrogen applied after preheating. Preheating took 30 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-17[a]

Temp.: 200 °C; Pressure: 7.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.19
20	1.86	1.99	1.93	1.93	1.37	112.97
50	9.53	2.95	8.97	12.02	5.97	90.27
80	31.48	14.04	47.60	3.63	42.12	12.80
110	53.09	2.71	81.06	3.11	70.02	
140						
170						
200						

a. Hydrogen applied after preheating. Preheating took 20 mins. *b*. unit is min. *c*. unit is mM.

Experiment #1-18[a]

Temp.: 200 °C; Pressure: 7.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.12
20	0.92	1.11	0.95	0.89	0.77	116.40
50	6.48	1.74	6.45	1.96	3.93	106.04
80	11.00	1.42	11.83	1.50	7.50	97.86
110	14.70	2.25	15.95	1.08	10.82	90.03
145	17.50	3.63	18.48	1.64	12.38	83.98
210	19.64	1.09	21.73	0.61	14.70	81.99

a. Hydrogen applied after preheating. Preheating took 20 mins. *b.* unit is min. *c.* unit is mM.

Experiment #1-19[a]

Temp.: 200 °C; Pressure: 3.0 MPa; Catalyst: 65% Ni on Kieselguhr (0.1 g); Base: 1N NaOH (0.4 *ml*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	0.00	0.00	0.00	0.00	120.16
25	2.02	2.73	1.32	2.40	0.68	113.04
55	10.45	5.75	9.07	5.42	5.44	94.49
85	22.28	12.03	22.22	7.29	13.94	64.68
115	46.34	19.79	47.81	14.66	29.48	8.43
145	51.55	17.47	53.61	14.62	31.96	2.50
175	50.59	17.52	53.09	16.23	30.93	2.39

a. Hydrogen applied after preheating. Preheating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #2-1[a]

Temperature: 210 °C; H_2 pressure: 3.5 MPa; Catalyst: 65% Ni on Kieselguhr; Base: 1N NaOH (0.20 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	2.45	0.00	0.00	0.00	118.70
30	19.77	7.60	13.32	7.51	10.22	80.62
60	27.84	6.66	20.72	6.64	16.60	67.84
90	31.56	6.53	24.35	6.53	20.06	60.89
120	35.28	6.49	27.63	6.42	23.00	54.58
150	35.90	6.15	28.28	6.00	23.60	53.94
180	37.86	5.77	30.07	5.58	25.07	51.21
210	44.28	6.53	35.43	6.13	29.30	40.14
240	43.19	5.94	34.76	5.78	29.26	41.72

[a] Hydrogen applied after pre-heating, pre-heating took 25 mins. [b] unit is min. [c] unit is mM.

Experiment #2-2[a]

Temperature: 210 °C; H_2 pressure: 3.5 MPa; Catalyst: Ni on silica/alumina; Base: 1N NaOH (0.21 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	2.24	0.00	1.22	0.00	117.07
30	19.93	10.01	11.65	9.18	9.60	77.50
60	30.03	10.01	20.81	9.84	17.58	59.22
90	32.69	8.01	25.06	8.31	22.08	53.80
120	37.59	6.84	29.47	6.51	25.29	48.32
150	39.12	5.16	31.43	5.98	17.70	45.05
180	39.19	6.35	31.25	6.33	27.63	44.71
210	44.56	6.98	35.57	6.73	31.31	35.48
240	48.63	7.49	39.06	7.09	34.18	28.22

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #2-3[a]

Temperature: 210 °C; H_2 pressure: 3.5 MPa; Catalyst: Raney Ni; Base: 1N NaOH (0.20 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	1.88	5.25	0.00	3.18	0.00	120.40
30	10.18	6.46	6.08	4.64	4.44	99.95
60	15.66	7.53	10.64	5.00	7.77	90.71
90	19.19	7.08	13.19	4.78	9.90	86.00
120	24.35	7.35	16.61	4.07	12.17	80.00
150	16.16	6.70	18.71	3.98	13.45	77.19
180	32.89	7.80	24.28	4.42	17.28	66.21
210	33.09	6.22	24.46	3.49	17.09	67.94
240	38.18	7.73	29.31	4.71	21.08	56.99

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #2-4[a]

