





LIBRARY Michigan State University

This is to certify that the

thesis entitled

Chemical Products From Hydrogenation of Succinate Esters

presented by

Sriraman Varadarajan

has been accepted towards fulfillment of the requirements for

M.S. Chem Engineering degree in _

Dennes Major professor

Date 7/10/96

O-7639

MSU is an Affirmative Action/Equal Opportunity Institution

PLACE IN RETURN BOX to remove this checkout from your record. TO AVOID FINES return on or before date due.

DATE DUE	DATE DUE	DATE DUE
AUG 53 35 2801		

MSU Is An Affirmative Action/Equal Opportunity Institution c\circ\deledus.pm3-p.1

CHEMICAL PRODUCTS FROM HYDROGENATION OF SUCCINATE ESTERS

By

Sriraman Varadarajan

A THESIS

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

MASTER OF SCIENCE

Department of Chemical Engineering

1996

.

ABSTRACT

CHEMICAL PRODUCTS FROM HYDROGENATION OF SUCCINATE ESTERS

By

Sriraman Varadarajan

The catalytic hydrogenation of succinic acid alkyl esters to a family of products including 1,4-butanediol (BDL), γ -butyrolactone (GBL), and tetrahydrofuran (THF) was investigated over simple, environmentally benign, silica-supported metal catalysts. A 30% - 40% solution of dimethyl succinate in methanol was vaporized in hydrogen and passed over a catalyst in a continuous flow, fixed bed reactor. A maximum BDL yield of 91% of theoretical with 83% selectivity was achieved over a silica supported copper catalyst at 1200 psig and 250°C. A maximum GBL yield of 61% was achieved over a copperpalladium catalyst. Copper favored the selective formation of THF on high surface area support, with a maximum yield of 73% with 88% selectivity obtained at 600 psig and 310°C.

Significant improvements were made over existing processes in yield and selectivity of 1,4-butanediol from dimethyl succinate. With highly efficient fermentation technologies now commercially available for production of succinate esters from starch hydrolysates, the current study provides the basis for development of an economically attractive process. I dedicate this work to my parents without whose love and encouragement nothing would

have been possible.

ACKNOWLEDGMENTS

The author wishes to thank Dr. Dennis J. Miller for his guidance, support and understanding throughout this project; Dr. James E. Jackson for his suggestions and comments; Dr. Kris A. Berghund for his comments; and finally Man Tam for his helpful suggestions.

TABLE OF CONTENTS

LIST OF TA	ABLES	viii		
LIST OF FIGURES				
Chapter 1.	Chapter 1. Introduction and Background			
1.1	Introduction	1		
1.2	Organic Acid Esters from Biomass	3		
1.3	Succinic Acid and Anhydride	4		
1.4	Literature Review	7		
1.5	Stobbe Condensation	8		
1.6	2-Pyrrolidinone	10		
1.7	1,4-Butanediol, γ -Butyrolactone, Tetrahydrofuran	11		
	1.7.1 Current Manufacturing Processes	12		
1.8	Research Objectives	18		
Chapter 2	Vapor Phase Reaction System	20		
2.1	Design Criteria for Vapor Phase Flow Through Reactor	20		
2.2	High Pressure, High Temperature Reactor Vessel	21		
2.3	Catalyst Loading and Unloading	22		
2.4	Reactor Furnace	25		

2.5	Liquid Feed System	26
2.6	Gas Flow System	27
2.7	Reaction Product Collection	28
2.8	Safety Equipment	30
Chapter 3	Experimental Conditions and Procedures	31
3.1	Introduction	31
3.2	Catalyst Preparation	32
3.3	Catalyst Loading and Reduction in Reactor	34
3.4	Operation of Reactor	35
3.5	Reactor Shutdown and Product Recovery	37
3.6	Reaction Product Analysis	38
	3.6.1 Product Identification	38
	3.6.2 Liquid Products	44
	3.6.3 Gas Products	45
3.7	Product Yield and Selectivity Calculations	46
Chapter 4	Results and Discussion of Vapor Phase Experiments	48
4.1	Preliminary Studies and Reaction Conditions	49
	4.1.1 Preliminary Experiments	49
	4.1.2 Reaction Conditions	50
4.2	Results of Vapor Phase Experiments	52
	4.2.1 Summary of Experiments	52
	4.2.2 Summary of Results	53

4.3	Discussion of Results			
	4.3.1 Catalyst Material	55		
	4.3.2 Catalysts Supports	57		
	4.3.3 Temperature	58		
	4.3.4 Pressure	60		
4.4	Carbon Balance	61		
4.5	Conclusions			
Chapter 5	Summary and Recommendations	78		
5.1	Summary of Results	78		
5.2	Improvements Over Existing Processes			
5.3	Recommendations	80		
Appendix A		82		
Appendix B		84		
LIST OF REI	FERENCES	128		

LIST OF TABLES

1.1	Physical Properties of Compounds Under Study (12, 43)	6
1.2	Previous Work on Succinic Acid Route to 1,4-Butanediol	17
3.1	Catalysts Studied with Composition and Loading	33
3.2	List of Retention Times and Response Factors	45
3.3	Sample Experimental Report	47
4.1	Reaction Conditions	53
A .1	Temperature Program for Gas Chromatograph	83
B .1	Preliminary Experiments	84
B.2	Run #13 Report	85
B .3	Run #14 Report	86
B.4	Run #15 Report	87
B .5	Run #16 Report	88
B.6	Run #17 Report	89
B.7	Run #22 Report	90
B.8	Run #23 Report	91
B .9	Run #24 Report	92
B .10	Run #25 Report	93

B .11	Run #28 Report	94
B .12	Run #29 Report	95
B .13	Run #30 Report	96
B .14	Run #31 Report	97
B .15	Run #32 Report	98
B .16	Run #33 Report	99
B .17	Run #34 Report	100
B .18	Run #35 Report	101
B .19	Run #36 Report	102
B.20	Run #37 Report	103
B .21	Run #38 Report	104
B.22	Run #39 Report	105
B.23	Run #40 Report	106
B.24	Run #41 Report	107
B.25	Run #42 Report	108
B.26	Run #43 Report	109
B.27	Run #44 Report	110
B.28	Run #45 Report	111
B.29	Run #46 Report	112
B.30	Run #47 Report	113
B .31	Run #48 Report	114
B .32	Run #49 Report	115

B .33	Run #50 Report	116
B.34	Run #51 Report	117
B.35	Run #52 Report	118
B .36	Run #53 Report	119
B .37	Run #54 Report	120
B.38	Run #55 Report	121
B.39	Run #56 Report	122
B.40	Run #57 Report	123
B.41	Run #58 Report	124
B .42	Run #59 Report	125
B.43	Run #60 Report	126
B.44	Run #61 Report	127

LIST OF FIGURES

1.1	Reaction Pathways From Succinic Acid (12)	2
2.1	Vapor Phase Reaction System	23
2.1	Cross-section of Vapor Phase Reactor	24
2.3	Liquid Product Trapping System	29
3.1 -A	Typical GC Spectrum of Product Sample	39
3.1 -B	Mass Spectrum of Methyl Lactate	40
3.1 -C	Mass Spectrum of Dimethyl Succinate	41
3.1 -D	Mass Spectrum of γ -Butyrolactone	42
3.1 -E	Mass Spectrum of 1,4-Butanediol	43
4.1	Effect of Pressure on DMS Conversion over Catalysts Supported on Si-Al (T = 320 C)	63
4.2	Effect of Temperature on DMS Conversion over Catalysts Supported on Silica-Alumina (P = 600 psig)	64
4.3	Effect of Pressure on BDL Yields over Catalysts Supported on Silica-Alumina (T=320 C)	65
4.4	Effect of Temperature on BDL Yields over Catalysts Supported on Silica-Alumina (P = 600 psig)	66
4.5	Effect of Pressure on GBL Yields over Catalysts Supported on Silica-Alumina (T = 320 C)	67

68 69
69
69
70
71
72
73
74
75
76
77

Chapter 1

INTRODUCTION AND BACKGROUND

1.1 Introduction

It is well established that current chemical production technology is deeply rooted in petroleum, coal, and other fossil carbonaceous materials. This immense resource is finite, however, and its limiting effect on industrial growth is being felt slowly but surely. Naturally, one major concern in research circles is to find alternate carbon sources for the production of basic feedstock, shifting from a fossil to a renewable carbon base. The focus of this research project is on the production of industrial commodity and specialty chemicals from renewable (crop-derived) succinic acid and esters. Some of the possible reaction pathways from succinic acid are given in Figure 1.1. The following sections in this chapter explain the need for biomass-derived instead of petroleum-derived feedstocks, the



(N-alkyl,2-pyrrolidinone)

- (1) Esterification process with methanol
- (2) Catalytic hydrogenation over copper chromite, copper, or copper-chromiummanganese
- Hydrogenation of solution of succinic acid and R'NH₂ where, R' = H (ammonia) or an alkyl group (alkyl amine)
- (4) Condensation with aldehydes or ketones and metal alkoxide
- (5) Condensation of γ -butyrolactone with R'NH₂, an alkyl amine

Figure 1.1 - Reaction Pathways from Succinic Acid (12)

technology behind the production of succinic acid and esters, and the chemicals identified as industrially valuable that could be produced from these chemicals. The properties, current production techniques and the work done to date on the production of these organic compounds from succinic acids and esters are also explained.

1.2 Organic Acid Esters from Biomass.

Biomass consists of collectible plant derived materials that are abundant in nature, inexpensive, and potentially convertible to feedstock chemicals by fermentation processes. Common sources of biomass as starch are corn, wheat, potato, sago palm, and other agricultural products. Corn syrup and molasses are also sources of biomass as monomeric sugars or soluble oligomers (1). However, lignocelhulose (wood, agricultural residue, grass) is the major source of biomass that is both available in large quantities and has no competing use as food (2). Various parameters have been documented for the production of organic acids, both volatile and non-volatile, from carbohydrates under anaerobic conditions (3, 4, 5). This process, acidogenic fermentation, yields the various organic acids using bacteria, fungi or yeast under mostly anaerobic conditions. Specifically, succinic acid, a non-volatile acid, is produced by bacterial fermentation under anaerobic conditions (6). Bigelis, *et. al.*, explain production of succinic acid by *candida brumptii* by a fermentation process or by *Rhizopus sp.* in a mixed fermentation with bacteria (7).

The major advantages in the bio-processing of commodity chemicals are (8) (a) An alternative to the use of petroleum feedstock through biomass conversion, hence replacing existing thermal and chemical routes to commodity chemicals.

3

(b) Milder reaction temperatures and pressures and high selectivity to end products.

(c) Higher selectivity also leads to reduction of undesirable by-products, thus making the process more environmentally benign.

These are just some of the advantages of bio-processing. Process economics, however, are dictated mostly by products separation. Some of the techniques currently followed for recovery of organic acids from fermentation are liquid-liquid extraction, distillation, electrodialysis separation using membranes, and fermentation and crystallization of acid salt followed by simple separation by sedimentation and filtration (6). Other issues to be addressed before bio-processing becomes economically feasible include reaction kinetics, sterility requirements, and heat and mass transfer requirements. These economic considerations and business related details of bio-processing are well documented (9,10,11). Clearly, further research needs to done to overcome these surmountable problems.

1.3 Succinic Acid and Anhydride

1,4-Butanedioic acid or succinic acid, $C_4H_6O_4$, is a constituent in almost all plant and animal tissues. The acid's uses range from scientific applications such as radiation dosimetry, and buffer standards to applications in agriculture, food, medicine, plastics, textiles, and cosmetics. It can be produced by numerous catalyzed oxidation processes as well as by chemical and biochemical oxidation of fats and by alcoholic fermentation of sugar. Succinic acid dehydrates to form the internal anhydride. The anhydride is also produced by the catalytic hydrogenation of maleic anhydride (12), and is relatively

4

insoluble in water and ether. Some of the physical properties of succinic acid and anhydride are given in Table 1.1.

Succinic acid is currently manufactured by catalytic hydrogenation of maleic acid or anhydride. Common catalysts preferred for the hydrogenation of maleic acid to succinic acid are palladium on carbon, palladium on calcium carbonate, and carbon carrier catalysts containing rhodium and ruthenium. Catalysts uses in the hydrogenation of maleic anhydride are nickel on kieselguhr, palladium on alumina, and calcined nickel aluminate (12). The production of succinic acid and esters has been studied extensively. Common feedstock include normal paraffins, sucrose, acetone, and isopropyl alcohol (13,14). Process economics and hence the market price of succinic acid, as described in section 1.2, is based mostly on separation methods employed to remove the acid from the product mixture. Succinic acid currently sells at \$2.72 per lb and the anhydride at \$1.71 per lb (15). The fermentation technology for the production of succinic acid and ester is gaining momentum with new innovations in process technology (16). This would lead to a definite drop in the price of the acid as a raw material. Hence the current project to study organic commodity and specialty chemicals that could be produced from these raw materials seems in order.

Succinic acid undergoes common reactions like dehydration to the anhydride, halogenation, esterification to mono and diesters, oxidation, and reduction. One important reaction that is specific to this acid or, more accurately, its esters is the Stobbe condensation. This reaction has lead to the preparation of a variety of unsaturated and saturated substituted succinic acids. A solution of succinic acid in ammonia produces Table 1.1 - Physical Properties of Compounds Under Study (12,43)

Properties	Succinic Acid	Succinic Anhydride	Butanediol	y-Butyrolactone
Molecular formula	C4H6O4	C,H,O3	C4H10O2	C,H ₆ O ₂
CAS registry number	110-15-6	108-30-5	110-63-4	96-48-0
Melting point	188.1 ⁰ C	119.6 ⁰ C	20.2 [°] C	- 44°C
Boiling point	dehydrates at mp	261°C	228°C at 101 kPa	204 ⁰ C at 101 kPa
Specific gravity	1.552-1.577	1.572	1.017	1.127
Solubility in water (per 100 g of soln)	2.88 g at 0 ⁰ C 121 g at 100 ⁰ C	relatively insoluble	miscible	miscible
Crystalline structure	Triclinic and monoclinic prisms	Rhombic pyramidal or bipyramidal crystals	liquid form	liquid form

2-pyrrolidinone on catalytic hydrogenation. Catalytic hydrogenation of succinic acid or anhydride yields 1,4-butanediol, γ -butyrolactone, and tetrahydrofuran, as discussed in section 1.7.

1.4 Literature Review

A comprehensive literature study has been conducted on the industrially viable commodity and specialty chemicals that could be produced from succinic acid, anhydride and esters. Reaction pathways were studied from these raw materials that lead to the commodity chemicals. Present and future industrial demand, production, and consumption, techniques followed in the industries currently for the production of these compounds, and costs involved were some of the key factors taken in to consideration in identifying these compounds. Three pathways were identified for the lab scale study based on their industrial value and rising demand. New uses are being discovered for these compounds and the current need is an alternative pathway, like fermentation derived raw materials, by which the chemicals could be produced that would make it economically attractive.

(A) The first set of reactions is the Stobbe condensation. This reaction is unique to succinic esters and leads to a host of potentially important chemicals. The applications include synthesis of new compounds by varying the aldehydes and ketones used in the condensation reaction. The reaction and its applications are detailed in the next section.

(B) The second set of products is from the hydrogenation of succinic acids and esters. Three main compounds formed are γ -butyrolactone, 1,4-butanediol, and tetrahydrofuran. All three chemicals are increasingly in demand in a variety of industries like polymers, pharmaceutical, and in synthesis of new organic compounds. The reduction reaction, properties of product compounds, and industrial application are discussed in detail in section 1.7

(C) The third reaction pathway is hydrogenation of a solution of succinic acid in ammonia to 2-pyrrolidinone, an intermediate in manufacture of 1-vinyl-2-pyrrolidinone. The latter is the monomer for polyvinyl pyrrolidinone (PVP) or Povidone, a specialty polymer that has a wide range of industrial applications including the pharmaceutical, textile, photochemical industries and medicine. The production of 2-pyrrolidinone from succinic acid is discussed briefly in section 1.6.

1.5 Stobbe Condensation.

The reaction between an ester of succinic acid and an aldehyde or ketone to form alkylidenesuccinic acid is called Stobbe condensation. The first Stobbe synthesis was done as early as 1893 (17). A mole of metal alkoxide is required per mole of carbonyl compound and ester. A typical Stobbe condensation reaction is shown below.

$$R_{2}C=O + \begin{array}{c} COOC_{2}H_{5} \\ \downarrow \\ CH_{2}CH_{2}COOC_{2}H_{5} \end{array} + \begin{array}{c} NaOR \\ NaOR \\ R_{2}C=CCH_{2}COONa \end{array} + \begin{array}{c} COOC_{2}H_{5} \\ \downarrow \\ R_{2}C=CCH_{2}COONa \end{array} + \begin{array}{c} C_{2}H_{5}OH \\ CH_{2}CH_{5}OH \\ R_{2}C=CCH_{2}COONa \end{array}$$

Isomers of the acid could also be formed by tautomeric shift of hydrogen. A variety of aldehydes and ketones have been studied for this condensation reaction (18, 19, 20, 21). Diethyl, dimethyl, di-t-butyl succinate as well as α -substituted aryl-, alkyl-, aralkyl-, and alkylidene-succinic ester have been studied as feed. The condensation reaction is said to

proceed via at least three routes. The most accepted one proceeds with the formation of an intermediate called paraconic esters (22).

The applications of Stobbe condensation are enormous, its primary use being in the synthesis of new compounds. Some of the common synthesis that could be conducted with succinic esters are listed below

(a) Lactonic acids : Bromo lactonic acids are prepared from alkylidene succinic acids, formed by Stobbe condensation, by treatment with bromine. These on boiling with water give α,β -unsaturated lactonic acids and dilactones (18).

(b) Naphthol synthesis : Alkylidene succinic acids and half-esters may undergo cyclodehydration and enolization to give substituted 1-naphthol, 3-carboxylic acid. Ring closure can be effected by zinc chloride in acetic acid-anhydride or by hydrogen fluoride (18).

(c) Indone synthesis: Alkylidene succinic acid having an aryl group cis to the carboxyl group may undergo cyclodehydration to form a substituted indanoneacetic acid accompanied by some isomeric lactone formation. A variety of substances have been studied for this ring closure (18).

Other compounds that could be synthesized include tetrahydroindanones, tetralones, and equilenones. The methods above have led to the synthesis of such substances as hinekinin, 2-methylazulene, structures related to the steroids and polycyclic aromatic compounds in the naphthacene, benzphenanthrene series (18).

1.6 2-Pyrrolidinone

2-Pyrrolidinone is produced commercially by the condensation of butyrolactone with ammonia. It can also be synthesized by hydrogenation of succinic acid in ammonia (23). The main application of 2-pyrrolidinone is as an intermediate in the manufacture of 1-vinyl-2-pyrrolidinone. This compound is used as a monomer in the manufacture of PolyVinyl Pyrrolidinone (PVP). PVP or Povidone is one of the key polymers used in a variety of applications owing to its unique physical and chemical properties. These include a uses in pharmaceuticals as a binder for tablets, and in medicine for long term preservation of blood. It is also used in the textiles, paper, and cosmetic industries (29). Other applications of pyrrolidinones include as an intermediate in the preparation of Nylon-4 and as an organic solvent.