Temperature: 210 °C; H_2 pressure: 3.5 MPa; Catalyst: Raney Cu; Base: 1N NaOH (0.20 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	1.59	0.00	0.00	0.00	120.50
30	3.29	4.35	1.30	1.91	0.97	113.15
60	6.07	5.70	2.82	2.76	1.96	108.49
90	9.08	6.80	4.74	3.42	3.21	103.56
120	10.69	6.73	6.17	3.33	4.06	101.31
150	13.16	7.11	7.87	3.49	5.07	97.87
180	14.25	6.11	8.70	2.80	5.16	98.01
210	16.91	7.49	11.36	3.76	7.15	91.71
240	21.18	8.01	13.41	4.11	8.51	86.57

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #2-5[a]

Temperature: 210 °C; H_2 pressure: 5.0 MPa; Catalyst: Raney Cu; Base: 1N NaOH (none); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	1.17	0.00	2.00	0.34	119.10
30	1.25	1.76	0.67	3.60	2.33	111.32
60	1.72	1.86	1.05	5.27	4.16	107.35
90	2.47	2.18	1.59	6.93	6.64	102.41
120	2.55	1.93	1.65	6.42	7.15	102.46
150	3.05	2.04	2.01	6.91	8.99	99.65
180	3.52	2.18	2.37	7.31	10.70	97.06
210	4.11	2.28	2.84	7.31	12.39	94.78
240	4.15	1.83	2.73	6.38	10.74	97.63

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #2-6[a]

Temperature: 220 °C; H_2 pressure: 5.0 MPa; Catalyst: Raney Cu; Base: 1N NaOH (0.51 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	1.06	1.93	0.60	1.47	1.20	119.10
30	5.83	6.80	4.14	3.62	3.02	104.08
60	10.26	7.49	8.05	3.91	4.98	97.30
90	8.93	7.01	8.83	3.53	5.85	97.33
120	13.78	7.70	11.94	3.93	7.70	90.76
150	15.86	7.04	12.43	3.53	7.89	90.01
180	19.93	7.91	14.87	3.98	9.48	84.29
210	20.95	7.98	15.96	4.00	9.84	82.82
240	22.44	7.84	16.48	3.93	9.99	81.81

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b*. unit is min. *c*. unit is mM.

Experiment #2-7[a]

Temperature: 220 °C; H_2 pressure: 5.0 MPa; Catalyst: Raney Cu; Base: 1N NaOH (0.21 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	2.52	0.00	1.29	0.39	119.40
30	7.20	7.77	4.78	5.40	7.61	96.51
60	10.85	9.05	7.89	7.09	12.79	85.63
90	11.63	8.43	8.88	7.02	14.06	83.86
120	12.33	7.53	9.64	5.96	14.49	84.21
150	13.94	8.11	11.54	7.24	17.88	77.49
180	13.39	6.84	11.31	6.44	17.34	79.85
210	15.19	7.01	12.99	6.84	19.72	75.24
240	12.65	6.11	12.85	6.13	19.03	78.43

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b*. unit is min. *c*. unit is mM.

Experiment #2-8[a]

Temperature: 220 °C; H_2 pressure: 5.0 MPa; Catalyst: Ranet Cu; Base: 1N NaOH (0.20 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	1.73	0.00	1.07	0.46	120.40
30	3.72	3.90	1.65	1.96	2.08	111.73
60	5.21	5.97	2.95	3.27	3.63	106.44
90	7.79	7.70	5.01	4.33	5.75	100.07
120	10.18	8.18	5.86	4.71	6.58	97.00
150	11.20	8.70	7.69	5.11	8.73	93.13
180	12.45	7.80	7.85	4.49	8.26	93.60
210	14.33	8.05	9.30	4.60	9.57	90.39
240	14.76	8.08	9.73	4.73	9.81	89.58

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b*. unit is min. *c*. unit is mM.

Experiment #2-9[a]

Temperature: 220 °C; H_2 pressure: 5.0 MPa; atalyst: Raney Cu; Base: 1N NaOH (0.21 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	1.25	2.69	0.63	1.91	0.77	122.80
30	2.39	2.87	1.54	1.96	1.31	116.14
60	11.43	5.66	7.96	4.29	7.61	98.38
90	14.64	4.14	11.09	3.00	10.53	94.33
120	11.39	2.69	9.43	1.73	10.34	98.96
150	12.18	3.07	10.53	2.71	11.58	95.62
180	18.95	3.63	15.96	2.96	16.46	84.11
210	26.12	4.14	21.01	3.64	21.04	72.48
240	26.59	3.83	22.33	3.49	21.69	71.24

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #2-10[a]

Temperature: 220 °C; H_2 pressure: 3.0 MPa; Catalyst: Raney Cu ; Base: 1N NaOH (0.21 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	2.86	4.97	1.39	3.24	1.65	128.95
30	12.96	11.57	6.46	10.33	6.54	96.58
60	15.78	13.43	8.52	13.56	9.05	87.48
90	17.74	13.54	10.17	14.93	10.98	82.31
120	18.32	11.98	11.13	14.16	12.05	82.02
150	19.77	12.64	12.65	16.13	14.41	75.87
180	26.78	16.78	17.33	22.98	20.06	55.47

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #2-11[a]

Temperature: 240 °C; H_2 pressure: 5.0 MPa; Catalyst: Raney Cu; Base: 1N NaOH (0.20 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	2.43	4.35	1.16	2.93	1.52	118.40
30	17.11	11.50	10.44	8.49	10.45	79.94
60	26.19	12.53	17.08	10.11	15.41	64.98
90	29.01	11.57	20.37	9.87	18.14	59.92
120	28.43	10.32	20.75	9.47	18.66	60.52
150	35.28	10.74	26.31	10.24	23.39	48.60
180	37.67	12.09	28.39	12.16	24.70	42.48

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b*. unit is min. *c*. unit is mM.

Experiment #2-12[a]

Temperature: 200 °C; H_2 pressure: 5.0 MPa; Catalyst: Raney Cu; Base: 1N NaOH (0.21 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	1.69	0.00	1.09	1.08	119.08
30	3.64	3.28	2.77	1.98	3.24	109.74
60	.34	3.56	5.41	2.31	5.51	104.32
90	7.64	3.00	6.86	2.11	6.95	101.98
120	11.12	3.25	9.84	2.24	10.31	95.14
150	10.96	2.38	9.39	1.51	8.11	98.81
180	13.86	2.66	12.50	1.87	11.98	91.45
210	15.04	2.66	13.53	1.96	13.39	89.04
240	15.39	2.45	13.97	1.84	13.61	88.44

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b.* unit is min. *c.* unit is mM.

Experiment #2-13[a]

Temperature: 220 °C; H_2 pressure: 7.0 MPa; Catalyst: Raney Cu; Base: 1N NaOH (0.20 *g*); Solvent: water (40 *ml*)

time[b]	ethanol[c]	acetone[c]	isopropanol[c]	2-pentanone[c]	2-pentanol[c]	2,4-PD[c]
0	0.00	2.18	0.00	1.38	0.30	120.80
30	4.03	4.73	2.59	2.64	2.88	109.59
60	6.19	4.77	4.58	2.73	4.84	105.46
90	7.71	4.32	6.24	2.60	6.49	102.57
120	8.10	3.69	6.75	2.18	6.70	102.65
150	9.83	4.01	8.63	2.44	8.34	98.79
180	11.16	3.80	9.55	2.24	8.97	97.33
210	12.76	3.87	10.75	2.27	9.99	94.86
240	15.15	4.04	13.26	2.44	12.81	89.32

a. Hydrogen applied after pre-heating, pre-heating took 25 mins. *b.* unit is min. *c.* unit is mM.

LIST OF REFERENCES

LIST OF REFERENCES

Alexander, 1954, Studies on enol titration. II. Enol content of some ketones and esters in the presence of methanol. *J. Org. Chem.*, **41**, 3299-3302.

Andrews, M. A. and Klaeren, S. A., 1989, Selective Hydrocracking of Monosaccharide Carbon-Carbon Single Bonds under Mild Conditions. Ruthenium Hydride Catalyzed Formation of Glycols. *J. Am. Chem. Soc.*, **111**, 4131-4133.

Arena B.J., 1983, Hydrogenolysis of polyhydroxylated compounds. US Patent 4,401,823.

Ariono, D., Moraes de Abreu, C., Roesyad, A., Declercq, G. and Zoulalian, A., 1986, Hydrogenolyse sur catalyseurs solides de solutions de glucose. *Bull. Soc. Chim. Fr.*, 703-710.

Baggett, N., Buck, K. W., Foster, A. B., Randall, M. H. and Webber, J. M., 1965, Aspects of Stereochemistry. Part IV. Absolute configuration of Benzylidene derivatives of some acylic polyhydric alcohols. *J. Chem. Soc.*, 3394-3400.