Considerable work has been done on the succinic acid route to 2-pyrrolidinone. As explained in the next section, γ -butyrolactone (GBL) is synthesized easily by hydrogenation of succinic acid or esters. On treatment with ammonia at around 250°C and 8-9 MPa, GBL yields 2-pyrrolidinone. The reactions involved in the typical industrial production of 2-pyrrolidinone from γ -butyrolactone are given below. The intermediate 4hydroxybutyramide is not ordinarily isolated.



Direct hydrogenation of succinic acid in ammonia using catalysts has been studied recently. A process for preparing 2-pyrrolidinone which consists of reacting succinic acid, hydrogen, and ammonia in an aqueous system and over ruthenium as catalyst is claimed in (24). Yields over 90% of theoretical are reported. A similar process with a yield of up to 90% using rhodium as catalyst is claimed in (25). A one-step process for the preparation of 2-pyrrolidinone by contacting succinic acid or anhydride with ammonia and a catalyst made of palladium on alumina is claimed in (26). Yields up to 78% is reported in the patent.

Thus the hydrogenation of succinic acid or anhydride to 2-pyrrolidinone is a well established process. The reaction step is however very sensitive to catalyst metal and yields of 2-pyrrolidinone are also affected by the succinic acid to ammonia ratio. Further study is required wherein the reduction could be conducted over more environmentally benign and economical catalysts.

1.7 1,4-Butanediol, γ-Butyrolactone, and Tetrahydrofuran

The catalytic reduction of succinic acid or ester yields 1,4-butanediol (BDL), γ butyrolactone (GBL), tetrahydrofuran (THF), or a mixture of these compounds, depending on catalyst and reaction conditions. Of the three compounds the industrial demand for the first two has been steadily increasing these past years. 1,4-Butanediol is produced by major manufacturers for internal use in the production of γ -butyrolactone. But demand for 1,4-butanediol has steadily increased, especially in Japan, owing to its use in the manufacture of polytetramethylene glycol (PTMEG) and polybutylene terephthalate (PBT) resin, along with a steady increase in the use of polyurethane (28). A review of current technologies used by industry shows that the Reppe process is still the method being followed by the majority of manufacturing companies for production of 1,4-butanediol. The low cost of acetylene as a raw material offsets any other alternative routes via propylene oxide, butadiene, and maleic or succinic anhydride. But because acetylene has problems caused by its explosive nature and high energy consumption in its preparation, as well as because of depletion in the petroleum feedstock, alternate routes for the above three compounds are becoming attractive. The cost estimates for the other routes, especially succinic acid, assume synthetic production of these raw materials. The recent development of fermentation technologies, however, is bound to make production of 1,4-butanediol and γ -butyrolactone economically viable. Estimated figures for 1994 put world demand at 304,000 metric tons with an annual growth of 7% (27).

1.7.1 Current Manufacturing Processes

The Reppe process proceeds via copper catalyzed condensation of acetylene with formaldehyde at 1 atm pressure and 80-95°C temperature to produce propargyl alcohol and 1,4-butynediol. The alcohols are then hydrogenated over Raney nickel to produce 1,4butanediol. Overall yields are approximately 90%. Major US suppliers include DuPont, BASF, and ARCO. The following shows the steps involved in the commercial Reppe process.

HC
$$\equiv$$
CH + 2HCHO \longrightarrow HO $-$ CH₂ $-$ C \equiv C $-$ CH₂ $-$ OH (acetylene) (formaldehyde)

^---

HO---CH₂---CH₂--OH + 2H₂
$$\xrightarrow{\text{(Raney Ni)}}$$
 HO---CH₂--CH

Other routes include butadiene acetoxylation, maleic anhydride hydrogenation, propylene oxide isomerisation, etc (43).

Butadiene acetoxylation has been employed by Mitsubishi Chemical for nearly a decade. The process involves liquid phase acetoxylation of butadiene on Pd-Te over carbon with acetic acid. The diacetate formed is further reduced over palladium on carbon catalyst at 1300 psia and 85°C to give 1,4-butanediol at about 95% yield of theoretical (28). The propylene oxide process involves isomerisation of the oxide to allyl alcohol, followed by hydrogenation at around 60°C under 100 atm pressure to 1,4-butanediol with 2-methyl-1,3-propanediol as by-product; yields are nearly 100% (27). The maleic or succinic acid pathways involve either direct hydrogenation to 1,4-butanediol or via the intermediate diesters. The former process is an old one and appears to be focused on primary production of tetrahydrofuran and γ -butyrolactone. Yields are typically 95% and the individual yields of the above two compounds are variable depending on reaction conditions.

The preferred route from maleic and succinic anhydride is by the Davy-Mckee process. It can produce both 1,4-butanediol and γ -butyrolactone. The original patents in the early 1980's involved a two-step esterification process with simple alcohols. The first step is non-catalytic and yields the succinic or maleic monoester which is then converted to the corresponding diester by ion-exchange catalysis. The yields were almost 100% in both cases. The hydrogenation is in the vapor phase and uses copper-chromium catalysis. The products had both 1,4-butanediol and γ -butyrolactone along with tetrahydrofuran. The yields of each compound varied depending on reaction conditions. Subsequent patents have adopted this process and have improved upon the yield and selectivity as well as varied the feed, reaction conditions and catalysts.

1.7.2 Succinic Acid route to 1,4-butanediol

Sharif *et. al.* claim a continuous process in which dimethyl maleate was smoothly converted to dimethyl succinate over a catalyst of surface area 85 m²/g comprising of 25% chromium and 35% copper before reduction (30). The diethyl succinate was further reduced to 1,4-butanediol with a maximum selectivity of 84% along with γ -butyrolactone and tetrahydrofuran at selectivities of 9% and 6%, respectively. A conversion of 97% was achieved and typical reaction conditions were 175°C and 56 bar with a hydrogen to ester ratio of 295 : 1.

Suzuki *et. al.* claim a continuous process in which succinic anhydride dissolved in γ -butyrolactone, in a molar ratio of 1:4, was reduced over a catalyst comprising copper, chromium and manganese with a weight percentage of 39%, 37%, and 36%, respectively (31). A 100% conversion of succinic anhydride on a molar basis was obtained with 41% yield of 1,4-butanediol, and 55% yield of tetrahydrofuran on a molar basis based on succinic anhydride supplied. Typical reaction conditions were a temperature of 210°C and a pressure of 200 psig.

Suzuki et. al. claim a gas phase reduction process for succinic anhydride in the presence of a catalyst comprising rhenium, copper and zinc (32). The reaction conditions

were a temperature of 200°C and pressure of 200 psig, with succinic anhydride undergoing 100% conversion to give 70% of 1,4-butanediol and 26% of tetrahydrofuran. The process also involved reducing the catalyst, which started in the form of oxides of rhenium, copper, and zinc, before the reaction to the respective metals. Reduction was carried out overnight with a mixture of hydrogen and nitrogen.

Hara *et. al.* describe a process in which succinic anhydride was reduced over a catalyst comprising ruthenium and phosphine (33). Reaction conditions were a temperature of 210°C and a pressure of 120 kg/cm² with the anhydride undergoing 97% conversion with 67% selectivity to 1,4-butanediol and 29% selectivity to γ -butyrolactone. The reaction could be in batch or continuous process but the hydrogenation step is conducted in liquid phase.

Turner *et. al.* claim a process for the preparation of 1,4-butanediol by hydrogenolysis of dialkyl esters over a copper chromite catalyst in a reactor with two heating zones (34). The second zone was at approximately 5°C higher than the first, thus increasing the 1,4-butanediol yield over that of γ -butyrolactone. Kouba *et. al.* illustrate the use of copper aluminum borate or copper chromite as hydrogenation catalyst for reducing succinic diesters (35). The reactions were carried out in batch reactors and the results disclosed show a maximum dimethyl succinate conversion of 38% over copper chromite with 1,4-butanediol and γ -butyrolactone selectivity of 57% and 19%, respectively. Reactions were carried out at 200°C and 1800 psig for about 6.5 hours. Narasimhan *et. al.* claim the use of supported and unsupported cobalt, a group IV A element and boron catalysts for the hydrogenation of diester of succinic acid (36). Dimethyl succinate is reduced over cobalt - tin boride catalyst supported on γ -alumina at 200°C to give 79% 1.4-butanediol and 10% tetrahydrofuran at 90% conversion.

Thomas *et. al.* claim a hydrogenation catalyst comprising copper, palladium and an alkali or alkaline earth metal supported on magnesium silicate or silica-alumina wherein the hydrogenation of γ -butyrolactone to 1,4-butanediol is reported (37). The procedure for preparing the catalyst was explained and this procedure was closely followed in the preparation of the catalyst in the lab for the present study.

Copper as a catalyst has been extensively studied by Monti, Trimm, and coworkers in hydrogenation of aliphatic esters. The reactions studied were primarily methanol synthesis from methyl formate (38, 39) and hydrogenolysis of dimethyl succinate (40, 41). It was shown that γ -butyrolactone was formed in the first step of hydrogenation of dimethyl succinate over copper chromite and copper on silica (41). The compound then reacted further to tetrahydrofuran or 1,4-butanediol depending on the reaction conditions, particularly pressure. It is also suggested, from equilibrium calculations, that 1,4butanediol is unlikely to be formed in any significant amounts from dimethyl succinate at pressure less than 700 psig (42).

A summary of work done so far, that is available in the patent literature, is given in Table 1.2. The table gives the best results that were obtained in the study of 1,4butanediol production from succinic acid and its derivatives including catalyst used, reaction conditions and yield. Table 1.2 - Previous Work on Succinic Acid Route to 1,4-Butanediol

	Reference		31	32	33	34	36	37	38
	Comments		Vapor Phase Reaction	Vapor Phase Reaction	Vapor Phase Reaction	Liquid Phase reaction	Batch reaction	Vapor Phase Reaction	Vapor Phase Reaction
(%)	THF		6.1	55.7	26.3	3.1	•	10	١
st Yield	GBL		6	1	I	28.4	7.4	I	N/A
Produk	BDL		82	41.1	70.4	65.5	22.1	61	94
	Conversion		97.3%	100%	100%	97.4%	39%	%06	95%
H ₂ : Feed		molar	295:1	200 : 1	ı	ſ	N/A	1:2 to 1:20	150:1
onditions	Pressure	(psig)	825	215	215	1700	1800	370	006
Reaction C	Temp.	(c)	177	200	200	200	200	200	160
	Feed		Diethyl maleate	Succinic anhydride (1) in GBL (4)	Succinic anhydride (1) in GBL (4)	Succinic anhydride in GBL	DMS	SMG	GBL
	Catalyst		Cu - 35%, Cr - 25% , unsupported	Cu - 39%, Cr - 37%, Mn - 4% (Commercial catalyst - G-89), unsupported	Cu - Zn - Rh, unsupported	Ru - Phosphine, unsupported	Strem - barium promoted copper chromite	Co, Sn (at. ratio - 4:1) on γ - Alumina	Cu (12%), Pd (0.3%), KOH (3%) on Magnesium silicate

17

1.8 Research Objectives

The rest of this section is devoted to setting out the research objectives in this project. As explained above the aim of this project is to develop catalytic pathways from succinic acid and derivatives to commodity and specialty chemicals. The major pathways were identified through extensive literature study. It was found that while the industry is currently producing these chemicals through other non-succinic routes, the demand for these chemicals is increasingly steadily and correspondingly the supply of petroleum based raw materials for these compounds has dwindled over the years. Hence alternate pathways are welcomed. Literature study also shows that considerable work has been done on the succinic pathways to the above chemicals. Hence the objectives of this project would be to improve upon the existing processes as well as to explore the possibilities of new routes from succinic acid, anhydride or esters to these chemicals. Some of the more important goals of this research are enumerated below.

(1) A literature review to study the following : current processes available for production of succinic acid and esters from biomass, identification of commodity and specialty chemicals that could be produced from succinic acid and its derivatives as an alternate pathway, and advancements made so far in this direction.

(2) The experimental study in the research laboratory is conducted in a high pressure, high temperature setup. Calculations will be done to design the reactor, taking into account the various parameters involved like optimum and maximum operating conditions, space restrictions, cost involved, and ease of operation among others. The setup also includes the design of liquid and gas feed flow and product collection, controlling and monitoring the flow rates as well as pressure and temperature in the reactor, method of catalyst loading. Safety plays an important part in the design of high pressure reactors and the design should also take into account the possible failure of the setup during operation.

(3) The production of 1,4-butanediol from succinic esters is taken up for further study in the lab scale. The by-products are γ -butyrolactone, tetrahydrofuran, and butanol and parameters would be studied to minimize or eliminate these compounds. A set of runs would be conducted initially to test the reactor and to identify a set of operating conditions. A series of experiments would be conducted to identify a catalyst material for dimethyl succinate hydrogenation that is environmentally benign and industrially economical. The conversion of the reactant, as well as the yield and selectivity of 1,4-butanediol in the product would be maximized.

Chapter 2

VAPOR PHASE REACTION SYSTEM

This chapter describes in detail the design and construction of the high pressure/high temperature fixed bed continuous flow reactor used in succinate hydrogenation studies. Section 2.1 gives the various criteria taken into account while designing the reactor and apparatus. Section 2.2 and onward describe in detail the components that form the reactor and experimental setup.

2.1 Design Criteria for the Vapor Phase Flow Through Reactor

A continuous flow fixed bed reactor was chosen for the study of catalytic conversion of succinic esters as the literature showed excellent results in similar studies. The reactor is designed for hydrogenation of succinic esters under conditions of high pressure and high temperature, as these have proven to be the most favorable conditions pressure and high temperature, as these have proven to be the most favorable conditions for reduction reactions with molecular hydrogen. The following were some of the criteria taken into account in designing the apparatus to ensure that it performs satisfactorily.

1) The system should be designed for a fixed bed of catalyst and a continuous flow of reactants and products.

2) The system should withstand extreme conditions of up to 400°C and 3000 psig simultaneously without leaking.

3) The reactor must be constructed of a material that is economical and capable of handling a wide range of reactant and product materials without corrosion or fracture.

4) The system must also be capable of allowing the introduction of liquid and gaseous reactants simultaneously.

5) The system must be designed to allow catalyst reduction prior to reactions.

6) Finally, the system should be designed so as to allow easy dismantling for catalyst loading and unloading.

The following sections describe in detail the procedure for designing and constructing the reactor setup.

2.2 High Pressure, High Temperature Reactor Vessel

A desired internal volume of approximately 10 milliliters for the actual reaction chamber was calculated using extreme conditions of pressure and temperature as well as optimum flow rates of liquid and gas feeds and catalyst loading. A cone closure tubing reactor, made of 316 stainless steel and completely assembled and factory tested at
Autoclave Engineers (Model # CC.985SS20) was chosen as the reaction vessel. The above model was capable of handling a maximum pressure of up to 16,800 psig at 800° F and thus exceeded the required pressure and temperature limits. The reactor body (P/N 103A-2454) is 102 mm long, 19.1 mm O.D., and 11.1 mm I.D., has a nominal capacity of 9.85 ml, and is easily replaceable. The length of the whole reactor (167 mm) was chosen based on the available standard heating element length from Mellen Furnace discussed later in the chapter. A schematic of the experimental setup is given in Figure 2.1.

A schematic of the cross-section of the reactor part of the experimental setup is shown in Figure 2.2. The two open ends of the reactor tube are connected to nipples (P/N-CN6608-316) by a coupling assembly made of 316 stainless steel with standard Autoclave Engineers high pressure connections (P/N-F375C). The reactor was opened and closed from the top for easy catalyst loading and unloading. To prevent leakage and possible explosions there was no machined part at or near the reactor, since the setup was to be used at extreme lab conditions and also since hydrogen was one of the reactants.

2.3 Catalyst Loading and Unloading

Initially the catalyst was loaded in a glass tube of length 102 mm and O.D. 10 mm and equipped with a quartz frit at the bottom. Glass was chosen to prevent any catalytic activity as well as to ensure easy weighing of the catalyst before and after the reaction. But the results showed poor conversion of dimethyl succinate owing to loss of feed in vapor phase through the gap between the glass outer wall and the reactor inner wall. Hence the idea was abandoned and was replaced with a very small glass tube about 6 mm in height,





23

.



Figure 2.2 - Cross-section of Vapor Phase Reactor

10 mm O.D. and fitted with a quartz frit in the middle. A steel screen was wrapped over it so as to fit snugly at the bottom of the reactor. This would hold the solid catalyst yet allow the liquid and vapor phase to flow through and would also enable the catalyst to be loaded and unloaded easily as well as increase the volume available for reaction. This method has worked well so far with the sizes of catalyst used. The two mesh sizes of catalyst material used were 16-30 mesh and 80 mesh and a medium quartz frit was chosen since it was nonporous to both, but still allowed flow of liquid and gas.

2.4 **Reactor Furnace**

The system is designed for vapor phase reactions. Hence, keeping in mind the high temperatures needed for vaporizing the feed at high pressures, Mellen Split Type tubular heaters were chosen. The furnace is made up of two 1.25 in (317 mm) I.D. by 9 in (228 mm) long, split type heating elements (Model # 12-155). The maximum hex size of the reactor was 254 mm and hence fitted the furnace correctly. The Mellen heating element utilizes a high quality ceramic holder and helical coiled iron - chromium - alumina wire embedded in high purity alumina cement. The furnace elements can reach up to a maximum of 1200°C and are wired in parallel so that they can be powered by a 120 Volt source. The furnace elements are enclosed by two K20 type fire bricks of dimensions 23 mm long, 11.5 mm wide and 12.5 mm deep. The bricks are cut and grooved to accommodate the furnace elements and the wiring without any gaps to give good insulation. Two more brick pieces of dimensions 6 mm by 11.5 mm by 12.5 mm are added at the top and bottom for insulation of the connecting assembly and a part of the nipple on

either side. The whole assembly including the bricks enclosing the furnace which encloses the reactor is mounted on an aluminum stand for stability and access.

The furnace is controlled by an Omega series CN-2010 programmable temperature controller with the temperature of the furnace being read on the inside with a thermocouple (T1) as shown in Figure 2.1. A few experiments were done using a thermocouple inside the reactor to measure the difference between the temperature outside in the furnace and the actual temperature inside the reactor. The set point was then adjusted to achieve the desired catalyst bed reaction temperature and the difference was always accounted for in later experiments by keeping a higher set point.

2.5 Liquid Feed System

The liquid reactant is introduced into the heated zone of the reactor by a Bio-Rad Soft-Start (Model 125-1350) pump (P1). The pump was chosen because the reactant had to be pumped against high pressures and because pressure in the reactor had to be monitored. The pump is capable of pumping fluids at pressures up to 6000 psig and has a flow rate range of 0.02 ml/min to 9.9 ml/min in increments of 0.01 ml/min and also measures the pressure it is pumping against. Earlier runs with an Eldex model A-30-S pump gave unreliable flow rates at high pressures. The present dual piston, positive displacement pump has proved accurate even at low flow rates. The pump also features an alarm system which stops the pump in case of increase in the pressure beyond a set point or a drop in the pressure below a set point. The liquid feed was stored in a burette and kept well above the pump heads. A draw-off valve is provided in the pump to pull the feed through the inlet tubing and to push it through the pump heads. This is done to eliminate any air bubbles in the lines. A Teflon tube of 1/16 in. O.D. was used for the inlet to the pump and a stainless steel tube of 1/16 in. O.D. was used for the outlet from the pump. The stainless steel outlet tube runs all the way to the reactor and is set up so that the liquid reactant drops slowly from the tip of the tube in the heating zone, thus providing easier vaporization. An on-off valve (V2) is provided in the middle of the outlet tube to isolate the pump from the reactor during purging of the reactor or reduction of the catalyst.