Baggett, N., Brimacombe, J. S., Foster, A. B., Stachey, M. and Weiffen, D. H., 1960, Aspects of Stereochemistry. Part IV. Configuration and some reactions of the 1,3-O-Benzylideneglycerols (5-hydroxy-2-phenyl-1,3-dioxans). *J. Chem. Soc.*, 2574-2581.

Barbirato, F., 1996, 3-Hydroxypropionaldehyde, an inhibitory metabolite of glycerol fermentation to 1,3-propanediol by enterobacterial species. *Appl. Environ. Microbiol.*, **62**, 1448-1451.

Barrier J. W. and Bulls M. M., 1992, Feedstock availability of biomass and wastes. In *Emerging Technologies for Materials and Chemicals from Biomass* (Edited by Rowell R. M. *et al.*), pp 410-421. Americal Chemical Society, Washington DC.

Biebl, H., 1995, Fermentation of glycerol to 1,3-propanediol: use of cosubstrate. *Appl. Microbiol Biotechnol*, **44**, 15-19.

Boelhouwer, C., Korf, D. and Waterman, H. I., 1960, Catalytic hydrogenation of sugars. *J. Appl. Chem.*, **10**, 292-296.

Boenigk, R., Bowien, S. and Gottschalk, G., 1993, Fermentation of glycerol to 1,3-propanediol in continuous cultures of citrobacter freundii. *Appl. Microbiol Biotechnol*, **38**, 453-457.

Brimacombe, J. S., Foster, A.B. and Haines, A. H., 1960, Aspects of Stereochemistry. Part V. Some properties of 1,2-O-methylideneglycerol and related compounds. *J. Chem. Soc.*, 2582-2586.

Cameron, D. C., 1998, Metabolic engineering of propanediol pathways. *Biotechnology Progress*, **14**, 116-125.

Casey, M., Lenoard, J. and Lygo, B., 1990, *Advanced Practical Organic Chemistry*. pp133-134. Blackie Academic and Professonal: London.

Chaloner P. A., 1986, *Handbook of Coordination Catalysis in Organic Chemistry*; Butterworths: Boston.

Chang, F. W., Kuo, K. T. and Lee, C.N., 1985, A kinetic study on the hydrogenolysis of sorbitol over Raney nickel catalysts. *J. Chin. I. Ch.E.*, **16** , 17-23.

Chao, J. C., Huibers, D. T. A. and Derk, T. A., 1982, Catalytic hydrogenolysis of alditols for producing glycerol and polyols. *Chem. Abtra.*, 98:18453.

Chapman, P., 1997, Shell advances plans for new polyester. *Chemical Market Reporter*, **250**, 1.

Chapman, P., 1996, Dupont in race to commercialize a new polyester. *Chemical Market Reporter*, **251**, 3.

Che, T. M., 1987, Catalytic conversion of glycerol and synthesis gas to propanediol. US Patent 5093537.

Chong, J. M. and Sokoll, K. K., 1993, Synthesis of 2-O-protected glycerol derivatives. *Org. Prep. Pro. int.*, **25**, 639-647.

Chum, H. L. and Power, A. J., 1992, The promise and pitfalls of biomass and waste conversion. In *Emerging Technologies for Materials and Chemicals from Biomass* (Edited by Rowell R. M. *et al.*), pp 339-353. Americal chemical Society: Washington DC.

Clark, I. T., 1958, Hydrogenolysis of Sorbitol. *Ind. Eng. Chem.*, **50**, 1125-1126.

Clausen, E. C. and Gaddy, J. L., 1987, The production of chemicals and fuels from municipal solid wastes. In *Global Bioconversions, vol II* (Ed. by Wise D. L.), pp 61-73. CRC: Boca Raton, FL

Collman, J. P., Hegedus, L. S. and Finke R. G., 1987, *Principles and Applications of Organotransition Metal Chemistry*. Universe Science Books, Mill valley, CA.

Connor, R. and Adkins, H., 1932, Hydrogenolysis of Oxygenated Organic Compounds. *J. Am. Chem. Soc*, **54**, 4678-4690.

Cook, J. and Mailis, P. M., 1981, *Formaldehyde as a Hydrogen-donor to Aldehydes and Ketones in Metal-catalyzed Reactions in Water. J. Chem. Soc., Chem. Comun.*, 924-925.

DeAthos, S. J., 1989, A preliminary study of the conversion of glycerol to 1,3-propanediol. M.S. Thesis, Chemical engineering Department, Michigan State University, East Lansing, Michigan.

Dobinson, B. and Foster, A. B., 1961, Aspects of Stereochemistry. Part IV. Configuration of the 5-hydroxy-2-p-nitrophenyl-1,3-dioxans and futher observations on *trans*-5-hydroxyl-2-phenyl-1,3-dioxan. *J. Chem. Soc.,* 2338.

Dubeck, M. and Knapp, G. G., 1984, Sulfide-modified ruthenium catalyst. US patent 4,430,253. *Chem. Abstr.,* 102:167115.

Dubois, J. E. and Viellard, H., 1964, Mecanisme de la decetolisation. *Tetra. Lett.,* 1809-1815.

Edashige, Y., Ishii, T. and Hiroi, T., 1990, Anhydrorous hydrogen fluoride sacchrification of lignocellulosis materials. *Chem. Abstr.* 120:301338.

Fieser, L. F. and Fieser, M, 1967, *Regents for Organic Synthesis, Vol.1,* pp1180. Weiley: New York.

Flowers, H. M., 1971, Protection of the hydroxyl group. In *The chemstry of the Hydroxyl Group, Part 2.* Ed. by Patai, S., pp 1001-1004. Interscience: London.

Furney, T. D., 1995, A mechanism and selectivity study of sugar and sugar alcohol hydrogenolysis using 1,3-diol model compounds. M.S. Thesis, Chemical Engineering Department, Michigan State University, East Lansing, Michigan.

Franz, R., Erckel, R., Riehm, T. and Worenle, R., 1982, Lignocellulose saccharification by HF, in *Energy from Biomass: Second E.C. Conference* (Edited by A. Strub, P. Chartier and G. Schleser), pp. 873-878. Applied Science, London.

Goldstein I. S., 1992, Chemicals and fuels from biomass. In *Emerging Technologies for Materials and Chemicals from Biomass* (Edited by Rowell R. M. *et al.*), pp 332-353. Americal Chemical Society, Washington DC.

Goldstein I. S., 1981, *Organic Chemicals from Biomass.* CRC: Boca Raton, FL

Grohman, K., Wyman, C. E. and Himmel M. E., 1993, Potential for fuels from biomass and wastes. In *Emerging Technologies for Materials and Chemicals from Biomass* (Edited by Rowell R. M. *et al.*), pp 354-392. Americal Chemical Society, Washington DC.

Gunzel, B., Yonsel, S. and Deckwer, W. D., 1991, Fermentative production of 1,3-propanediol from glycerol by clostridium butyicum up to a scale of 2 m^2. *Appl. Microbiol Biotechnol*, **36**, 289-294.

Guthrie, J. P., 1977, Equibilibrium constants of a series of simple aldol condensations, and linear free energy relations with other carbonyl addition reactions. *Can. J. Chem.* **56**, 962-972.

Guthrie, J. P., 1974, The aldol condensation of acetaldehyde: the equibilibrium constant for the reaction and the rate constant for the hydroxide catalyzed retroaldol reaction. *Can. J. Chem.* **52**, 2037-2040.

Hawley, M. C., Downey, D. W., Selke, S. M. and Lamport, D. T. A., 1986, Hydrogen fluoride saccharification of lignocellulose materials, in *Cellulose: Structure, Modification, and Hydrolysis* (Edited by R. A. Young and R. M. Rowell), pp. 297-321. Wiley, New York.

Hawley, M. C., Selke, S. M. and Lamport, D. T. A., 1983, Comparision of hydrogen fluoride saccharification of lignocellulose materials with other saccharification technologies. *Energy Agric.* **2**, 219-244.

Hessel, L. W., van Lohuizen, O. E. and Verkade, P. E., 1954, Glycerol-α– and β-monoiodohydrin. *Rec. Trav. Chim.*, **73**, 842-848.

Hibbert, H. and Carter, N. M., 1928, Studies on the reactions relating to carbonydrates and polysaccharides. XVIL. Structure of the isomeric methylidene glycerols. *J. Am. Chem. Soc.*, **50**, 3120-3127.