2.6 Gas Flow System

The gaseous feed system is designed to switch between any two gas sources. This allows the use of an inert gas like helium for pressure testing the setup for possible leaks before an experiment and then switching to hydrogen during reduction and reaction. Tubing of 1/8 in. O.D. runs from the two regulators connected to the gas cylinders to a switching valve (V1). Another 1/8 in. O.D. tubing runs from the valve (V1) to the nipple at the top of the reactor heating zone. The pressure delivered to the reactor is controlled by the cylinder regulators, and the reactor pressure is monitored using the digital readings from the pump as well as the analog readings from the regulator. The product stream then passes through switching valve (V3) to a system designed for collection of condensable product in the stream.

2.7 Reaction Product Collection

The liquid product was collected in a single ended Whitey sample cylinder (C1) (P/N - SS-4CS-TW-10) of internal volume 10 ml and made of stainless steel. A second double ended sample cylinder (C2) fitted with a stem valve for draining the collected liquid is set in the bypass route for collection of the condensable products as waste. The switching valve (V3) is designed to set the flow through either the collection or the bypass route. The liquid product recovery system is given in Figure 2.3 and the procedure for collection of the products is explained in Chapter 3. A mixture of water and ice is used as a cold trap to collect the non-volatile products in the stream. A second switching valve (V4) is set at the downstream side of the collection system to de-pressurize the collection vessel (C1) at the end of the desired collection time since the vessel is still at reaction pressure.

The pressure of the exiting gas from collection is stepped down to atmospheric pressure using a Linde step-down regulator (R1) (P/N - SG3810) before passing through a gas flow controller (F1) consisting of a Nupro metering valve (P/N - SS-4L) and a Matheson flow monitor for regulating the flow rate of the gas through the reactor. A switching valve (V5) was placed after the flow controller to direct the flow of the effluent to either a gas collection system or to the exhaust in the hood. The gas products were collected for a specific amount of time in a gas bag which is evacuated prior to collection with a GE vacuum pump (P2) by turning the switching valve (V6) placed after V5. The gas is finally vented through a soap bubble meter (M1) which measures the gas flow rate



Figure 2.3 - Liquid Product Trapping System

with reasonable accuracy. The design of the system is shown in Figure 2.1 and is explained in detail in Chapter 3.

2.8 Safety Equipment

A Fike rupture disk is provided downstream of the regulators but upstream of the reactor (Figure 2.1) to protect the system from failure of the cylinder regulator or operator error in handling equipment. The disk is designed to rupture if the inlet pressure exceeds 3200 psig, safely venting the gas into the hood. All the Swagelok and NPT fittings as well as the valves and tubing are made of stainless steel and rated for high pressures and temperatures. The whole reactor setup was constructed inside a fume hood with Plexiglass doors for safety reasons owing to the high pressures involved as also to the combustible nature of the reactant gas, hydrogen.

CHAPTER 3

EXPERIMENTAL CONDITIONS AND PROCEDURES

3.1 Introduction

This chapter enumerates the methods and procedures used for catalyst preparation, vapor phase conversion, liquid and gas product collection, reactant and product analysis and calculation of the various study parameters for dimethyl succinate conversions. Section 3.1 details the catalyst preparation and reduction process. Sections 3.2 discusses the procedure used in loading and operating the reactor. Section 3.3 discusses the techniques used in collecting and analyzing the products obtained, both liquid and gas. Section 3.4 briefly deals with the methods used in calculating the various parameters like yield and selectivity.

3.2 Catalyst Preparation :

The catalysts chosen for initial study were based on previously published or patented catalysts. Hence the procedure for preparing the catalysts for further research was built upon this original method of preparation. The supports taken up for study were silica-alumina of surface area $10 \text{ m}^2/\text{g}$ (measured by BET method) from Sigma, and two silica supports, XOA-400 and XOB-30 from Phase Separations of surface areas $400 \text{ m}^2/\text{g}$ and $31 \text{ m}^2/\text{g}$, respectively. The following describes the procedure used in preparing a catalyst.

To prepare the catalyst, 0.5 g of palladium nitrate, 8 g of copper nitrate and 1 g of 85% potassium hydroxide were added to 10 g of 16-30 mesh silica-alumina support. Approximately 10 ml of HPLC water was added to the mixture and stirred at room temperature for 2 hours to allow dissolution of the salts and to form a homogeneous mixture with the support. The mixture was then dried under vacuum of 10 in. Hg and at a temperature of 60° C - 70° C for 2 hours. The final dry mixture has the metals in the form of salts and is calcined in air in a furnace at 500° C for 11 to 12 hours. The catalyst thus formed has the metals in the form of their oxides and is reduced with hydrogen to the metal as explained in Section 3.3.

The above general method of catalyst preparation has been followed throughout the research. The various catalysts studied and their loading per gram of support are given in Table 3.1. The actual metallic loading was calculated from the weights of metallic salt taken and the support initially mixed together. The metal composition in each catalyst was calculated before calcination whereas, the loading as reported in Table 3.1, is the same

Catalyst	Catalyst	Support	Metal %	Metal Loading	
No:		$(SA - m^2/g)$		(mmol/g of support)	
			Cu - 11 %	Cu - 3.22	
A1	Cu / Pd / KOH	Si-Al (10)	Pd - 0.2 %	Pd - 0.035	
			КОН - 4 %	КОН - 1.37	
			Cu - 11%	Cu - 3.44	
A2	Cu / Pd / KOH	Si-Al (10)	Pd - 1.1 %	Pd - 0.203	
			КОН - 4 %	КОН - 1.51	
			Fe - 7.4 %	Fe - 3.22	
A3	Fe / Pd / KOH	Si -Al (10)	Pd - 0.17 %	Pd - 0.038	
			KOH -3.4 %	KOH - 1.43	
		· · · · · · · · · · · · · · · · · · ·	Fe - 7.3 %	Fe - 3.21	
A4	Fe / Pd / KOH	Si - Al (10)	Pd - 0.88 %	Pd - 0.202	
			КОН -3.3 %	KOH - 1.46	
A6	Pd	Si -Al (10)	Pd - 2.02 %	Pd - 0.201	
A7	Fe	Si -Al (10)	Fe - 7.8 %	Fe - 3.21	
A8	КОН	Si - Al (10)	KOH -7.8 %	КОН - 1.53	
A10	Cu	Si - Al (10)	Cu - 11.7 %	Cu - 3.22	
A11	Cu	XOB-30 (31)	Cu - 11.7 %	Cu - 3.25	
A12	Cu	XOA-400 (400)	Cu - 11.7 %	Cu - 3.25	

Table 3.1 - Catalysts Studied with Composition and Loading

.

before and after calcination. The various metals studied for catalytic activity were iron, copper, potassium, palladium and combinations of these. The copper catalyst was taken up for further studies since it gave the best results among the catalysts tested. The supports by themselves were also tested for possible reactions.

3.3 Catalyst Loading and Reduction in Reactor

After calcining, the catalyst, with the metals in the form of oxides, was taken up for reduction since metal oxides are known dehydrogenation catalysts. The reduction was done in the reactor itself, since this would eliminate the need for transporting the catalyst twice for each experiment. Also, the reactor was designed for in-situ reduction. The reactor tube was accessed by opening the quick connects Q1 and Q2, as shown in Figure 2.1 and moving the reactor up and clamping it at the top. The connection at the top of the reactor is then opened and the reactor is pulled down and removed. This procedure is followed since the quick connects are easy to connect and disconnect and also removing the furnace elements and the insulating fire bricks each time a new experiment has to be conducted is avoided. The catalyst material was then added through the top of the reactor and was held in place at the bottom by a glass tube fitted with a quartz frit as shown in Figure 2.2. A similar procedure was followed for unloading the catalyst after completion of an experiment. The catalyst after completion of reaction was weighed for possible weight gain and stored. The standard reduction procedure used for all catalysts involved passing pure hydrogen at a catalyst bed temperature of 200°C, pressure of 200 psig, and a gas flow rate of around 40 ml/min for about 3 hours. During the reduction process the valve V2 was kept closed to isolate the pump from the reactor. Normally, the reaction was carried out the end of the reduction time by heating the catalyst bed to the required temperature and pumping in the feed. In selected experiments, the catalyst was removed and examined after reduction but prior to exposure to succinate; the reduction process seemed complete from the fact that catalyst weight loss was observed and also catalyst color had changed to that of the metal. Catalyst density was also measured in every experiment in order to calculate the residence time.

3.4 **Operation of Reactor**

The reactor was charged with the calcined catalyst in oxide form and the subsequent reduction process has been described above. The reactor was then fed with a solution of the desired reactant in methanol as the liquid feed and hydrogen as the gaseous reactant. The two reactants studied here were dimethyl succinate (Aldrich, 98%) and γ -butyrolactone (Aldrich, 99 + %); a feed concentration of 30 weight percent reactant in methanol was used throughout. Pure methanol was also used as the feed in control experimental runs to check for side reactions. The following describes the procedure for conducting the reaction after reducing the catalyst. The symbols referred to are shown in Figure 2.1 in Chapter 2.

Each catalyst was tested under two conditions, one at constant temperature and varying pressure and the other at constant pressure and varying temperature. Fresh catalyst was loaded into the reactor for each of these experiments. In the constant temperature experiment, the catalyst bed temperature was increased to the reaction temperature by increasing the furnace temperature, as measured by the thermocouple (T1), and allowed to stabilize. The hydrogen inlet valve (V1) was then turned to allow hydrogen to be fed into the reactor and the reactor was pressurized to the desired initial value. Hydrogen flow rate was set using the flow controller (F1), and the actual flow rate was measured with the bubble meter (M1).

With the reactor heated up and pressurized to the desired conditions, the liquid feed valve (V2) was opened and the liquid feed was pumped using the BioRad HPLC pump (P1). Liquid flow rate was set with the digital tuner in the pump and monitored along with reactor pressure; this flow rate was verified by measuring the differential volume of liquid pumped from the burette over time and was typically within $\pm 5\%$ of the set point. The outlet valves (V3 and V4) were turned to allow flow of the reactant and products to the collection vessel (C2). About 2.5 to 3 ml of the reactant was pumped in to ensure that the reactor internals, tubing, and catalyst were completely wetted. Once the reactor reached steady state, the collection vessel (C1) was immersed in an ice bath and outlet valves (V3 and V4) were turned to direct flow through C1. Liquid sample was collected for a fixed amount of time, usually 60 to 70 min.

The product stream was then passed through a step-down regulator (R1) and passes through the switching value (V5) to be directed either to the exhaust in the hood or to the gas collection system. A gas sample was collected in an evacuated gas bag for a shorter time interval of about 10 min. One line from the three way valve (V6) was connected to a vacuum pump and the other end to the gas bag through a needle outlet to allow evacuation of the gas bag. The valve (V6) was then turned back to prevent any back flow of air into the bag. The valve (V5) was turned to allow flow of the gaseous products into the gas bag and turned back to resume normal flow once collection is over.

Reactant pressure was then changed to the next desired value, allowed time to stabilize and the above procedure repeated. In this way, a series of runs were done by varying pressures at a constant temperature, and a series of products were collected for analysis. The procedure was the same for the experiments conducted at constant pressure and varying temperatures.

3.5 Reactor Shutdown and Product Recovery

Procedures for collecting and analyzing liquid and gas phase samples in each run are described below.

The liquid product was collected in the collection vessel (C1) and analyzed in a Gas Chromatograph using a flame ionization detector. At the end of the steady state reaction period, the valve V3 was turned to direct effluent through C2. The valve V4 was kept turned to C1 to depressurize the vessel (C1) to atmospheric pressure. As described earlier, the pressure was stepped down from the reactor pressure to that of the atmosphere with a step down pressure regulator (R1). The regulator is capable of delivering a maximum pressure of 20 psig, which eliminates any possibility of high pressure at the vent

side of the reactor system. The bubble meter was monitored until the flow dropped to zero, which confirmed that the pressure in the vessel C1 had dropped to atmospheric. The valve V4 was then turned to C2 and the ice trap removed from C1. Liquid sample volume was measured in a graduated cylinder, the sample was examined for any color changes, and stored in a labeled vial for analysis. The gas product was collected in a gas bag and analyzed in a Gas Chromatograph with a thermal conductivity detector.

3.6 **Reaction Product Analysis**

3.6.1 **Product Identification**

The reaction products in the initial reactions were identified using Gas Chromatograph Mass Spectrometry (GC-MS). All GC-MS data were generated by a LKB Bromma 2091 Mass Spectrometer located in the Michigan State University Mass Spectrometry Facility. The spectrometer is attached to a Shimadzu Model GC-9A Gas Chromatograph fitted with a SPB-5 capillary column. The temperature program, and flow rates of the gases used for a typical GC-MS run is given in Appendix A. The sample contained several unkowns reaction products and the internal standard, methyl lactate, described in the next section. The various compounds in the sample collected were identified by matching the mass spectra and retention time of each compound with reference spectra collected by analyzing a standard sample. The database in the GC-MS facility enabled easy comparison, and a near-perfect match was made for almost all compounds. A typical GC and MS spectra results for a sample product are given in Figure 3.1-A to Figure 3.1-E





















3.6.2 Liquid Products

Liquid products were analyzed in a Varian (Model 3300) Gas Chromatograph (GC) equipped with a Flame Ionization Detector (FID). The detector oven and injector were kept at constant temperatures of 290°C and 250°C, respectively, and helium was used as the carrier gas. The column used for liquid analysis was a Supelco fused silica capillary column (SPB-1) of 0.53 mm ID. The output signal generated from the GC was collected using a Perkin Elmer Single Channel Interface and the data were analyzed using Omega-2 software from Perkin Elmer. The column gave excellent separation, based on boiling points, of the different compounds in an injected sample with the lower boiling compounds coming out first. The temperature program for the column was developed via a trial and error method to obtain maximum separation of the peaks in the product distribution. A typical Gas Chromatograph is shown in Figure 3.1-A.

To determine species concentrations in liquid samples, the GC was initially run with a series of standard samples of known concentrations to determine response factors. Methyl lactate was used as an internal standard in these calibrations since its retention time does not interfere with that of the expected products. The response factor of methyl lactate was assumed to be one; using its area and concentration, the response factors of the various compounds in the standard were calculated. Values of retention times and response factors of the more commonly observed compounds are given in Table 3.2. The method for calculating these values, the actual product concentrations and the conditions under which the GC was run are given in Appendix A.

Compound	Retention Time	Response Factor	
	(min)		
Methanol	2.4	2.159	
1-Propanol	2.8	0.371	
iso-Propanol	3.4	0.42	
Tetrahydrofuran	4.4	0.378	
1-Butanol	5.1	0.328	
Methyl butyrate	6.4	0.436	
Methyl Lactate (Internal Standard)	6.7	1	
1-Hexanol	11.4	0.291	
γ-Butyrolactone	12.1	0.539	
1,4-Butanediol	14.5	0.772	
1-Heptanol	15.2	0.276	
Dimethyl succinate	17.1	0.708	

Table 3.2 - List of Retention Times and Response Factors

3.6.3 Gas Products

Gas products were analyzed using a Thermal Conductivity Detector (TCD) in the same Varian 3300 GC described above. The TCD oven was kept at 210° C and the injector at 250° C. Helium was used as the carrier gas. The column used for gas analysis was a 80/100 carbosieve SII Supelco column of 1/8 in. O.D. and 5 ft length. The gas separation in the packed column is based on the molecular size of the gases and are detected based on their thermal conductivity. A gas standard consisting of 4.93% CO, 5.02% CO₂, 5.06% methane was run each time before the sample and used to calculate concentrations of the these species. The temperature program for a standard GC run in the TCD is given in Appendix A. 46

3.7 Product Yield and Selectivity Calculations

Products identified initially by GC-MS and quantitatively analyzed using GC (Section 3.6) were reported in terms of yields and selectivities on a molar basis. The percentage conversion of reactant is given by

$$Conversion (\%) = \frac{Moles of reactant in feed - Moles of reactant in product}{Moles of reactant in feed} X 100$$

A spreadsheet in MS-Excel 5.0 was developed to calculate product yields from liquid concentrations in grams per liter obtained from the GC runs. Reactant concentration of the feed and the product formed were converted to the number of moles on a basis of one hour. The percentage yield of a product based on feed was then calculated by the relation,

Yield of product A (%) =
$$\frac{\text{Moles of A in product}}{\text{Moles of reactant in feed}} \times 100$$

A typical spreadsheet result is reproduced in Table 3.3, for the sample analyzed in the GC-MS, and the results of all the experiments conducted are reproduced in Appendix B and the some of the parameters calculated are explained in Appendix A.

	Catalyst	A11				
REPORT	R51.1	R51.2	R51.3			
Experiment Date	1/17/96	1/17/96	1/17/96			
Entry Date	4/13/96	4/13/96	4/13/96			
	700.00					
P (psig)	700.00	270.00	370.00			
	270.00	270.00	10.00			
$R_1(S)$	0.40	12 02	6.20			
	-0.77	13.82	0.20			
Conv(BOF)	90.12	97.70	90.07	<u> </u>		
	89.30	111.70	104.87			
H2 : DMS (molar)	202.26	202.73	200.23			
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00			
Iso-Propanol	0.00	0.00	0.00			
THF	9.71	7.87	13.81			
1-Butanol	2.38	2.50	6.87			
Methyl Butyrate	0.00	0.00	0.00			
4-Methyl,1-Pentanol	0.00	0.00	0.00			
1-Hexanol	0.00	0.00	0.00			
GBL	37.55	32.86	26.91			
1,4-Butanediol	39.15	67.63	56.31			
1-Heptanol	0.56	0.84	0.97			
Others	0.00	0.00	0.00			
Selectivity(79)	0.00	0.00	0.00			
leo-Propanol	0.00	0.00	0.00			
	10.00	7.05	13 17			
1-Rutenol	2 66	2.24	13.17			
Methyl Butyrata	2.00	2.24	0.55			
A_Methyl 1_Dentanol	0.00	0.00	0.00			
1_Hevenol	0.00	0.00	0.00			
GRI	12 02	20.00	25 66			
1 4 Butanediol	43.82	20.42 60.55	53 70			
1-Hentanol	0.02	0.35	0 02			
Intervation	0.03	0.75	0.92			

Table 3.3 Sample Experimental Report

Chapter 4

RESULTS AND DISCUSSION OF VAPOR PHASE EXPERIMENTS

This chapter presents the studies of dimethyl succinate conversion in the vapor phase over various catalyst materials. Section 4.1 enumerates the preliminary experiments that were done to test the reactor equipment discussed in Chapter 2. Section 4.2 details the series of experiments that were conducted in the vapor phase to study the effect of different catalyst materials, temperature, and pressure on the hydrogenation of dimethyl succinate. Results of these experiments are presented in Section 4.3 in terms of product yields and selectivity. Section 4.4 discusses the effect of various parameters in the hydrogenation process, gives the best results obtained in the above series of reaction studies, and describes improvements the current study has made over the existing processes in terms of yields and selectivity.

4.1 **Preliminary Studies and Reaction Conditions**

A set of preliminary experiments were conducted to test the performance of the vapor phase reactor constructed for this study. These experiments helped to further refine the reactor setup before the actual study was done. They also helped to define reaction conditions favorable for vaporizing dimethyl succinate at the desired operating pressures. The preliminary reactions also tested the collection methods for liquid and gases in the product streams, allowed identification of the products via GC and mass spectrometry, and determine their retention times and response factors.