Hill, H. S., Whelen, M. S. and Hibbert, H., 1928, Studies on the reactions relating to carbonydrates and polysaccharides. XV. The isomeric benzylidene glycerols. *J. Am. Chem. Soc.*, **50**, 2235-2242.

Hydrocarbon Research Inc., 1981, Two step conversion of aldoses to polyols. *Neth. Appl.* NL 8,105,092.

Irvine, J. C., Macdonald, J. L. A. and Soutar, C . W., 1915, XXXIX. Condensation of acetone and benadehyde with glycerol. Preparation of glycerol α–methyl ether. *J. Chem. Soc.*, **107**, 337-351.

James, B. R., 1973, *Homogeneous Hydrogenation.* John Wiley & sons, New York.

Jensen, J. L. and Hashtroudi, H., 1976, Base-catalyzed hydration of *a*,β-unsaturated ketones. *J. Org. Chem.* **41**, 3299-3302.

Jensen, J. L. and Carre, D. J., 1974, Kinetics and Mechanism of Reaction of 3-Buten-2-one and Related Compounds in Aqueous Perchloric Acid. *J. Org. Chem.* **39**, 2103-2107.

Jochims, J. C. and Kobayashi, Y., 1974, Sterospecific synthesis of 5-substituted 1,3-dioxanes by application of Dimroth's principle. *Tetra. Lett.*, 575-578.

Juaristi, E. and Antunez, S., 1992, Conformational analysis of 5-substituted 1,3-dioxanes. 6. Study of the attractive *gauche* effect in O-C-C-O Segments. *Tetrahedron*, **48**, 5941-5950.

Kuhad, R. C., 1993, Lignocellulose biotechnology: current and future prospects. *Critical Reviews in Biomass*, **13**, 151-172.

Latosh, M. V., 1984, Gas chromatographic identification of polyols in products of carbonhydrate hydrogenolysis. *Chem. Abstr.*, 102:26593.

Lipinsky, E. S., 1981, Chemical from biomass: petrochemical substitution options. *Science*, **212**, 1465-1471.

Luers, H., 1938, Das holzverzucherungsverfahren mit fluorwasserstoff von Hock und Bohunek. *Holz Roh- werkst* **1**, 342-344.

Maksimenko, O. A., Zyukova, L. A., Ignat'eva, E. V. and Fedorovich, R. M., 1975, Quantitative gas chromatographic analysis of the hydrogenolysis products of carbohydrate. *Chem. Abstr.*, 84:31333.

Masters C., 1981, *Homogeneous Transition-metal Catalysis: A gentle Art.* Chapman and Hall, New York.

Matheson, N. K. and Angyal, S. J., 1952, The replacement of secondary tosyloxy-groups by iodine in polyhydroxy-compounds. *J. Chem. Soc.*, 1133-1138.

Mestroni, G., Spogliarich, R., Camus, A. Martinelli, F. and Zassinovich, G., 1978, Selective hydrogenation of unsaturated ketones by rhodium (I) complexes containing 2,2'-bipyridine ligand. *J. orgnometal. chem.*, **157**, 345-352.

Mohring, W. R. and Hawley, M. C., 1989, Gravimetric analysis of hydrogen fluoride vapor adsorption by big-tooth-aspen wood. *Ind. Eng. Chem. Res.* **28**, 237-243.

Molnar, A., Felfoldi, K. and Bartok, M., 1981, Transformation of 1,3-diols on homogeneous and heterogeneous rhodium catalysts. *J. Mol. Catal.*, **11**, 225-232.

Montassier, C., Menezo, J. C., Hoang, L. C., Renaud, C. and Barbier, J., 1991, Aqueous polyol conversion on ruthenium and on sulfur-modified ruthenium. *J. Mol. Catal.*, **70**, 99-100.

Montassier C., Giraud D., Barbier J. and Boitiaux J. P., 1989, Transformation de polyols par catalyse heterogene en phase liquide sur les metaux. *Bull. Soc. Chim. Fr.*, 148-155.

Montassier C., Giraud D. and Barbier J., 1988, Polyol Conversion by Liquid Phase Heterogeneous Catalysis over Metals. In *Heterogeneous Catalysis and Fine Chemicals*; Guisnet M. *et. al.* Ed.; Elsevier: Amsterdam.

Neilsen, A. T. and Houlihan., W. J., 1968, The Aldol Condensation. In *Organic Reactions, vol.6,* Adams R. *et. al.* Ed., Weiley: New York.