4.1.1 Preliminary Experiments

A set of runs were conducted to test the reactor and ancillary equipment such as the HPLC pump, the regulators and controllers. These experiments were not successful as far as product formation was concerned but gave valuable insight into the operation of the reactor and the operating conditions. These are not taken into account when discussing the results of vapor phase reactions. Some early experiments were conducted with an Eldex pump which failed to deliver a steady flow at high pressures, and hence the experiment had to be terminated whenever the pump stopped. This problem was resolved with replacement of the Eldex pump with a more efficient Bio-Rad (Model 125-1350) HPLC pump. A list of these experiments and results are given in Appendix B. A set of blank runs testing the catalyst supports for possible side reactions with dimethyl succinate were also conducted. The results are discussed in Section 4.3.2.

4.1.2 Reaction Conditions

. .

The reaction studies involved primarily dimethyl succinate as the feed with methanol as the solvent. Dimethyl succinate was chosen to be used as the actual feed in the reactions since succinic acid is a solid at room temperature with no volatility, very low solubility in water and with a melting point of 190° C. Other feeds tested for reduction with hydrogen over catalysts were γ -butyrolactone in methanol and pure methanol by itself.

The reaction conditions for the vapor phase system were set by both experimental considerations and the properties of dimethyl succinate and methanol. Previous work in the literature was also examined to identify the optimum operating conditions. The lower and upper temperature limits were the most important operating parameters to be set. The other reaction parameters included the reactant concentration, dimethyl succinate and hydrogen flow rate, amount of catalyst material needed, and liquid and gas product collection times. The catalyst, as prepared, was in the form of metal oxides and needed to be reduced to the metal as well. The reduction procedure was standardized so as to be uniform throughout the study and was explained in Chapter 3.

The lowest temperature at which the reaction could be conducted was limited by the boiling point of dimethyl succinate. The normal boiling point of dimethyl succinate is 200°C and this temperature varies with the operating pressure. Hence 250°C was set as the lower temperature limit for dimethyl succinate reactions. Preliminary experiments showed that dimethyl succinate did not degrade at temperatures as high as 350°C, thus the upper limit was set only by kinetic constraints.

50

The reaction under study was hydrogenation and hence the operating pressures had to be reasonable high. Previous work (42) showed hydrogenation of dimethyl succinate to be practical only above pressures of 400 psig, which was thus used as the minimum operating pressure. The upper pressure was limited by the Fike rupture disk in the experimental system set to rupture at 3200 psig.

A reactant concentration of 30% - 40% dimethyl succinate by weight in methanol was used as the liquid feed in the reactions. The relatively low concentration was to ensure the vaporization of the feed even at high reactant pressures. The liquid and hydrogen feed rates were fixed after a set of preliminary experiments. The experiments were initially conducted at an average liquid flow rate of 0.1 ml/min and hydrogen flow rate of 50 ml/min. At these rates, analysis of the product showed hardly any conversion and calculations showed that the molar ratio of hydrogen to dimethyl succinate was only 8:1 with 40% dimethyl succinate in methanol. Since excess hydrogen is required to push the reaction to completion a 200:1 molar ratio of hydrogen to dimethyl succinate was fixed for all subsequent experiments. This was accomplished with a liquid flow rate of 0.05 ml/min and a hydrogen flow rate of 400 ml/min with 30% dimethyl succinate in methanol.

The amount of catalyst material used in each experiment depended upon the support used. The weight of the catalyst taken, and hence the height of the catalyst bed, along with the reactor dimensions, reaction conditions, and reactant flow rates were used to calculate the residence times. The residence time was allowed to vary only with operating pressures, ensuring that the weight hourly space velocity (WHSV) in the reactor was a constant. Three materials were studied as catalyst supports as explained in Chapter

51

2, and of the three XOA-400 and XOB-30 had almost the same density and low surface area Si-Al support had a lower density. Thus, 3.5 g of catalyst material supported on Si-Al and 1.0 g of catalyst supported on XOA-400 or XOB-30 resulted in similar residence time. The residence time and the WHSV calculations are shown in the Appendix A.

The liquid and product collection times were fixed according to the flow rates of the feed and hydrogen. At liquid feed and hydrogen flow rates of 0.05 ml/min and 400 ml/min respectively, the liquid product was collected for 1 hour and the gas product for about 10 min. This gave adequate quantity of the products for analysis.

4.2 **Results of Vapor Phase Experiments**

4.2.1 Summary of Experiments

A series of experiments were carried out in the vapor phase reactor to study the catalytic hydrogenation of dimethyl succinate with hydrogen. Two kinds of experiments were conducted with each catalyst, one in which the temperature was varied and the other in which the pressure was varied. In several experiments, γ -butyrolactone was used as feed in the place of dimethyl succinate. The standard reactant concentrations and flow rates were explained in Section 4.1.1 and are summarized in Table 4.1. The set of materials used as hydrogenation catalysts for dimethyl succinate are listed in Table 3.1. The experiments were conducted with the goal of maximizing the conversion of dimethyl succinate as well as the yield and selectivity to 1,4-butanediol. The by-products included γ -butyrolactone, tetrahydrofuran, and 1-butanol.

Table 4.1 - Reaction Conditions

Experimental conditions :					
		Dimethyl succinate : 0.47%			
Feed molar composition (vapor phase)		Methanol: 5.03%			
		Hydrogen: 94.49%			
Hydrogen : dimethyl succinate (molar)		200 : 1			
Dimethyl succinate concentration		~255 g/l in methanol			
Liquid flow rate		0.05 ml/min			
Gas flow rate		400 ml/min			
Product collection times					
Liquid	=	60 mins			
Gas	=	10 mins			
Catalyst :					
Supports	=	Si-Al, XOA-400, XOB-30			
Weight of catalyst					
with Si-Al support		3.5 g			
with XOA-400, XOB-30		1.0 g			
Reduction conditions					
Catalyst bed temperature		200°C			
Pressure	=	200 psig			
Hydrogen flow rate		40 ml/min			

4.2.2 Summary of Results

The results of these experiments are given in terms of four main products that were observed in all the runs viz. 1,4-butanediol, y-butyrolactone, tetrahydrofuran, and 1butanol. The effect of different catalyst materials on conversion of dimethyl succinate are presented in Figures 4.1 - 4.2. These also illustrate the effect of variation in pressure and temperature on the conversion. Variation in 1,4-butanediol and y-butyrolactone yields with pressure and temperature over all the catalyst materials tested except copper are shown in Figures 4.3 - 4.6. The yield of both products dropped with increase in temperature beyond an optimum point. The yields of 1,4-butanediol and γ -butyrolactone obtained over copper catalyst on the three supports tested (silica-alumina, XOA-400, and XOB-30) are shown in Figures 4.11 - 4.14. Copper on XOB-30 gave the highest yield of 1,4-butanediol and γ butyrolactone, combined. The effect of pressure and temperature on yields of 1-butanol and tetrahydrofuran are given in Figures 4.7 - 4.10 for all the catalysts tested. Both products were formed in significant yields at high temperatures, especially over 300°C and showed little changes in yield with increase in pressure.

 γ -Butyrolactone in methanol was used as reactant in place of dimethyl succinate in several experiments and 1,4-butanediol yields obtained over the catalysts tested are shown in Figure 4.15. Methanol was also used as the feed to test for possible side reactions and the results are given in Run #37 in Appendix B; no products were formed except for small quantities of propanol.

4.3 Discussion of Results

Most of the reaction parameters, like the flow rates of the feed, the molar ratio of hydrogen to dimethyl succinate, and the space hourly velocity of the feed in the catalyst bed were kept constant. Thus the conversion of dimethyl succinate and the product distribution were dependent only on the catalyst material used, catalyst support in the case of copper, and operating temperature and pressure. The following sections discuss the effect of these factors. Composition of the various catalysts referred to in the following sections and their metal loading per gram of support are given in Table 3.1 in Chapter 3.

4.3.1 Catalyst material

The first set of experiments were conducted over a catalyst comprising copper, palladium, and potassium hydroxide supported on silica-alumina (A1). A catalyst of the same composition was reported in the literature (38) in the hydrogenation of γ -butyrolactone to 1,4-butanediol. A conversion of 90% of γ -butyrolactone with 95% selectivity to 1,4-butanediol was also claimed. Hence a similar catalyst was used in an effort to duplicate the results with dimethyl succinate as the reactant. A maximum dimethyl succinate conversion of 97% at 600 psig and 360°C was obtained. But 1,4-butanediol yields were significantly low with a maximum of only 13% at 330°C and 1000 psig, as shown in Figure 4.3. An increase in loading of palladium in the catalyst (A2) led to lower conversions of dimethyl succinate and increased yield of 1,4-butanediol. A maximum yield of 28% 1,4-butanediol at 330°C and 1300 psig was obtained. γ -Butyrolactone and 1-butanol were the other products formed in significant yields as shown in Figures 4.5 - 4.8.

In the next set of experiments, a catalyst comprising iron, palladium, and potassium hydroxide supported on silica-alumina (A3) was used in hydrogenation of dimethyl succinate. Complete conversion of dimethyl succinate was achieved with very little toward 1,4-butanediol and γ -butyrolactone. 1-Butanol was formed in significant yields with a maximum of 38% at 320°C and 1000 psig. An increase in the palladium loading in the next batch of catalyst (A4) did not affect the conversion of dimethyl succinate. 1,4-Butanediol yields were still low, with a maximum yield of 6% at 330°C and 600 psig. γ -Butyrolactone yields were higher as shown in Figure 4.6 with a maximum of 52% at 290°C and 600 psig. 1-Butanol and tetrahydrofuran yields were not affected by the increase in loading of palladium.

Iron, palladium, and copper supported on silica-alumina were tested individually as catalysts in the hydrogenation of dimethyl succinate. The conversion of dimethyl succinate over iron (A7) increased at higher temperatures with a maximum of 91% at 320° C and 1000 psig. While no 1,4-butanediol was formed, γ -butyrolactone and 1-butanol were the two main products with a maximum yield of 48% and 21%, respectively at 320° C and 1000 psig. Thus iron was not a good catalyst for the production of 1,4-butanediol even though it reduced dimethyl succinate to γ -butyrolactone, a possible intermediate toward formation of 1,4-butanediol, since the lactone was further reduced to 1-butanol.

The use of palladium (A6) as reduction catalyst resulted in lower conversion of dimethyl succinate (Figures 4.1 - 4.2). A maximum conversion of 69%, with 24% yield of γ -butyrolactone and 14% yield of tetrahydrofuran, was obtained at 330°C and 600 psig. Several other products were observed when palladium as well as a mixture of metals containing palladium were used as catalyst. These include methyl butyrate, 1-propanol, iso-propanol, hexanol, and heptanol. One interesting result was the formation of methyl butyrate in significant yields over palladium supported on Si - Al as shown in Run #41 - 42 in Appendix B.

When copper (A10) was used as hydrogenation catalyst, very high conversion of dimethyl succinate was achieved, with complete conversion at 330° C and 600 psig (Figure 4.2). A significant increase in yield of 1,4-butanediol was obtained with a maximum of 66% at 270° C and 1000 psig (Figure 4.11). γ -Butyrolactone yields were lower at the same
conditions (Figure 4.13). The formation of 1-butanol and tetrahydrofuran were inhibited at low temperatures over copper catalyst (Runs #47 - #48). No other by-products were formed in noticeable yields and, except for heptanol, were not observed over copper catalysts.

To summarize, addition of palladium to copper resulted in lower conversion of dimethyl succinate. Copper catalyst showed the maximum activity with respect to formation of 1,4-butanediol and γ -butyrolactone, followed by the mixture of copper with palladium. The yield of 1,4-butanediol over copper was further increased at lower temperatures with increase in pressure. These are discussed in subsequent sections.

4.3.2 Catalyst Supports

Since copper showed the maximum yields with respect to 1,4-butanediol, the effect of support on its activity was studied. The support used in the first set of experiments (Figures 4.1 - 4.10) was silica-alumina manufactured by Johnson Mathey. The experiments conducted showed significant formation of 1,4-butanediol and γ -butyrolactone only over copper as a catalyst material. Hence, copper was tested over two silica supports, XOA -400 of surface area 400 m²/g and XOB - 30 of surface area 31 m²/g. The supports by themselves were initially used as hydrogenation catalyst for possible side reactions and showed little conversion of dimethyl succinate (Figure 4.1 - 4.2).

The conversion of dimethyl succinate did not change significantly with the change in support except at lower temperatures and pressures, where copper on XOA - 400 showed lower conversions. The conversion of dimethyl succinate as well as the formation

57

of 1,4-butanediol and γ -butyrolactone were definitely favored by low surface area supports. Copper on XOB - 30 proved to be the best catalyst among those tested with almost 100% conversion of dimethyl succinate, and a maximum yield of 89% 1,4butanediol at a temperature of 270°C and 1200 psig pressure (Figure 4.12).

An interesting result obtained in the study of copper catalyst over various supports was the high yield of tetrahydrofuran obtained over copper on XOA-400 support. A maximum yield of tetrahydrofuran of 73% with 88% selectivity was obtained over copper on XOA-400 (A12) at 310°C and 600 psig (Run #52 in Appendix B). Thus the major concern of formation of tetrahydrofuran as by-product in the hydrogenation of dimethyl succinate can easily be dealt with by lowering the surface areas of the supports used, since low surface areas showed less proclivity toward formation of tetrahydrofuran.

To summarize, low surface area supports for copper favored selective hydrogenation of dimethyl succinate to 1,4-butanediol. XOB - 30 showed slightly better yields and significant selectivity towards 1,4-butanediol than silica-alumina. Use of high surface area supports resulted primarily in the reduction of dimethyl succinate to tetrahydrofuran.

4.3.3 Temperature

The conversion of dimethyl succinate always increased with an increase in temperature (Figure 4.2). A conversion of 90% or higher was obtained at temperatures above 310°C over all the catalysts used. 1,4-Butanediol formation was severely affected with increase in temperature especially for copper catalysts. A significant drop in the yield

of 1,4-butanediol was observed at temperatures above 270° C over copper on the various supports, falling from 89% at 270° C to 70% at 290° C in the case of A11. Hence high yields of 1,4-butanediol were not obtained over catalyst A1 and A2, even though they contained copper in same loading as A11, since the experiments were conducted at 330° C. The formation of γ -butyrolactone was also dictated by temperature considerations with the yield increasing with increasing temperature. But again similar to 1,4-butanediol, yields of γ -butyrolactone showed a drop beyond certain temperatures, the actual temperature depending on the catalyst. In the case of copper the yields dropped beyond 290° C - 300° C; in other cases the temperature limit was slightly higher at 320° C - 330° C.

The drop in the yield of 1,4-butanediol and γ -butyrolactone can be explained by the increase in yields of other byproducts, especially tetrahydrofuran and 1-butanol, suggesting that they are further reduced. Tetrahydrofuran and 1-butanol showed an increase in yield with an increase in temperature for almost all the catalyst materials tested (Figures 4.8 and 4.10). As mentioned earlier significant yields of tetrahydrofuran were observed at temperatures above 300°C in the case of copper on high surface area silica support.

In summary, an increase in temperature beyond a certain limit produced a significant loss in the production of 1,4-butanediol and γ -butyrolactone. Increase in temperature also increased conversion of dimethyl succinate, and the production of tetrahydrofuran and 1-butanol. Thus the results of the set of experiments conducted by varying the temperature gave an optimum temperature for the production of 1,4-butanediol at 270°C over copper catalyst and an optimum of 290°C to 320°C for the

production of γ -butyrolactone over any of the catalyst tested. Almost 100% conversion of dimethyl succinate was achieved at these temperatures.

4.3.4 Pressure

The conversion of dimethyl succinate was found to be more dependent on temperature than on the operating pressure, and showed no significant increase with pressure except when pure metals were used as catalysts (Figure 4.1). High pressure favored the conversion of dimethyl succinate to 1.4-butanediol which agreed with literature. An optimum pressure for the maximum yield of 1,4-butanediol was not apparent within the pressure limits tested but a maximum yield of 89% was obtained at 270°C and 1200 psig, the highest pressure tested over copper on XOB - 30 catalyst. The yield of γ butyrolactone decreased with increase in pressure. Previous work (39, 40) postulated that γ -butyrolactone is an intermediate in the hydrogenation of dimethyl succinate to 1,4butanediol. It is clear that γ -butyrolactone is further reduced to 1,4-butanediol as the pressure is increased. A look at the trend in the yields of 1,4-butanediol and γ butyrolactone over catalyst A2 in Figures 4.3 and 4.5, respectively shows the decline in the yield of y-butyrolactone as the pressure is increased at 320°C and the corresponding increase in the yield of 1,4-butanediol. The yields of tetrahydrofuran and 1-butanol are not affected significantly by and increase in pressure except at high temperatures when there is a slight increase in the yields.

The formation of γ -butyrolactone as an intermediate in the hydrogenation of dimethyl succinate to 1,4-butanediol prompted the use of the compound by itself as the

feed. The catalysts used were A3, A11, and A12 and the results are given in Figure 4.15. The iron catalyst (A3) produced no 1,4-butanediol but a significant amount of butanol. The copper catalysts were tested at 270° C and gave a high yield of 1,4-butanediol even over the high surface area support, XOA - 400. An increase in yield of 1,4-butanediol with pressure was observed with a maximum yield of 84% with 92% selectivity over copper on XOB - 30 at 270° C and 1100 psig.

4.4 Carbon Balance

One of the factors taken into consideration in the quantitative analysis of the reaction products was the carbon balance, reported as error (%C) in the results in Appendix B. It is the amount of carbon recovered in the products out of the total amount of carbon fed to the reactor in a fixed amount of time. Thus a carbon error of 0% would indicate a total recovery of feed in the product distribution. A look at results of all the experiments given in Appendix B shows a carbon error in the range of $\pm 20\%$ with better carbon recovery over copper catalysts where the error is $\pm 15\%$ This suggests that there is very little coke formation when dimethyl succinate is fed over the catalysts even at high temperatures. It is also verified by the fact that very little weight gain of the catalyst was observed at the end of each experiment.

4.5 Conclusions

Thus the series of experiments had shown the effect of some the more important parameters in the reduction of dimethyl succinate to 1,4-butanediol and γ -butyrolactone. Copper catalyst on low surface area support was identified among those studied to give high yields of 1,4-butanediol and γ -butyrolactone. An optimum temperature and pressure was also noted for maximizing the yield of 1,4-butanediol. The overall success of the current study and the improvements made over the existing processes are explained in Chapter 5, as well as the future work that needs to be done on this project.



Figure 4.1 - Effect of Pressure on DMS Conversion over Catalysts Supported on Si-Al (T = 320 C)

























































CHAPTER 5

SUMMARY AND RECOMMENDATIONS

This chapter summarizes the results obtained in this research project and outlines further work that could be done. Section 5.1 discusses some of the more important results achieved in this study and highlights the improvements made over existing processes for the production of 1,4-butanediol. Section 5.2 sets forth the direction in which the current study could proceed to further understand the role of copper as a catalyst material in the production of 1,4-butanediol from dimethyl succinate.