Palsson, B. O., Fathi-Afshar, S., Rudd, D. F. and Lightfoot, E. N., 1981, Biomass as a source of chemical feedstocks: an economic evaluation. *Science*, **213**, 513-517.

Perry, R. H., Green, D. W. and Maloney J. O., 1984, *Perry's Chemical Engineer's Handbook, 6th.* pp 3-144 to 3-146. MaGraw-Hill, New York.

Piasecki, A. and Burczyk, B., 1980, Acetals and ethers. Part VI. Synthesis of selected *cis*- and *trans*-2-alkyl-4-hydroxylmethyl-1,3-dioxolanes and *cis*- and *trans*-2-alkyl-5-hydroxy-1,3-dioxanes. *Pol. J. of Chem.*, **54**, 367-372.

Pignolet L. H, 1983, *Homogeneous Catalysis with Metal Phosphine Complexes*. Plenum Press: New York.

Pikkov, L. M., Sokovov, N. M. and Tearo, E. N., 1973, Isolation of glycerol from products of sucrose hydrogenolysis in spray apparatus. *Chem. Abstr.*, 80:97637.

Reath, M. L., 1989, Bench scale studies of HF saccharification of wood with 1.5 liter packed-bed reactor. M.S. Thesis, Chemical Engineering Department, Michigan State University, East Lansing, Michigan.

Reimann, A., 1998, Production of 1,3-propanediol by *Clostrium Butrium* in continuous culture with cell recycling. *Appl. Microbiol Biotechnol.*, **49**, 359-363.

Rorrer, G. L., 1989, Solvolysis of a single lignocellulose particles by anhydrous hydrogen fluoride vapor: reaction rate studies, sugar yield studies and development of a detailed kinetic and heat transfer model. Ph.D. dissertation, Chemical Engineering Department, Michigan State University, East Lansing, Michigan.

Rorrer, G. L., Mohring, W. R., Hawley, M. C. and Lamport D. T. A., 1988, Adsorption and reaction processes of HF solvolysis of wood and pure cellulose by anhydrous hydrogen fluoride vapor. *J. Energy Fuels*, **2**, 556-566.

Rylander, P. N., 1985, *Hydrogenation Methods*. Academic Press, Orlando, Florida.

Selke, S. M., Hawley, M. C. and Lamport, D. T. A., 1983, Reaction rates for liquid phase hydrogen fluoride saccharification of wood, in *Wood and Agriculture Residues: Research on Use for Feed, Fuels, and Chemicals* (Edited by E. J. Soltes), pp. 329-349. Academic Press, New York.

Selke, S. M., Hawley, M. C., Hardt, H., Lamport, D. T. A., Smith, G. and Smith, J., 1982, Chemicals from wood via HF. *Ind. Eng. Chem. Prod.* Res. Dev., **21**, 11-16.

Showler, A. J. and Darley, P. A., 1967, Condensation products of glycerol with aldehydes and ketones: 2-substituted *m*-dioxan-5-ols and 1,3-dioxolane-4-methanols. *Chem. Rev.*, **67**, 427-440.

Smith, G. G. and Yates, B. L., 1964, Pyrolysis Studies. XV. Thermal retrograde aldol condensation of β-hydroxyl ketones. *J. Chem. Sci.*, 7242.

Smith, J., Lamport, D. T. A., Hawley, M. C. and Selke, S. M., 1983, Feasibility of using anhydrous hydrogen fluoride to "crack" cellulose. *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, **37**, 641-651.

Sohounloue, D. K., Montassier, C. and Barbier, J., 1983, Catalytic Hydrogenolysis of Sorbitol. *React. Kinet. Catal. Lett.*, 391-397.

Sokolvo, N. M., Tearo, E. and Siirde, E., 1977, Isolation of glycols and glycerol from sucrose hydrogenolysis products by extraction. *Chem. Abstr.*, 88:23287.

Sokolvo, N. M., Shtrom, M. I., Zhavronkov, N. M., 1975, Separartion and purification of sucrose hydrogenolysis products. *Chem. Abstr.*, 83:166124.

Stefoglo, E. F., Ermakova, A. Vasyunina, N. A. and Klabunovskii, E. I., 1973, Kinetic model for the preparation of glycerol by the catalytic hydrogenolysis of glucose. *Chem. Abstr.*, 80:61336.