5.1 Summary of Results

The hydrogenation of dimethyl succinate was performed in a fixed bed, continuous flow reactor. A 30% - 40% solution of dimethyl succinate in methanol was used as the liquid feed along with hydrogen as the gaseous reactant with a hydrogen to succinate molar ratio of 200. Several catalyst materials were studied including copper, iron, and palladium; silica-alumina of surface area 10 m²/g, and silicas of surface area 30 m²/g (XOB-30) and 400 m²/g (XOA-400) were used as catalyst supporting materials. The three primary hydrogenation products observed were γ -butyrolactone, tetrahydrofuran, and 1,4-butanediol. Further reduction products included 1-butanol, 1-propanol, methyl butyrate, and iso-propanol. Product distribution depends on reaction conditions and catalyst material.

Conversion of dimethyl succinate was almost complete above 300° C over all studied catalysts with pressure having negligible effect on the conversion. Iron and palladium were shown to be poor catalyst materials for formation of 1,4-butanediol from dimethyl succinate, but iron was effective in the formation of γ -butyrolactone. Copper on XOB-30 gave the best yield of 91% 1,4-butanediol from dimethyl succinate with 83% selectivity at 1200 psig and 250°C. Conversion of dimethyl succinate in that case was 97%. The yield of 1,4-butanediol went down to less than 30% with high surface area silica support, XOA-400. The significant result was that 1,4-butanediol production increased with higher pressure, thus opening the possibility of further improving the yields. γ -Butyrolactone formation followed a trend similar to 1,4-butanediol. It is clearly shown in the current study that γ -butyrolactone is an intermediate in the reduction of dimethyl succinate to 1,4-butanediol.

A surprising result obtained was the significant yield of tetrahydrofuran over high surface area silica support, XOA-400. A maximum yield of 73% tetrahydrofuran with 88% selectivity was obtained at 600 psig and 310°C. The formation of tetrahydrofuran increased strongly with temperature, and higher yields should be obtainable above 310°C.

5.2 Improvements Over Existing Processes

The current study made several significant improvements over the existing processes for the production of 1,4-butanediol. Turner *et. al* (34) claimed a process in which 65% yield of 1,4-butanediol was reported with 97% conversion of succinic anhydride over a catalyst of unsupported ruthenium and phosphine. Thomas *et. al.* (37) report a 1,4-butanediol yield of 79% from hydrogenation of dimethyl succinate over cobalt-tin catalyst. Copper chromite was claimed to give best conversion of dimethyl succinate to 1,4-butanediol (31, 32); however, it was shown in this study that dimethyl succinate could be selectively converted to 1,4-butanediol in higher yields than achieved in any other process reported with a simple copper catalyst; it was also shown that tetrahydrofuran could be formed in high selectivity on a high surface area silica support.

5.3 Recommendations

The surface area of the catalyst material before and after calcination, as well as after reduction in the reactor, needs to be studied to see changes that may affect product formation. The well known BET method could be used for finding the surface area. The effect of surface area of the support itself in product distribution needs to be further understood, especially in the reduction of dimethyl succinate to tetrahydrofuran at high surface area. Tetrahydrofuran is a commodity chemical that finds increasing uses in the pharmaceutical and polymer industries and hence the selective production of this chemical shown in our lab needs to be further explored. The role of metallic copper loading on the supported catalyst needs also to be investigated. The results discussed above were obtained over a catalyst with a copper loading of 3.4 mmol/g of support. Hence a typical study could include lower copper loadings of 1.2, 0.5 and 0.25 mmol/g of support. Several operating parameters like hydrogen to dimethyl succinate molar ratio in the feed and residence time of vapor phase reactants in the catalyst bed were not systematically varied in this study to observe thier effects on product distribution. Preliminary studies had shown that a excess hydrogen to dimethyl succinate ratio lead to increased conversion. Dimethyl succinate was also the only ester of succinic acid that was studied. Hence a set of experiments could be designed in which the above parameters were varied and their effects in production of 1,4-butanediol and γ -butyrolactone observed.

APPENDICES

APPENDIX A

Appendix A - Calculation of Common Parameters

(1) To find the concentration of an unknown compound using the Internal Standard method :

$$C_i (g/ml) = \frac{(Area)_i}{(Area)_{is}} * C_{is} * (RF)_i$$

where,

- C i = concentration of compound 'i'
- C_{IS} = concentration of internal standard
- $(Area)_i = peak area of compound 'i' in a GC output$

 $(Area)_{IS} = peak of internal standard in GC output$

(2) To find the carbon error :

Carbon Error (%) = $\frac{\sum (Moles of compounds in product) - \sum (Moles of compounds in feed)}{\sum (Moles of compounds in feed)}$

(3) To find the residence time :

Residence Time (s) = $\pi(\mathbf{R}_{\circ})^2 \mathbf{L} - \left[\frac{\mathbf{M}_{\circ}}{\rho_{\circ}}\right] \left[\frac{60}{\mathbf{V}_{\circ}}\right]$

where,

R_o = Radius of reactor tube (cm)

L = Length of catalyst bed (cm)

- $M_c = Mass of catalyst (g)$
- $\rho_{\rm c}$ = Density of catalyst (g/ml)
- V_c = Total vapor flow in reactor (ml/min)

			GC	2
Temperature	··· •·	GC-MS	FID	TCD
Ramp - I	Temperature (°C)	50	40	50
	Hold time (min)	0	0	1
	Rate (°C/min)	5	4	15
Ramp - II	Temperature (°C)	175	160	200
	Hold time (min)	0	0	4
	Rate (°C/min)	15	12	-
Ramp - III	Temperature (°C)	200	200	-
	Hold time (min)	3	2	-
	Rate (°C/min)	-	-	-
Flow Rates	Hydrogen	30 ml/min	30 ml/min	-
	Helium	30 ml/min	30 ml/min	30 ml/min
	Air	300 ml/min	300 ml/min	-

APPENDIX B

Runs	Date	Catalvst	Feed	Conditions	kesults from GC analysis	Comments
# 1-9	till 4/27/95	Si-Al support, etc.	DMS, GBL in MeOH	Press <= 400 psig Temp <= 320C	N/A	Since the GC was hooked up to the plotter, integration is not reliable. Also all the expts were repeated later w/ integrator connected to GC
#10	4/27/95	Cu / Pd / KOH on Si-Al dust	35 wt% DMS in MeOH	Press - 400 psig 10.1 - 280C 10.2 - 310C	GBL, THF formed	Since support was high SA, THF was formed. The expt. was repeated later with XOA-400
#11	5/26/95	XOA - 400 alone	40 wt% DMS in MeOH	Press - 350 psig Temp - 300C	No product formation	Same expt. was repeated in Run #50 under better conditions
# 12	6/1/95	Cu - 5.2, Pd-0.3, KOH - 2.77	40 wt% DMS in MeOH	Press -600 psig 12.1 - 290C 12.2 - 315C	12.1, 12.2 - GBL formed	12.2 - very low product recovery. Expt. was repeated later under same conditions in Run #30-31
# 18	7/6/95	KOH in XOA-400 - 4 mmol /g	40 wt% DMS in MeOH	Temp - 310C 18.1 - 500 psig 18.2 - 600 psig	18.1, 18.2 No GC run	Poor carbon balance due to low product recovery. The expts were repeated in Run #45
# 19	7/7/95	Fe (4 mmol/g) on XOA - 400	40 wt% DMS in MeOH	Press - 500 psig Temp - 300C	Product not run thru GC	No product formation for no known reason. Again experiment repeated in Run #39 on Si-Al support.
# 20	7/10/95	Fe(1.25) / Pd(0.52) / KOH(0.96) on XOA-400	40 wt% DMS in MeOH	Press - 500 psig Temp - 300C	Product not run thru GC	Less than 1 ml of product collected from 7 ml of feed, again for no reason. The expt. was later repeated in Run #32 on Si Al support

Table B.1 - Preliminary Experiments

84

Table B.2 - Run # 13 report

FEED = GBL	Catalyst	Cu (5.2) / P	Pd (0.3) / KOH (2.7) on XOA-400
REPORT	R13.1	R13.2	T
Experiment Date	6/4/95	6/4/95	
Entry Date	4/9/96	4/9/96	
P (psig)	600.00	600.00	
T(C)	290.00	310.00	
RT(s)	45.61	39.86	
Err(%C)	1.34	2.20	
Conv(BOF)	30.96	20.03	
Conv(adj)	32.30	22.23	
H2 : DMS (molar)	3.63	3.73	
Yield BOF(%)			+
1-Propanol	0.00	0.00	
Iso-Propanol	0.00	0.00	
THF	0.33	0.72	
1-Butanol	1.10	3.13	
Methyl Butyrate	1.71	8.11	
4-Methyl,1-Pentanol	0.00	0.00	
1-Hexanol	0.00	0.00	
DMS	11.57	1.14	
1,4-Butanediol	11.46	5.39	
1-Heptanol	0.58	0.67	
Others	5.55	3.06	
Selectivity(%)	-		
1-Propanol	0.00	0.00	
Iso-Propanol	0.00	0.00	
THF	1.23	3.76	
1-Butanol	4.11	16.34	
Methyl Butyrate	6.39	42.33	
4-Methyl,1-Pentanol	0.00	0.00	
1-Hexanol	0.00	0.00	
DMS	43.25	5.95	
1,4-Butanediol	42.84	28.13	
1-Heptanol	2.17	3.50	

 Table B.3
 Run # 14 Report

.

•

	Catalyst	Cu (5.2) / Pd (0.3) / KOH (2.7) on XOA-400		
REPORT	R14.1	R14.2	R14.3	
Experiment Date	6/7/95	6/7/95	6/7/95	
Entry Date	4/9/96	4/9/96	4/9/96	
P (psig)	600.00	600.00	750.00	
T(C)	295.00	320.00	320.00	
RT(s)	47.12	42.96	54.57	
Err(%C)	-4.86	6.71	15.12	
Conv(BOF)	60.06	69.38	85.85	
Conv(adj)	55.19	76.10	100.97	
H2 : DMS (molar)	7.79	5.72	5.91	
Yield BOF(%)				
1-Prop anol	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	
THF	0.44	0.72	0.89	
1-Butanol	1.02	2.82	6.60	
Methyl Butyrate	1.83	3.59	4.06	
4-Methyl,1-Pentanol	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	
GBL	40.60	57.40	64.08	
1,4-Butanediol	9.06	9.09	24.49	
1-Heptanol	0.42	0.53	0.85	
Others	1.82	1.94	0.00	
Selectivity(%)				
1-Propanol	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	
THF	0.82	0.97	0.88	
1-Butanol	1.91	3.80	6.54	
Methyl Butyrate	3.43	4.84	4.02	
4-Methyl,1-Pentanol	0.00	0.00	0.00	
1-Hex anol	0.00	0.00	0.00	
GBL	76.07	77.41	63.46	
1,4-Butanediol	16.98	12.26	24.25	
1-Heptanol	0.79	0.71	0.84	

 Table B.4 Run # 15 report

<u>,</u>	Catalyst	XOA-400 su	pport
REPORT	R15.1	R15.2	
Experiment Date	6/9/95	6/9/95	
Entry Date	4/9/96	4/9/96	
P (psig)	600.00	600.00	
T(C)	300.00	320.00	
RT(s)	22.93	14.45	
Err(%C)	-2.75	3.53	
Conv(BOF)	10.00	4.29	
Conv(adj)	7.25	7.82	
H2 : DMS (molar)	9.13	6.12	
Yield BOF(%)			
1-Propanol	0.00	0.00	
Iso-Propanol	0.00	0.00	
THF	0.00	0.00	
1-Butanoi	0.00	0.00	
Methyl Butyrate	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	
1-Hexanol	0.00	0.00	
GBL	7.25	7.82	
1,4-Butanediol	0.00	0.00	
1-Heptanol	0.00	0.00	
Others	0.00	0.00	
Selectivity(%)			
1-Propanol	0.00	0.00	
Iso-Propanol	0.00	0.00	
THF	0.00	0.00	
1-Butanol	0.00	0.00	
Methyl Butyrate	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	
1-Hexanol	0.00	0.00	
GBL	100.00	100.00	
1,4-Butanediol	0.00	0.00	
1-Heptanol	0.00	0.00	

T	able	B .5	; -	Run	#	16	report
---	------	-------------	-----	-----	---	----	--------

FEED = GBL Catalyst	Cu (5.2) / Pd (0.3) / KOH (2.7) on XOA-400				
REPORT	R16.1	R16.2			
Experiment Date	6/7/95	6/7/95	1		
Entry Date	4/9/96	4/9/96			
P (psig)	600.00	600.00			
T(C)	300.00	340.00			
RT(s)	63.23	59.27			
Err(%C)	-12.73	-27.80			
Conv(BOF)	44.56	71.38			
Conv(adj)	31.84	43.58			
H2 : DMS (molar)	3.37	3.39			
Yield BOF(%)					
1-Propanol	0.00	0.00			
Iso-Propanol	0.00	0.00			
THF	0.84	2.10			
1-Butanol	1.38	2.01			
Methyl Butyrate	5.77	11.25			
4-Methyl,1-Pentanol	0.00	0.00			
1-Hexanol	0.00	0.00			
GBL	0.66	0.17			
1,4-Butanediol	12.83	7.81			
1-Heptanol	0.71	1.15			
Others	9.64	19.08			
Selectivity(%)					
1-Propanol	0.00	0.00			
Iso-Propanol	0.00	0.00			
THF	3.79	8.57			
1-Butanol	6.22	8.21			
Methyl Butyrate	26.00	45.94	1		
4-Methyl,1-Pentanol	0.00	0.00	1		
1-Hexanol	0.00	0.00			
GBL	2.97	0.69			
1,4-Butanediol	57.82	31.89			
1-Heptanol	3.20	4.70	1		

	Catalyst Cu (5.2) / Pd (0.3) / KOH (2.7) on XOA-400			
REPORT	R17.1	R17.2	R17.3	
Experiment Date	6/7/95	6/7/95	6/7/95	
Entry Date	4/9/96	4/9/96	4/9/96	
P (psig)	600.00	600.00	750.00	
T(C)	295.00	320.00	320.00	
RT(s)	47.12	42.96	54.57	
Err(%C)	-4.86	6.71	15.12	
Conv(BOF)	60.06	69.38	85.85	
Conv(adj)	55.19	76.10	100.97	
H2 : DMS (molar)	7.79	5.72	5.91	
Vield BOF(%)				
1-Pronanol	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	
THF	0.44	0.72	0.89	
1-Butanol	1.02	2.82	6.60	
Methyl Butyrate	1.83	3.59	4.06	
4-Methyl,1-Pentanol	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	
GBL	40.60	57.40	64.08	
1,4-Butanediol	9.06	9.09	24.49	
1-Heptanol	0.42	0.53	0.85	
Others	1.82	1.94	0.00	
Selectivity (%)				
1-Propanoi	0.00	0 00	0 00	
Iso-Propanol	0.00	0.00	0.00	
THF	0.82	0.97	0.88	
1-Butanol	1.91	3.80	6.54	
Methyl Butyrate	3.43	4.84	4.02	
4-Methyl,1-Pentanol	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	
GBL	76.07	77.41	63.46	
1,4-Butanediol	16.98	12.26	24.25	
1-Heptanol	0.79	0.71	0.84	

Table B.6 - Run # 17 report
Table B.7 - Run # 22 report

	Catalyst	Fe/Pd/KOH	on XOA-40	0
	,			
REPORT	R22.1	R22.2	R22.3	
Experiment Date	7/15/95	7/15/95	7/15/95	
Entry Date	12/20/95	12/20/95	12/20/95	
-				
P (psig)	480.00	480.00	480.00	
T(C)	290.00	320.00	345.00	
RT(s)	9.90	9.51	6.66	
Err(%C)	-58.04	-62.60	-50.64	
Conv(BOF)	66.94	74.72	61.42	
Conv(adj)	8.90	12.12	10. 78	
H2 : DMS (molar)	3.11	3.17	4.99	
Yield BOF(%)				
1-Propanol	0.00	0.41	0.27	
Iso-Propanol	0.00	0.00	0.00	
THF	0.17	0.35	0.62	
1-Butanol	0.09	0.39	0.27	
Methyl Butyrate	0.14	0.32	0.65	
4-Methyl,1-Pentanol	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	
GBL	8.50	10.65	8.97	
1,4-Butanediol	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	
Others	0.00	0.00	0.00	
Selectivity(%)				
1-Propanol	0.00	3.38	2.50	
Iso-Propanol	0.00	0.00	0.00	
THF	1.91	2.89	5.75	
1-Butanol	1.01	3.22	2.50	
Methyl Butyrate	1.57	2.64	6.03	
4-Methyl,1-Pentanol	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	
	95.51	87.87	83.21	
1,4-Butanediol	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	

Table B.8 - Run # 23 report

(

	Catalyst	Cu (5.32) / 1	Pd (0.13) / KOH (0.84) on Si-Al
		Da 2 A	
REPORT	R23.1	R23.2	
Experiment Date	7/17/95	7/17/95	
Entry Date	4/8/96	4/8/96	
P (neig)	400.00	400.00	
- () T(C)	290.00	310.00	
RT(s)	15.43	14.64	
Err(%C)	-13.64	-26.71	
Conv(BOF)	26.71	58.02	
Conv(adi)	13.07	31.31	
H2 : DMS (molar)	7.71	7.48	
Yield BOF(%)			
1-Propanol	0.00	0.00	
Iso-Propanol	0.00	0.00	
THF	3.29	10.19	
1-Butanol	0.48	0.32	
Methyl Butyrate	0.00	0.49	
4-Methyl,1-Pentanol	0.00	0.00	
1-Hexanol	0.00	0.00	
GBL	8.13	10.05	
1,4-Butanediol	0.00	0.00	
1-Heptanol	1.17	1.34	
Others	0.00	8.92	
Selectivity(%)			
1-Propanol	0.00	0.00	
Iso-Propanol	0.00	0.00	
THF	25.17	45.51	
1-Butanol	3.67	1.43	
Methyl Butyrate	0.00	2.19	
4-Methyl,1-Pentanol	0.00	0.00	
1-Hexanol	0.00	0.00	
GBL	62.20	44.89	
1,4-Butanediol	0.00	0.00	
1-Heptanol	8.95	5.98	

Table B.9 - Run # 24 report

	Catalyst	Fe/Pd/KOH	on Si-Al		
	•				
REPORT	R24 .1	R24.2	R24.3	R24.4	
Experiment Date	7/21/95	7/21/95	7/21/95	7/21/95	
Entry Date	12/20/95	12/20/95	12/20/95	12/20/95	
	1				
P (psig)	620.00	620.00	620.00	620.00	
T(C)	290.00	312.00	332.00	350.00	
RT(s)	11.94	15.02	14.85	14.82	
Err(%C)	3.21	-0.98	-5.65	2.69	
Conv(BOF)	1.95	23.91	54.29	68.24	
Conv(adj)	5.17	22.93	48.64	70.93	
H2 : DMS (molar)	16.00	29.42	31.85	30.82	
Yield BOF(%)					
1-Propanol	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	0.00	
THF	0.76	3.76	10.54	13.92	
1-Butanol	0.00	0.16	0.56	1.87	
Methyl Butyrate	0.00	0.26	1.49	4.83	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	4.41	18.75	36.05	50.30	
1,4-Butanedioł	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	
Others	0.00	0.00	0.00	0.00	
Selectivity(%)					
1-Propanol	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	0.00	
THF	14.70	16.40	21.67	19.63	
1-Butanol	0.00	0.70	1.15	2.64	
Methyl Butyrate	0.00	1.13	3.06	6.81	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	85.30	81.77	74.12	70.92	
1,4-Butanediol	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	

Table B.10 - Run # 25 report

	Catalyst	A1				
REPORT	R25.1	R25.2	R25.3	R25.4	R25.5	
Experiment Date	7/26/95	7/26/95	7/26/95	7/26/95	7/26/95	
Entry Date	12/20/95	12/20/95	12/20/95	12/20/95	12/20/95	
P (psig)	500.00	600.00	750.00	900.00	900.00	
T(C)	330.00	330.00	330.00	330.00	330.00	
RT(s)	10.05	14.39	16.76	20.28	7.94	
Err(%C)	-49.00	-4.14	-1.24	-0.90	-3.08	
Conv(BOF)	79.65	74.21	79.23	85.88	90.09	
Conv(adj)	30.66	70.08	77.99	84.97	87.02	
H2 : DMS (molar)	20.73	29.19	33.75	35.34	108.76	
Yield BOF(%)	<u> </u>					
1-Propanol	1.30	1.82	1.93	0.48	1.35	
Iso-Propanol	0.91	1.38	1.62	1.72	0.75	
THF	0.36	0.81	1.27	1.59	1.66	
1-Butanol	0.93	2.73	5.18	13.35	13.34	
Methyl Butyrate	2.53	5.16	5.78	7.75	4.19	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	23.77	56.82	60.38	58.59	59.22	
1,4-Butanediol	0.87	1.37	1.83	1.49	6.50	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	
Others	0.00	0.00	0.00	0.00	0.00	
Selectivity(%)						
1-Propanol	4.24	2.60	2.47	0.56	1.55	
Iso-Propanol	2.97	1.97	2.08	2.02	0. 8 6	
THF	1.17	1.16	1.63	1.87	1.91	
1-Butanol	3.03	3.89	6.64	15.71	15.33	
Methyl Butyrate	8.25	7.36	7.41	9.12	4.82	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	77.50	81.07	77.42	68.95	68.06	
1,4-Butanediol	2.84	1.95	2.35	1.75	7.47	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	

Table B.11 - Run # 28 report

	Catalyst	A1			
REPORT	R28.1	R28.2	R28.3	R28.4	
Experiment Date	9/18/95	9/18/95	9/18/95	9/18/95	
Entry Date	12/20/95	12/20/95	12/20/95	12/20/95	
P (psig)	600.00	600.00	600.00	600.00	
T(C)	290.00	320.00	340.00	360.00	
RT(s)	7.88	7.78	7.36	7.14	
Err(%C)	-27.75	-13.41	-10.38	-47.92	
Conv(BOF)	46.15	81.59	90.51	97.53	
Conv(adj)	18.40	68.18	80.13	49.62	
H2 : DMS (molar)	225.00	313.00	243.00	253.00	
Yield BOF(%)					
1-Propanol	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	1.31	2.01	3.52	
THF	1.09	5.78	5.69	1.38	
1-Butanol	0.00	9.26	26.30	26.07	
Methyl Butyrate	0.00	4.08	8.43	6.80	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0	0.00	
GBL	17.31	47.75	35.64	9.48	
1,4-Butanediol	0.00	0.00	1.78	2.21	
1-Heptanol	0.00	0.00	0.29	0.15	
Others	0.00	0.00	0.00	0.00	
Selectivity(%)					
1-Propanol	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	1.92	2.51	7.10	
THF	5.92	8.48	7.10	2.78	
1-Butanol	0.00	13.58	32.82	52.55	-
Methyl Butyrate	0.00	5.98	10.52	13.71	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	94.08	70.04	44.47	19.11	
1,4-Butanediol	0.00	0.00	2.22	4.45	
1-Heptanol	0.00	0.00	0.36	0.30	

Table B.12 - Run # 29 report

	Catalyst	Cu/Pd/KOH				
				D 00 4		
REPORT	R29.1	R29.2	R29.3	R29.4	R29.5	R29.0
Experiment Date	9/19/95	9/19/95	9/19/95	9/19/95	9/19/95	9/19/95
Entry Date	9/20/95	9/20/95	9/20/95	9/20/95	9/20/95	9/20/95
P (psig)	400.00	500.00	600.00	750.00	900.00	1000.00
T(C)	330.00	330.00	330.00	330.00	330.00	330.00
RT(s)	5.05	6.35	7.60	11.76	14.64	16.40
Err(%C)	-9.87	-11.73	-13.89	-12.26	-12.36	-9.24
Conv(BOF)	70.55	82.98	90.34	92.21	95.66	95.34
Conv(adj)	60.68	71.24	76.45	79.95	83.31	86.11
H2 : DMS (molar)	190.00	189.00	197.00	163.00	194.00	189.00
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
THF	1.16	2.06	3.01	3.83	4.84	4.96
1-Butanol	2.31	3.40	6.0 8	7.61	10.51	12.55
Methyl Butyrate	3.45	4.42	5.24	6.24	5.92	5.98
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexanol	0.00	0.00	0.00	0.00	0.00	0.00
GBL	52.93	60.31	60.62	58.49	53.07	49.62
1,4-Butanediol	0.82	1.07	1.50	3.78	8.97	13.00
1-Heptanol	0.00	0.00	0.00	0.00	0.00	0.00
Others	5.37	0.00	0.00	0.00	0.00	0.00
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
THF	1.91	2.89	3.94	4.79	5.81	5.76
1-Butanol	3.81	4.77	7.95	9.52	12.62	14.57
Methyl Butyrate	5.69	6.20	6.85	7.80	7.11	6.94
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexanol	0.00	0.00	0.00	0.00	0.00	0.00
GBL	87.24	84.63	79.29	73.16	63.70	57.62
1,4-Butanediol	1.35	1.50	1.96	4.73	10.77	15.10
1-Heptanol	0.00	0.00	0.00	0.00	0.00	0.00

Table	B .1	3 -	Run	#	30	report
-------	-------------	-----	-----	---	----	--------

	Catalyst	A2			
REPORT	R30.1	R30.2	R30.3	R30.4	
Experiment Date	9/25/95	9/25/95	9/25/95	9/25/95	
Entry Date	9/26/95	9/26/95	9/26/95	9/26/95	
P (psig)	600.00	600.00	600.00	600.00	
Γ(C)	290.00	314.00	340.00	360.00	
RT(s)	8.00	7.59	7.43	8.84	
Err(%C)	-16.13	-10.14	-5.19	-11.16	
Conv(BOF)	36.67	49.63	73.24	88.34	
Conv(adj)	20.54	39.49	68.05	77.18	
H2 : DMS (molar)	197.00	200.00	192.00	195.00	
Yield BOF(%)					
1-Prop anoi	0.00	0.00	0.00	0.00	
iso-Propanol	0.00	0.00	0.00	0.00	
THF	0.60	1.67	3.09	3.05	
1-Butanol	0.00	0.00	3.75	12.68	
Methyl Butyrate	0.00	2.58	8.61	16.33	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	19.30	34.01	50.41	41.93	
1,4-Butanediol	0.65	1.23	2.19	3.20	
l-Heptanol	0.00	0.00	0.00	0.00	
Others	0.00	0.00	0.00	0.00	
Selectivity(%)					
l-Propanol	0.00	0.00	0.00	0.00	
iso-Propanol	0.00	0.00	0.00	0.00	
ГНГ	2.92	4.23	4.54	3.95	
l-Butanol	0.00	0.00	5.51	16.43	
Methyl Butyrate	0.00	6.53	12.65	21.16	
f-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
l-Hexanol	0.00	0.00	0.00	0.00	
GBL	93.92	86.12	74.08	54.32	
1,4-Butanediol	3.16	3.11	3.22	4.15	
i-Heptanol	0.00	0.00	0.00	0.00	
	1				

Table B.14 - Run # 31 report

	Catalyst	A2				
REPORT	R31.1	R31.2	R31.3	R31.4	R31.5	R31.6
Experiment Date	9/27/95	9/27/95	9/27/95	9/27/95	9/27/95	9/27/95
Entry Date	10/3/95	10/3/95	10/3/95	10/3/95	10/3/95	10/3/95
P(psig)	500.00	600.00	750.00	900.00	1100.00	1300.00
T(C)	330.00	330.00	330.00	330.00	330.00	330.00
RT(s)	6.06	7.22	9.04	13.35	17.83	20.60
Err(%C)	-9.73	2.24	-6.84	-5.27	2.86	4.50
Conv(BOF)	82.11	82.93	89.35	92.00	86.36	95.87
Conv(adj)	72.38	85.15	82.52	86.73	89.22	100.38
H2 : DMS (molar)	209.00	202.00	201.00	202.00	203.00	206.00
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
Iso-Prop an ol	0.00	0.00	0.00	0.00	0.00	0.00
THF	1.39	1.98	2.41	2.63	3.83	4.12
1-Butanol	12.47	16.61	19.55	22.34	21.63	32.82
Methyl Butyrate	10.67	11.85	10.70	9.62	7.78	8.65
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexanol	0.00	0.00	0.00	0.00	0.00	0.00
GBL	45.36	53.47	43.86	36.56	31.58	27.04
1,4-Butanediol	1.58	1.24	6.00	15.58	24.39	27.74
1-Heptanol	0.00	0.00	0.00	0.00	0.00	0.00
Others	0.90	0.00	0.00	0.00	0.00	0.00
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
THF	1.94	2.33	2.92	3.03	4.29	4.10
1-Butanol	17.45	19.51	23.69	25.76	24.25	32.70
Methyi Butyrate	14.93	13.92	12.97	11.09	8.72	8.62
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexanol	0.00	0.00	0.00	0.00	0.00	0.00
GBL	63.47	62.80	53.15	42.15	35.40	26.94
1,4-Butanediol	2.21	1.46	7.27	17.96	27.34	27.64
1-Heptanol	0.00	0.00	0.00	0.00	0.00	0.00

Table B.15 - Run # 32 report

	Catalyst	A3			
REPORT	R32.1	R32.2	R32.3	R32.4	
Experiment Date	10/1/95	10/1/95	10/1/95	10/1/95	
Entry Date	10/27/95	10/27/95	10/27/95	10/27/95	
P (psig)	600.00	600.00	600.00	600.00	
T(C)	290.00	320.00	340.00	360.00	
RT(s)	7.74	7.43	7.08	8.52	
Err(%C)	-8.30	33.17	31.29	-14.46	
Conv(BOF)	100.00	100.00	100.00	100.00	
Conv(adj)	91.70	133.17	131.28	85.51	
H2 : DMS (molar)	206.00	204.00	192.30	194.00	
Viald BOEM					
1 Drenenel		22.10	20.41	47 20	
	8.80 0.00	22.19	39.41	47.29	
ISO-Propanoi Tur	0.00	0.00	0.00	0.00	
1 ELF	1.43	1.15	17.10	0.75	
1-Dulanoi Methyl Butymete	20.71	20,70	17.12	J.14 0.00	
Methyl Dutyrate	1.11	1.14	0.00	0.00	
4-Methyl,1-rentanoi	0.00	0.00	0.00	0.00	
CRI	17.54	0.00	0.00	0.00	
GBL 1 A-Butenedial	3 44	3 77	0.85	0.00	
1.Hentenol	0.00	0.00	0.00	0.00	
Others	32 67	77 58	0.00 60 09	34 37	
Selectivity(%)	52.01	11,50	07.07	54.57	
1-Propanol	14 91	39 92	63 36	92 44	
Iso-Propanol	0.00	0.00	0.00	0.00	
THF	2.42	2.07	0.96	1.43	
1-Butanol	45.25	48.03	27.52	6.14	
Methyl Butyrate	1.88	2.05	1.06	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	29.71	1.15	1.37	0.00	
1.4-Butanediol	5.83	6.78	5.72	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	
•					

Table B.16 - Run # 33 report

	Catalyst A3							
		500.0	500.0	D 00 4	D 22.6			
REPORT	R33.1	R33.2	R33.3	K33.4	K33.5			
Experiment Date	10/3/95	10/3/95	10/3/95	10/3/95	10/3/95			
Entry Date	12/29/95	12/29/95	12/29/95	12/29/95	12/29/95			
P (psig)	500.00	600.00	750.00	900.00	1000.00			
T(C)	320.00	320.00	320.00	320.00	320.00			
RT(s)	6.22	7.52	9.46	11.06	12.12			
Err(%C)	6.20	10.89	21.97	20.23	37.61			
Conv(BOF)	98.92	99.32	100.00	100.00	100.00			
Conv(adj)	105.13	110.21	121.97	120.32	137.61			
H2 : DMS (molar)	203.00	201.00	196.00	202.00	202.00			
Yield BOF(%)								
1-Propanol	5.39	6.31	7.82	7.96	8.00			
Iso-Propanol	21.09	22.20	24.58	24.62	27.41			
THF	0.28	0.83	0.67	0.57	0.67			
1-Butanol	20.46	24.25	27.75	27.61	37.75			
Methyl Butyrate	0.80	0.71	0.66	0.49	0.00			
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00			
1-Hexanol	4.45	3.70	3.78	3.41	3.55			
GBL	0.00	0.00	0.00	0.00	0.00			
1,4-Butanediol	7.09	4.65	4.06	3.33	3.44			
1-Heptanol	0.00	0.00	0.00	0.00	0.00			
Others	45.57	47.58	52.64	52.23	56.79			
Selectivity(%)								
1-Propanol	9.05	10.07	11.28	11.71	9.90			
Iso-Propanol	35.41	35.43	35.46	36.21	33.91			
THF	0.47	1.32	0.97	0.84	0.83			
1-Butanol	34.35	38.71	40.03	40.61	46.71			
Methyl Butyrate	1.34	1.13	0.95	0.72	0.00			
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00			
1-Hexanol	7.47	5.91	5.45	5.02	4.39			
GBL	0.00	0.00	0.00	0.00	0.00			
1,4-Butanediol	11.90	7.42	5.86	4.90	4.26			
1-Heptanol	0.00	0.00	0.00	0.00	0.00			

	Catalyst A4								
DFDODT	P 34 1	R34 2	R34 3	R34 4	R34 5				
Francisment Date	10/5/95	10/5/95	10/5/95	10/5/95	10/5/95				
Euter Date	12/28/05	12/28/05	12/28/05	12/28/95	12/28/95				
	12 20 33	12 20 75	142075	12/20/33	1220/22				
P (asia)	600.00	600.00	600.00	600.00	600 00				
r (peig)	250.00	270.00	290.00	310.00	330.00				
	230.00	270.00 9.13	290.00	7 58	7 31				
$R_{1}(s)$	-1.85	2 00	-11.00	-17 27	-31.66				
	-1.65	2.30	-11.00	07 55	-91.00				
Conv(BOF)	0.53	20.43	74 35	80.27	67.67				
$U_2 \cdot DMS$ (molor)	203.00	107.00	203.00	200.00	194.00				
HZ. DIVIS (MOLAI)	203.09	197.00	205.00	200.00	194.00				
Yield BOF(%)									
1-Propanol	0.00	0.00	0.00	1.44	4.91				
Iso-Propanol	0.00	0.00	5.52	14.43	22.03				
THF	2.13	0.77	2.24	1.93	1.30				
1-Butanol	0.00	0.00	8.18	2.89	22.59				
Methyl Butyrate	0.00	0.00	0.32	0.77	0.94				
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00				
1-Hexanol	0.00	0.00	0.00	1.63	2.72				
GBL	7.40	28.52	50.93	27.75	3.23				
1,4-Butanediol	0.00	2.02	2.55	3.30	4.88				
1-Heptanol	0.00	0.00	0.00	0.00	0.89				
Others	0.00	0.00	4.62	8.14	4.20				
Selectivity(%)									
1-Propanol	0.00	0.00	0.00	2.66	7.73				
Iso-Propanol	0.00	0.00	7.92	26.65	34.70				
THF	22.35	2.46	3.21	3.56	2.05				
1-Butanol	0.00	0.00	11.73	5.34	35.58				
Methyl Butyrate	0.00	0.00	0.46	1.42	1.48				
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00				
1-Hexanol	0.00	0.00	0.00	3.01	4.28				
GBL	77.65	91.09	73.03	51.26	5.09				
1,4-Butanediol	0.00	6.45	3.66	6.10	7.69				
1-Heptanol	0.00	0.00	0.00	0.00	1.40				

Table B.18 -	Run # 35	report
--------------	----------	--------

	Catalyst A4								
PFDODT	D25 1	P25 2	D25 2	D25 A	D25 5				
EFORI Experiment Date	10/12/05	10/12/05	10/12/05	10/12/05	10/12/05	<u> </u>			
Experiment Dute	10/12/95	10/12/95	10/12/95	10/12/95	10/12/95				
Entry Date	10/20/93	10/20/93	10/20/93	10/20/95	10/20/95				
P (noig)	500.00	600.00	750.00	880.00	1000.00				
	320.00	320.00	730.00	320.00	320.00				
	520.00	7 52	520.00	12 45	JZ0.00				
	5.07	7.55	9.23 2.24	13.45	20.30				
	-5.57	9.01	2.34	12.67	20.30				
Conv(BOF)	97.32	109.66	101.94	77.47	76.77				
$U_2 \cdot DMS$ (moloc)	91.34	108.00	101.64	112.33	119.29				
FIZ . DIVIS (MOIAT)	200.00	202.00	192.00	201.00	201.00				
Yield BOF(%)									
1-Propanol	7.09	7.66	7.17	8.01	8.65				
Iso-Propanol	0.00	0.00	0.00	0.00	0.00				
THF	1.14	1.33	1.17	1.16	1.18				
1-Butanol	17.52	23.36	23.88	27.66	30.67				
Methyl Butyrate	0.00	0.34	1.07	1.07	1.05				
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00				
1-Hexanol	0.00	0.00	0.00	0.00	0.00				
GBL	14.81	9.11	4.48	3.03	2.48				
1,4-Butanediol	4.54	4.75	3.66	3.20	3.76				
1-Heptanol	0.00	0.00	0.00	0.00	0.00				
Others	46.63	62.12	60.41	68.22	71.49				
Selectivity(%)									
1-Prop anol	15.72	16.46	17.31	18.15	18.10				
Iso-Propanol	0.00	0.00	0.00	0.00	0.00				
THF	2.53	2.86	2.82	2.63	2.47				
1-Butanol	38.85	50.18	57.64	62.68	64.18				
Methyl Butyrate	0.00	0.73	2.58	2.42	2.20				
4-Methyi,1-Pentanoi	0.00	0.00	0.00	0.00	0.00				
1-Hexanol	0.00	0.00	0.00	0.00	0.00				
GBL	32.84	19.57	10. 8 1	6. 8 7	5.19				
1,4-Butanediol	10.07	10.20	8.83	7.25	7.87				
1-Heptanol	0.00	0.00	0.00	0.00	0.00				