Stinson, S. C., 1995, Fine and intermediate chemicals makers emphasize new products and processes. *C&E News*, **73**, 10.

Swinnen, J. and Tollens, E., 1991, Bulk chemicals from biomass in the EC: feasibility and potential outlets. *Bioresource Technology*, **36**, 277-291.

Szeja, S., 1983, Separation of 2-substituted 5-hydroxy-1,3-dioxanes by esterification in catalytic two-phase system. *Pol. J. of Chem.*, **57**, 609-612.

Szmant, H. H., 1986, *Industrial Utilization of Renewable Resources*. Technomic Publishing Company: Lancaster, PA.

Tanikella, M. S. S. R., 1983a, Hydrogenolysis of polyols to ethylene glycol. *Eur. Appl.* EP 72,629.

Tanikella, M. S. S. R., 1983b, Hydrogenolysis of polyols to ethylene glycol in non-aqueous solvents, *Eur. Appl.* EP 86,296.

Tipson, R. S., 1953, Sufonic esters of carbohydrate. In *Advances in Carbohydrate Chemistry, vol.8*. Academic: New York.

Tronconi, E., Ferlazzo, N., Forzatti, P., Pasquon, I., Casale, B. and Marini, L., 1992, A Mathematical Model for the Catalytic Hydrogenolysis of Carbohydrates. *Chem. Eng. Sci.*, **47**, 2451-2456.

Trosr, B. M., 1991, *Comprehensive Organic Synthesis*, vol. 6, pp 659. Pergamon, New York.

Van Ling, G, Driessen, A.J., Piet, A.C. and Vlugter, J.C., 1970, Continuous Production of Glycerol by Catalytic High Pressure Hydrogenolysis of Sucrose. *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 210-212.

Van Ling G. and Vlugter J. C., 1969, Catalytic Hydrogenolysis of Saccharides II. Formation of Glycerol. *J. Appl. Chem.*, **19**, 43-45.

Van Ling G., Ruijterman G. and Vlugter J. C., 1967, Catalytic Hydrogenolysis of Saccharides I. Qualitative and Quantitaive Methods for the Identification and Determination of the Reaction Products. *Carbohyd. Res.*, **4**, 380-386.

Verma, R. and Gehlawat, J. K., 1989, Kinetics of hydrogenation of D-glucose to sorbitol. *J. Chem. Tech. Biotech.*, **46**, 259-301.

Wang, K., Furney, T. D. and M. C. Hawley, 1995b, A mechanism study of sugar and sugar alcohol hydrogenolysis using 1,3-diol model compounds. *Ind. & Eng. Chem.*, **34**, 3766-3770.

Wang, K., Furney, T. D. and Hawley, 1995a, Modeling the HF adsorption process on wood chips in a packed-bed reactor. *Chem. Eng. Sci.*, **50**, 2883-2897.

Wang, K., Hawley, M. C. and Reath, M. L., 1994, Adsorption model of HF on wood chips in a packed-bed reactor. *Chem. Eng. Sci.*, **49**, 2321-2329.

Weclas, L., Sokolowski, A. and Burczyk, B, 1982, Acetals and ethers. Part X. Synthesis of selected *cis*- and *trans*-2-alkyl-4-[(2-hydroxyethoxy)methyl]-1,3-dioxolanes and *cis*- and *trans*-2-alkyl-5-(2-hydroxyethoxy)-1,3-dioxanes. *Pol. J. of Chem.*, **56**, 485-490.

Wilson, R. A and Martin C. G., 1992, Paper tree, A solution to environmental problems. *Paper Technology*, **2**, 26-31.

Wise D. L., 1983, *Organic Chemicals from Biomass.* The Benjamin/Cummings Pulishing Company: Menlo park, CA.

Yates, B. L. and Quijano, J., 1969, The thermal decomposition of β-hydroxyl ketones. *J. Org. Chem.*, **34**, 2506-2068.

Young, C. L., 1981, *Solubility Data Series, Volume 5/6, Hydrogen and Deuterium.* Pergamon Press, New Yorek.

Zeng, A. P., Biebl, H, Schlieker, H. and Deckwer, W.D., 1993, Pathway analysis of glycerol fermentation by *Klebsiella pneumoniae:* Regulation of reducing equivalent balance and product formation. *Enzyme Microb. Technol.*, **15**, 770-773.