Table B.19 - Run # 36 report

	Catalyst	A4				
	•					
REPORT	R36 .1	R36.2	R36.3	R36.4	R36.5	
Experiment Date	10/24/95	10/24/95	10/24/95	10/24/95	10/24/95	
Entry Date	11/21/95	11/21/95	11/21/95	11/21/95	11/21/95	
P (psig)	800.00	800.00	800.00	800.00	800.00	
T(C)	240.00	260.00	280.00	300.00	330.00	
RT(s)	11.67	11.23	10.82	10.20	9.70	
Err(%C)	-14.66	-11.70	-21.97	-20.43	-10.54	
Conv(BOF)	26.30	41.49	83.03	95.43	98.45	
Conv(adj)	11.64	29.79	61.06	75.00	87.94	
H2 : DMS (molar)	200.00	199.00	199.00	201.47	204.00	
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	1.29	7.90	
Iso-Propanol	0.00	0.00	3.54	14.34	27.19	
THF	0.68	1.65	3.34	2.91	1.16	
1-Butanol	0.88	1.49	7.54	20.77	23.32	
Methyl Butyrate	0.00	0.00	0.00	0.78	0.83	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	1.24	3.33	
GBL	8.54	24.88	40.66	30.47	3.26	
1,4-Butanediol	0.00	0.00	3.73	2.74	0.00	
1-Heptanol	1.55	1.77	0.85	0.46	0.00	
Others	0.00	0.00	1.40	0.00	20.91	
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	1.72	11.79	
Iso-Propanol	0.00	0.00	5.93	19.12	40.59	
THF	5.84	5.54	5.60	3.88	1.73	
1-Butanol	7.55	5.00	12.64	27.69	34.81	
Methyl Butyrate	0.00	0.00	0.00	1.04	1.24	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	1.65	4.97	
GBL	73.30	83.52	68.15	40.63	4.87	
1,4-Butanediol	0.00	0.00	6.25	3.65	0.00	
1-Heptanol	13.30	5.94	1.42	0.61	0.00	

PURE METHANOL F	EED	Catalyst	Á4			
		-	202.0	505 4	505.5	
REPORT	<u>R37.1</u>	R37.2	R37.3	R37.4	R37.5	R37.6
Experiment Date	11/1/95	11/1/95	11/1/95	11/1/95	11/1/95	11/1/95
Entry Date	11/21/95	11/21/95	11/21/95	11/21/95	11/21/95	11/21/95
P (psig)	600.00	600.00	600.00	600.00	600.00	600.00
T(C)	250.00	260.00	280.00	300.00	330.00	350.00
RT(s)	8.69	11.23	10.82	10.20	9.70	7.39
Yield BOF(%)						
1-Propanol	0.00	0.00	0.41	1.02	2.24	5.51
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
THF	0.00	0.00	0.00	0.00	0.00	0.64
1-Butanol	0.00	0.00	0.00	0.00	0.00	0.08
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00	0.00
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexanol	0.00	0.00	0.00	0.00	0.00	0.00
GBL	0.00	0.00	0.00	0.00	0.00	0.00
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	0.00
1-Heptanol	0.00	0.00	0.00	0.00	0.00	0.00
Others	0.00	0.00	0.00	0.00	0.42	0.00
Selectivity(%)						
1-Propanol	0.00	0.00	100.00	100.00	100.00	88.44
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	0.00
THF	0.00	0.00	0.00	0.00	0.00	10.27
1-Butanol	0.00	0.00	0.00	0.00	0.00	1.28
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00	0.00
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	0.00
1-Hexanol	0.00	0.00	0.00	0.00	0.00	0.00
GBL	0.00	0.00	0.00	0.00	0.00	0.00
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	0.00
1-Heptanol	0.00	0.00	0.00	0.00	0.00	0.00

Table B.20-Run # 37report

•

Table B.21 - Run #38 Report

	Catalyst	A5				
REPORT	R38.1	R38.2	R38.3	R38.4	R38.5	
Experiment Date	11/4/95	11/4/95	11/4/95	11/4/95	11/4/95	
Entry Date	11/21/95	11/21/95	11/21/95	11/21/95	11/21/95	
P (psig)	600.00	600.00	600.00	600.00	600.00	
T(Ĉ)	350.00	330.00	310.00	290.00	270.00	
RT(s)	5.40	7.41	7.50	7.59	8.04	
Еп(%С)	-86.58	-28.19	-16.29	-12.88	-14.04	
Conv(BOF)	100.00	99.55	98.33	93.61	74.05	
Conv(adj)	13.42	71.36	82.03	80.73	60.02	
H2 : DMS (molar)	274.49	194.89	204.99	210.84	201.22	
Yield BOF(%)						
1-Propanol	10.82	5.00	2.02	1.34	0.00	
Iso-Propanol	2.50	15.17	11.72	6.25	2.06	
THF	0.10	0.92	1.07	1.08	1.03	
1-Butanol	0.00	15.82	16.27	13.14	7.05	
Methvi Butvrate	0.00	0.82	0.76	0.36	0.00	
4-Methvi.1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	2.15	1.59	0.53	0.00	
GBL	0.00	6.53	29.09	45.99	46.39	
1.4-Butanediol	0.00	2.58	2.52	4.41	1.29	
1-Heptanol	0.00	0.36	0.38	0.33	0.00	
Others	0.00	22.02	16.62	7.29	2.19	
Selectivity(%)						
1-Propanol	80.63	10.13	3.09	1.82	0.00	
iso-Propanoi	18.63	30.74	17.92	8.51	3.56	
THF	0.75	1.86	1.64	1.47	1.78	
1-Butanol	0.00	32.06	24.87	17.89	12.19	
Methyl Butyrate	0.00	1.66	1.16	0.49	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	4.36	2.43	0.72	0.00	
GBL	0.00	13.23	44.47	62.63	80.23	
1,4-Butanediol	0.00	5.23	3.85	6.01	2.23	
1-Heptanol	0.00	0.73	0.58	0.45	0.00	

Table D.ZZ - Ruit was Report	Table	B.22	-	Run	#39	Report
------------------------------	-------	-------------	---	-----	-----	--------

. -

	Catalyst	A7				
REPORT	R30 1	R39.2	R39 3	R39.4	R39.5	
Experiment Date	11/8/95	11/8/95	11/8/95	11/8/95	11/8/95	
Entry Date	11/21/95	11/21/95	11/21/95	11/21/95	11/21/95	
	1.12.1.00		1.1.2.1.00			
P (osia)	500.00	600.00	750.00	900.00	1000.00	
T(C)	320.00	320.00	320.00	320.00	320.00	
RT(s)	5.24	6.50	7.89	9.15	10.54	
Еп(%С)	-10.82	-10.44	-14.20	-10.27	-16.50	
Conv(BOF)	56.63	70.02	82.05	87.20	91.73	
Conv(adj)	45.81	59 .57	67.84	76.93	75.23	
H2 : DMS (molar)	202.38	197.68	195.99	206.13	194.77	
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	1.10	1.89	2.73	3.11	
THF	0.55	0.70	1.00	1.37	1.61	
1-Butanol	5.45	9.94	15.15	21.56	24.51	
Methyl Butyrate	0.00	0.52	0.63	0.66	0.69	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	39.81	47.31	47.13	47.93	42.48	
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	
Others	0.00	0.00	2.04	. 2.68	2.83	
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	1.85	2.87	3.68	4.30	
THF	1.20	1.18	1.52	1.85	2.22	
1-Butanol	11.90	16.69	23.02	29.04	33.85	
Methyl Butyrate	0.00	0.87	0.96	0.89	0.95	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	86.90	79.42	71.63	64.55	58.67	
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	

	Catalyst	A7				
PEDOPT	P40 1	P40 2	R40 3	R40 4	R40 5	
Evneriment Date	11/12/05	11/12/95	11/12/95	11/12/95	11/12/95	
Entry Data	11/2/05	11/20/05	11/20/05	11/20/05	11/20/95	
	11/20/85	11/20/00	11/20/00	11/20/00	11/20/00	
P (osia)	600.00	600.00	600.00	600.00	600.00	
T(C)	250.00	270.00	290.00	310.00	330.00	
RT(s)	6.91	6.62	6.61	6.21	6.18	
Err(%C)	-4.65	-9.96	-5.99	-5.83	-14.85	
Conv(BOF)	4.65	11.67	19.94	29.93	72.59	
Conv(adi)	0.00	1.70	13.95	24.11	57.73	
H2 : DMS (molar)	222.97	211.20	207.95	214.00	207.45	
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
iso-Propanol	0.00	0.00	0.00	0.00	1.27	
THF	0.00	0.00	0.00	0.00	0.83	
1-Butanol	0.00	0.00	0.35	1.59	9.19	
Methyl Butyrate	0.00	0.00	0.00	0.00	0.57	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	0.00	1.70	9.39	22.51	45.87	
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	
Others .	0.00	0.00	4.21	0.00	0.00	
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
iso-Propanol	0.00	0.00	0.00	0.00	2.20	
THF	0.00	0.00	0.00	0.00	1.44	
1-Butanol	0.00	0.00	3.59	6.60	15.92	
Methyl Butyrate	0.00	0.00	0.00	0.00	0.99	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	0.00	100.00	96.41	93.40	79.46	
1 ,4-Butanedi ol	0.00	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	

•

	Catalyst	A6				
	-					
REPORT	R41.1	R41.2	R41.3	R41.4	R41.5	
Experiment Date	11/19/95	11/19/95	11/19/95	11/19/95	11/19/95	
Entry Date	11/21/95	11/21/95	11/21/95	11/21/95	11/21/95	
P (psig)	500.00	600.00	750.00	900.00	1000.00	
T(C)	320.00	320.00	320.00	320.00	320.00	
RT(s)	4.82	6.37	7.93	9.37	10.3 9	
Еп(%С)	-27.58	-11.89	-12.40	-9.61	-14.80	
Conv(BOF)	56.47	52.56	49.74	58.60	66.81	
Conv(adj)	28.89	40.67	37.34	48.99	52.01	
H2 : DMS (molar)	223.94	202.85	207.36	204.88	205.36	
Yield BOF(%)						
1-Propanoi	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.71	0.00	1.18	1.41	
THF	6.40	8.21	6.45	7.56	7.18	
1-Butanol	0.30	0.72	0.87	2.10	3.24	
Methyl Butyrate	5.26	8.86	9.11	13.07	14.49	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	16.94	22.16	20.91	25.08	25.70	
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	
Others	0.00	0.00	0.00	0.00	0.00	
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	1.75	0.00	2.41	2.71	
THF	22.15	20.19	17.27	15.43	13.80	
1-Butanol	1.04	1.77	2.33	4.29	6.23	
Methyl Butyrate	18.20	21.79	24.40	26.68	27.85	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	58.62	54.50	56.00	51.19	49.40	
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	

	Catalyst A6							
REPORT	R42.1	R42.2	R42.3	R42.4	R42.5			
Experiment Date	11/27/95	11/27/95	11/27/95	11/27/95	11/27/95			
Entry Date	12/5/95	12/5/95	12/5/95	12/5/95	12/5/95			
P (psig)	600.00	600.00	600.00	600.00	600.00			
T(C)	250.00	270.00	290.00	310.00	330.00			
RT(s)	7.27	7.06	6.49	6.48	5.81			
Еп(%С)	3.03	0.86	-13.85	-16.06	-15.81			
Conv(BOF)	1.19	4.53	27.05	45.02	69.24			
Conv(adj)	4.22	5.39	13.20	28.96	53.43			
H2 : DMS (molar)	219.35	204.83	203.94	196.66	221.29			
Yield BOF(%)								
1-Propanol	0.00	0.00	0.00	0.00	0.00			
lso-Propanol	0.00	0.00	0.00	0.00	0.71			
THF	0.00	0.75	2.38	6.20	14.03			
1-Butanol	0.00	0.00	0.00	0.00	0.66			
Methyl Butyrate	0.86	0.80	2.31	5.93	13.68			
4-Methyi,1-Pentanoi	0.00	0.00	0.00	0.00	0.00			
1-Hexanol	0.00	0.00	0.00	0.00	0.00			
GBL	3.36	3.85	8.51	16.83	24.35			
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00			
1-Heptanol	0.00	0.00	0.00	0.00	0.00			
Others	0.00	0.00	0.00	0.00	0.00			
Selectivity(%)								
1-Propanol	0.00	0.00	0.00	0.00	0.00			
Iso-Propanol	0.00	0.00	0.00	0.00	1.33			
THF	0.00	13.89	18.03	21.41	26.26			
1-Butanol	0.00	0.00	0.00	0.00	1.24			
Methyl Butyrate	20.38	14.81	17.50	20.48	25.60			
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00			
1-Hexanol	0.00	0.00	0.00	0.00	0.00			
GBL	79.62	71.30	64.47	58.11	45.57			
1 ,4-Butanediol	0.00	0.00	0.00	0.00	0.00			
1-Heptanol	0.00	0.00	0.00	0.00	0.00			

	Catalyst A3							
REPORT	R43.1	R43.2	R43.3	R43.4	R43.5			
Experiment Date	12/3/95	12/3/95	12/3/95	12/3/95	12/3/95			
Entry Date	4/14/96	4/14/96	4/14/96	4/14/96	4/14/96			
P (psig)	500.00	600.00	750.00	900.00	1000.00			
T(C)	320.00	320.00	320.00	320.00	320.00			
RT(s)	4.95	5.83	7.09	8.80	9.65			
Еп(%С)	-21.78	-9.72	-9.28	-2.61	-1.53			
Conv(BOF)	56.47	65.37	74.00	79.11	84.81			
Conv(adj)	34.69	55.66	64.72	76.50	83.28			
H2 : DMS (molar)	117.94	117.22	121.57	120.66	121.41			
Yield BOF(%)								
1-Propanol	0.00	0.00	0.00	0.00	0.00			
iso-Propanol	8.97	15.73	18.76	22.69	26.99			
THF	1.08	0.99	0.98	1.04	1.04			
1-Butanol	13.38	20.09	22.96	27.20	30.43			
Methyl Butyrate	0.76	0.52	0.53	0.55	0.52			
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00			
1-Hex a noi	0.74	1.42	1.55	1.69	1.64			
GBL	2.57	0.30	0.24	0.00	0.00			
1,4-Butanediol	0.00	0.00	1.24	1.69	1.72			
1-Heptanol	0.00	2.04	2.04	2.18	0.00			
Others	7.19	14.56	16.41	19.47	20.94			
Selectivity(%)								
1-Propanol	0.00	0.00	0.00	0.00	0.00			
Iso-Propanol	32.62	38.28	38.84	39.78	43.29			
THF	3.93	2.41	2.03	1.82	1.67			
1-Butanol	48.65	48.89	47.54	47.69	48.81			
Methyl Butyrate	2.76	1.27	1.10	0.96	0.83			
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00			
1-Hexanol	2.69	3.46	3.21	2.96	2.63			
GBL	9.35	0.73	0.50	0.00	0.00			
1,4-Butanediol	0.00	0.00	2.57	2.96	2.76			
1-Heptanol	0.00	4.96	4.22	3.82	0.00			

	Catalyst	A8				
REPORT	R44.1	R44.2	R44.3	R44.4	R44.5	
Experiment Date	12/9/95	12/9/95	12/9/95	12/9/95	12/9/95	
Entry Date	12/12/95	12/12/95	12/12/95	12/12/95	12/12/95	•
P (psig)	500.00	600.00	750.00	900.00	1000.00	
T(Ĉ)	320.00	320.00	320.00	320.00	320.00	
RT(s)	6.24	7.11	9.25	11.07	11.60	
Еп(%С)	43.83	-16.34	-15.08	-2.02	-5.59	
Conv(BOF)	20.84	18.32	16.43	3.53	7.35	
Conv(adj)	205.29	1.98	1.35	1.51	1.76	
H2 : DMS (molar)	219.35	211.25	201.31	201.31	213.74	
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	
THF	1.62	0.00	0.00	0.00	0.00	
1-Butanol	0.00	0.00	0.00	0.00	0.00	
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00	
4-Methyi,1-Pentanoi	0.00	0.00	0.00	0.00	0.00	
1-Hex a nol	6.06	1.98	1.35	1.51	1.76	
GBL	0.00	0.00	0.00	0.00	0.00	
1,4-Butanediol	13.16	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	
Other s	0.00	0.00	0.00	0.00	0.00	
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	
THF	7.77	0.00	0.00	0.00	0.00	
1-Butanol	0.00	0.00	0.00	0.00	0.00	
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hex a nol	29.08	100.00	100.00	100.00	100.00	
GBL	0.00	0.00	0.00	0.00	0.00	
1,4-Butanediol	63.15	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	

	Catalyst	A8				
REPORT	R45.1	R45.2	R45.3	R45.4	R45.5	
Experiment Date	12/13/95	12/13/95	12/13/95	12/13/95	12/13/95	
Entry Date	4/13/96	4/13/96	4/13/96	4/13/96	4/13/96	
P (psig)	600.00	600.00	600.00	600.00	600.00	
T(C)	290.00	310.00	330.00	350.00	370.00	
RT(s)	6.30	5.86	5.67	5.74	5.50	
Еп(%С)	-8.85	-7.09	-3.61	-4.82	-12.90	
Conv(BOF)	8.85	7.09	6.25	9.48	18.75	
Conv(adj)	0.00	0.00	2.64	4.67	5.85	
H2 : DMS (molar)	212.81	210.11	212.91	198.82	205.95	
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	
THF	0.00	0.00	0.00	Ó. O O	0.00	
1-Butanol	0.00	0.00	0.00	0.69	1.24	
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	0.00	0.03	2.64	3.97	4.61	
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	
Others	0.00	0.00	0.00	0.00	0.00	
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	0.00	0.00	
THF	0.00	0.00	0.00	0.00	0.00	
1-Butanol	0.00	0.00	0.00	14.81	21.20	
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	0.00	100.00	100.00	85.19	78.80	
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	

Catalyst A10								
REPORT	R46 .1	R46.2	R46.3	R46.4	R46.5			
Experiment Date	12/15/95	12/15/95	12/15/95	12/15/95	12/15/95			
Entry Date	4/13/96	4/13/96	4/13/96	4/13/96	4/13/96			
P (osia)	500.00	600.00	750.00	900.00	1000.00			
T(C)	320.00	320.00	320.00	320.00	320.00			
RT(s)	4.76	6.09	6.92	8.75	9.83			
Еп(%С)	-12.38	-16.34	-13.51	-23.87	-19.53			
Conv(BOF)	99.24	97.67	98.45	98.71	99.16			
Conv(adj)	86.86	81.33	84.94	74.84	79.62			
H2 : DMS (molar)	211.86	191.02	215.24	200.68	200.23			
Yield BOF (%)								
1-Propanol	0.00	0.00	0.00	0.00	0.00			
iso-Propanol	2.02	1.76	1.65	1.46	1.31			
THF	13.66	13.64	14.99	14.34	13.87			
1-Butanol	15.06	13.14	13.64	12.23	11.99			
Methyl Butyrate	2.05	1.88	1.54	1.11	1.04			
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00			
1-Hexanol	0.00	0.00	0.00	0.00	0.00			
GBL	54.07	49.94	44.46	33.50	32.18			
1,4-Butanediol	0.00	0.00	7.40	11.11	18.11			
1-Heptanol	0.00	0.97	1.27	1.09	1.13			
Others	0.00	0.00	0.00	0.00	0.00			
Selectivity(%)								
1-Propanol	0.00	0.00	0.00	0.00	0.00			
Iso-Propanol	2.33	2.16	1.94	1.95	1.65			
THF	15.73	16.77	17.65	19.16	17.42			
1-Butanol	17.34	16.16	16.06	16.34	15.06			
Methyl Butyrate	2.36	2.31	1.81	1.48	1.31			
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00			
1-Hexanol	0.00	0.00	0.00	0.00	0.00			
GBL	62.25	61.40	52.34	44.76	40.41			
1,4-Butanediol	0.00	0.00	8.71	14.85	22.74			
1-Heptanol	0.00	1.19	1.49	1.46	1.42			

	Catalyst	A10				
REDORT	D474	D 47 0	D47.9	D47 4	D47 5	
REPORT	R47.1	R47.2	R47.3	R47.4	R47.5	
Experiment Date	12/1//95	12/1//95	12/1//95	12/1//95	12/17/95	
Entry Date	12/20/95	12/20/95	12/20/95	12/20/95	12/20/95	
	600.00	600.00			800.00	
P (psig)	000.00		800.00	220.00	250.00	
	270.00	290.00	310.00	330.00	350.00	
	7.85	7.50	7.28	7.23	5.77	
Em(%C)	-12.67	-10.89	-13.83	-12.60	-17.02	
Conv(BOF)	94.20	98.62	99.32	100.00	100.00	
Conv(adj)	81.53	87.73	85.49	87.40	82.98	
H2 : DMS (molar)	209.31	216.72	210.80	202.39	210.53	
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
iso-Propanol	0.00	0.00	0.00	1.97	5.14	
THF	7.45	9.95	13.78	22.89	28.39	
1-Butanol	0.70	2.44	8.11	21.53	34.97	
Methyl Butyrate	0.00	0.75	1.85	3.58	2.33	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	5.56	
GBL	46.95	52.60	54.37	37.06	6.60	
1,4-Butanediol	24.73	20.05	6.05	0.00	0.00	
1-Heptanol	1.70	1.95	1.33	0.36	0.00	
Others	0.00	0.00	0.00	0.00	0.00	
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
iso-Propanol	0.00	0.00	0.00	2.25	6.19	
THF	9.14	11.34	16.12	26.19	34.21	
1-Butanol	0.86	2.78	9.49	24.64	42.14	
Methyl Butyrate	0.00	0.85	2.16	4.10	2.81	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	6.70	
GBL	57.59	59.95	63.60	42.41	7.95	
1,4-Butanediol	30.33	22.85	7.08	0.00	0.00	
1-Heptanol	2.09	2.22	1.56	0.41	0.00	
-						

	Catalyst A	.10			
REPORT	R48.1	R48.2	R48.3	R48.4	
Experiment Date	1/3/96	1/3/96	1/3/96	1/3/96	
Entry D ate	1/5/96	1/5/96	1/5/96	1/5/96	
P (psig)	800.00	900.00	1000.00	1200.00	
T(C)	270.00	270.00	270.00	270.00	
RT(s)	9.14	10.01	11.13	13.33	
Епт(%С)	-12.16	10.70	10.82	6.24	
Conv(BOF)	92.85	98.31	96.28	92.55	
Conv(adj)	80.70	109.02	107.10	98.79	
H2 : DMS (molar)	205.23	202.99	210.24	210.58	
Yield BOF(%)					
1-Propanol	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	0.00	
THF	6.84	5.77	5.06	4.01	
1-Butanol	2.20	0.90	0.66	0.73	
Methyl Butyrate	0.00	0.00	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	38.03	36.81	35.31	29.18	
1,4-Butanediol	32.41	65.53	66.07	64.88	
1-Heptanol	1.23	0.00	0.00	0.00	
Others	0.00	0.00	0.00	0.00	
Selectivity(%)					
1-Propanol	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	0.00	
THF	8.47	5.29	4.72	4.06	
1-Butanoi	2.73	0.83	0.62	0.74	
Methyl Butyrate	0.00	0.00	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	47.12	33.77	32.97	29.53	
1,4-Butanediol	40.16	60.11	61.69	65.67	
1-Heptanol	1.52	0.00	0.00	0.00	

	Catalyst	A12				
REPORT	R49.1	R49.2	R49.3	R49.4	R49.5	
Experiment Date	1/9/96	1/9/96	1/9/96	1/9/96	1/9/96	
Entry Date	1/10/96	1/10/96	1/10/96	1/10/96	1/10/96	
P (psig)	700.00	800.00	900.00	1000.00	1100.00	
T(C)	270.00	270.00	270.00	270.00	270.00	
RT(s)	8.13	9.37	10.14	11.27	12.39	
Еп(%С)	3.60	-5.71	-6.73	-0.51	2.40	
Conv(BOF)	65.01	81.96	84.38	88.40	90.83	u .
Conv(adj)	68.61	76.25	77.65	87.89	93.23	:
H2 : DMS (molar)	201.01	20 0.71	218.29	205.82	209.02	
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
Iso-Propanol	1.13	1.19	1.00	0.91	0.85	
THF	26.94	29.99	26.94	27.04	28.82	
1-Butanol	1.25	1.21	1.18	1.24	1.38	
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hex a nol	0.00	0.00	0.00	0.00	0.00	
GBL	21.06	16.65	14.33	13.06	12.68	
1,4-Butanediol	2.69	6.90	13.35	24.44	27.18	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	
Others	15.52	20.31	20.85	21.21	22.32	
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00	0.00	
iso-Propanol	2.13	2.13	1.76	1.36	1.20	
THF	50.76	53.61	47.43	40.55	40.64	
1-Butanol	2.36	2.16	2.08	1.86	1.95	
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00	
4-Methyi,1-Pentanol	0.00	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	0.00	
GBL	39.68	29.76	25.23	19.58	17.88	
1,4-Butanediol	5.07	12.33	23.50	36.65	38.33	
1-Heptanol	0.00	0.00	0.00	0.00	0.00	

115

Catalyst -	XOA-400	support	
-			
R50.1	R50.2	R50.3	
1/15/96	1/15/96	1/15/96	
7/5/96	7/5/96	7/5/96	
600.00	800.00	1000.00	
270.00	270.00	270.00	
7.26	9.29	11.58	
-7.63	-1.96	-1.96	
7.63	1.96	1.96	
0.00	0.00	0.00	
187.83	205.38	198.65	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
0.00	0.00	0.00	
l ol	o	о	
o	ō	Ō	
l ol	0	0	
	0	0	
0	0	0	
o	0	0	
	0	0	
	0	0	
	0	0	
	0	0	
	R50.1 1/15/96 7/5/96 600.00 270.00 7.26 -7.63 7.63 0.00 187.83 0.00 0 0 0 0 0 0 0 0 0 0 0 0 0	Caranyst XOA-400 R50.1 R50.2 1/15/96 1/15/96 7/5/96 7/5/96 600.00 800.00 270.00 270.00 7.26 9.29 -7.63 -1.96 7.63 1.96 0.00 0.00 187.83 205.38 0.00 0.00 0 0	Caranyst - XOA-400 support R50.1 R50.2 R50.3 1/15/96 1/15/96 1/15/96 7/5/96 7/5/96 7/5/96 600.00 800.00 1000.00 270.00 270.00 270.00 7.26 9.29 11.58 -7.63 -1.96 -1.96 7.63 1.96 1.96 0.00 0.00 0.00 187.83 205.38 198.65 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00

	Catalyst	A11		
	-			
REPORT	R51.1	R51.2	R51.3	
Experiment Date	1/17/96	1/17/96	1/17/96	
Entry Date	4/13/96	4/13/96	4/13/96	
P (psig)	700.00	800.00	900.00	
T(C)	270.00	270.00	270.00	
RT(s)	8.48	9.66	10.98	
Еп(%С)	-0.77	13.92	6.20	
Conv(BOF)	90.12	97.78	98.67	
Conv(adj)	89.36	111.70	104.87	
H2 : DMS (molar)	202.26	202.73	200.23	
Viold POE(%)				
1 Propagol		0.00	0.00	
I-Propanol	0.00	0.00	0.00	
TUE	0.00	0.00	12.91	
	9.71	7.07	13.01	
I-Dularioi Mothyl Butyrata	2.30	2.50	0.07	
Methyl 1 Dentanol	0.00	0.00	0.00	
4-Meuryi, I-Fentanoi 1-Meyanol	0.00	0.00	0.00	
GRI	37 55	32.86	26 91	
1 A -Butanediol	39 15	67.63	56.31	
1,4 Buancalor	0.56	0.84	0.01	
Others	0.00	0.04	0.07	
	0.00	0.00	0.00	
Selectivity(%)				
1-Propanol	0.00	0.00	0.00	
Iso-Propanol	0.00	0.00	0.00	
THF	10.87	7.05	13.17	
1-Butanol	2.66	2.24	6.55	
Methyl Butyrate	0.00	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	
GBL	42.03	29.42	25.66	
1,4-Butanediol	43.82	60.55	53.70	
1-Heptanol	0.63	0.75	0.92	

REPORT	R52.1	R52.2	R52.3	R52.4	
Experiment Date	1/18/96	1/18/96	1/18/96	1/18/96	
Entry Date	1/29/96	1/29/96	1/29/96	1/29/96	
-					
P (psig)	600.00	600.00	600.00	600.00	
T(C)	250.00	270.00	290.00	310.00	
RT(s)	7.34	7.06	6.70	6.64	
Еп(%С)	-6.56	-0.61	-17.09	-14.62	
Conv(BOF)	40.41	58.63	93.87	100.00	
Conv(adj)	33.85	58.02	76.79	85.38	
H2 : DMS (molar)	206.80	205.38	190.88	195.85	
Yield BOF(%)					
1-Propanol	0.00	0.00	0.00	0.00	
Iso-Propanol	0.00	1.18	1.81	0.00	
THF	7.87	16.53	40.27	73.26	
1-Butanol	0.86	0.97	1.28	6.80	
Methyl Butyrate	0.00	0.00	0.00	0.29	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	16.39	21.01	18.79	2.98	
1,4-Butanediol	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	
Others	8.73	18.34	14.63	2.05	
Selectivity(%)					
1-Propanol	0.00	0.00	0.00	0.00	
iso-Propanol	0.00	2.97	2.91	0.00	
THF	31.33	41.65	64.79	87.92	
1-Butanol	3.42	2.44	2.06	8.16	
Methyl Butyrate	0.00	0.00	0.00	0.35	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	65.25	52.94	30.23	3.58	
1,4-Butanediol	0.00	0.00	0.00	0.00	
1-Heptanol	0.00	0.00	0.00	0.00	

Catalyst A11								
REPORT	R53 .1	R53.2	R53.3	R53.4				
Experiment Date	1/22/96	1/22/96	1/22/96	1/22/96				
Entry Date	4/13/96	4/13/96	4/13/96	4/13/96				
P (psig)	600.00	600.00	600.00	600.00				
T(C)	250.00	270.00	290.00	310.00				
RT(s)	7.62	7.23	6.5 9	6.51				
Еп(%С)	16.00	11.51	4.68	-15.49				
Conv(BOF)	78.25	97.14	99 .31	99.46				
Conv(adj)	94.25	108.65	103.99	83.98				
H2 : DMS (molar)	202.42	194.56	206.65	204.87				
Yield BOF(%)								
1-Propanol	0.00	0.00	0.00	0.00				
iso-Propanol	0.00	0.00	0.41	1.06				
THF	6.43	11.37	23.44	23.10				
1-Butanol	0.94	2.10	5.55	14.52				
Methyl Butyrate	1.41	0.00	0.38	0.76				
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00				
1-Hexanol	0.00	0.00	0.00	0.00				
GBL	37.31	46.90	43.99	32.80				
1,4-Butanediol	47.60	47.43	29.70	7.41				
1-Heptanol	0.55	0.84	0.51	0.31				
Others	0.00	0.00	0.00	4.03				
Selectivity(%)								
1-Propanol	0.00	0.00	0.00	0.00				
iso-Propanol	0.00	0.00	0.39	1.33				
THF	6.82	10.47	22.54	28.89				
1-Butanol	1.00	1.93	5.34	18.16				
Methyl Butyrate	1.50	0.00	0.37	0.95				
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00				
1-Hexanol	0.00	0.00	0.00	0.00				
GBL	39.59	43.17	42.31	41.02				
1,4-Butanediol	50.51	43.66	28.56	9.27				
1-Heptanol	0.58	0.77	0.49	0.39				

REPORT	R51.1	R51.2	R51.3	R51.4	
Experiment Date	2/4/96	2/4/96	2/4/96	2/4/96	
Entry Date	4/4/96	4/4/96	4/4/96	4/4/96	
P (psig)	600.00	800.00	900.00	1100.00	
T(C)	270.00	270.00	270.00	270.00	
RT(s)	6.83	9.19	10.45	12.72	
Епт(%С)	-5.20	14.63	16.45	20.16	
Conv(BOF)	62.45	56.62	71.84	76.89	
Conv(adj)	57.25	80.25	88.29	97.05	
H2 : DMS (molar)	119.31	121.01	121.06	119.07	
Yield BOF(%)					
1-Propanol	0.00	0.00	0.00	0.00	
iso-Propanol	1.30	0.81	0.53	0.39	
THF	8.76	7.21	5.25	5.70	
1-Butanol	0.70	0.57	0.44	0.50	
Methyl Butyrate	0.16	0.00	0.14	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
DMS	1.33	0.32	0.26	0.00	
1,4-Butanediol	40.23	65.17	76.17	85.05	
1-Heptanol	0.00	2.17	2.16	2.33	
Others	4.77	4.01	3.35	3.06	
Selectivity(%)					
1-Propanol	0.00	0.00	0.00	0.00	
iso-Propanol	2.48	1.06	0.62	0.42	
THF	16.69	9.46	6.18	6.07	
1-Butanol	1.33	0.75	0.52	0.53	
Methyl Butyrate	0.30	0.00	0.16	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
DMS	2.53	0.42	0.31	0.00	
1,4-Butanediol	76.66	85.47	89.66	90.51	
1-Heptanol	0.00	2.85	2.54	2.48	

	Catalyst	A11			
REPORT	R55.1	R55.2	R55.3	R55.4	
Experiment Date	2/4/96	2/4/96	2/4/96	2/4/96	
Entry Date	4/4/96	4/4/96	4/4/96	4/4/96	
-					
P (psig)	600.00	800.00	900.00	1100.00	
T(C)	270.00	270.00	270.00	270.00	
RT(s)	7.28	9.57	10.48	12.78	
Еп(%С)	10.96	13.29	15.54	15.31	
Conv(BOF)	53.02	62.42	69 .75	76.53	
Conv(adj)	63.97	75.71	85.29	91.84	
H2 : DMS (molar)	108.69	116.17	114.97	116.69	
Yield BOF(%)					
1-Propanol	0.00	0.00	0.00	0.00	
Iso-Propanol	0.24	0.00	0.00	0.00	
THE	5.50	5.56	4.30	4.43	
1-Butanoi	1.86	1.81	0.70	1.73	
Methyl Butyrate	0.24	0.00	0.00	0.00	
4-Methyl.1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
DMS	0.00	0.00	0.00	0.00	
1.4-Butanediol	52.44	65.48	78.07	83.54	
1-Heptanol	0.35	0.66	0.89	0.65	
Others	3.36	2.21	1.33	1.50	
Selectivity(%)					
1-Propanol	0.00	0.00	0.00	0.00	- - -
iso-Propanol	0.40	0.00	0.00	0.00	
THF	9.07	7.56	5.12	4.90	
1-Butanol	3.07	2.46	0.83	1.91	
Methyl Butyrate	0.40	0.00	0.00	0.00	
4-Methyi,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
DMS	0.00	0.00	0.00	0.00	
1,4-Butanediol	86.49	89.08	92.98	92.46	
1-Heptanol	0.58	0.90	1.06	0.72	

121

	Catalyst	A11			
REPORT	R56.1	R56.2	R56.3	R56.4	
Experiment Date	3/23/96	3/23/96	3/23/96	3/23/96	
Entry Date	3/25/96	3/25/96	3/25/96	3/25/96	
P (psig)	1200.00	1200.00	1200.00	1200.00	
T(C)	250.00	270.00	290.00	310.00	
RT(s)	14.67	13.35	13.30	12.84	
Err(%C)	63.23	27.52	5.71	-10.94	
Conv(BOF)	99.42	100.00	98.68	99 .02	
Conv(adj)	162.66	127.52	104.39	88.07	
H2 : DMS (molar)	211.98	231.00	214.60	214.60	
Yield BOF(%)					
1-Propanol	0.00	0.00	0.00	0.00	
iso-Propanol	0.00	0.00	0.00	0.96	
THF	1. 6 9	4.60	12.03	20.76	
1-Butanol	0.00	1.04	4.87	11.21	
Methyl Butyrate	0.00	0.00	0.00	0.00	
4-Methyi,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	19.92	14.11	17.89	16.40	
1,4-Butanediol	135.65	101.69	69.60	29.86	
1-Heptanol	0.00	0.00	0.00	0.00	
Others	5.40	6.08	0.00	8.87	
Selectivity(%)					
1-Propanol	0.00	0.00	0.00	0.00	
iso-Propanoi	0.00	0.00	0.00	1.21	
THF	1.07	3.79	11.52	26.22	
1-Butanol	0.00	0.86	4.67	14.16	
Methyl Butyrate	0.00	0.00	0.00	0.00	
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	
1-Hexanol	0.00	0.00	0.00	0.00	
GBL	12.67	11.62	17.14	20.71	
1,4-Butanediol	86.26	83.74	6 6.67	37.71	
1-Heptanol	0.00	0.00	0.00	0.00	

Table B.40 - Run #57 Report

Catalyst A11						
REPORT	R57.1	R57.2	R57.3	R57.4		
Experiment Date	4/5/96	4/5/96	4/5/96	4/5/96		
Entry Date	4/6/96	4/6/96	4/6/96	4/6/96		
-						
P (psig)	1200.00	1200.00	1200.00	1200.00		
T(C)	210.00	230.00	250.00	270.00		
RT(s)	16.01	15.07	14.66	14.10		
Еп(%С)	2.21	13.00	10.06	14.96		
Conv(BOF)	87.43	72.36	95.01	97.96		
Conv(adj)	89.64	85.36	105.07	112.91		
H2 : DMS (molar)	314.25	202.02	196.20	193.38		
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00		
Iso-Propanol	0.00	0.00	0.00	0.00		
THF	1.10	1.19	2.25	6.46		
1-Butanol	1.12	0.00	0.00	1.22		
Methyl Butyrate	0.00	0.00	0.00	0.00		
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00		
1-Hex a nol	0.00	0.00	0.00	0.00		
GBL	11.57	11.28	14.59	14.80		
1,4-Butanediol	74.83	72.01	87.25	89.19		
1-Heptanol	1.03	0.87	0.98	1.26		
Others	0.00	0.00	0.00	0.00		
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00		
Iso-Propanol	0.00	0.00	0.00	0.00		
THF	1.23	1.39	2.14	5.72		
1-Butanol	1.25	0.00	0.00	1.08		
Methyl Butyrate	0.00	0.00	0.00	0.00		
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00		
1-Hexanol	0.00	0.00	0.00	0.00		
GBL	12.91	13.22	13.89	13.11		
1,4-Butanediol	83.47	84.37	83.04	78.98		
1-Heptanol	1.15	1.02	0.93	1.12		

Catalyst A13						
REPORT	R58 .1	R58.2	R58.3	R58.4		
Experiment Date	6/13/96	6/13/96	6/13/96	6/13/96		
Entry Date	6/14/96	6/14/96	6/14/96	6/14/96		
P (psig)	1200.00	1200.00	1200.00	1200.00		
T(Ĉ)	230.00	250.00	270.00	290.00		
RT(s)	15.93	15.35	15.02	14.79		
Еп(%С)	-7.86	2.71	13.23	-18.36		
Conv(BOF)	8.76	55.68	93.39	99 .10		
Conv(adj)	0.90	58.39	106.62	80.72		
H2 : DMS (molar)	204.80	212.39	228.76	401.41		
Yield BOF(%)						
1-Propanol	0.00	0.00	0.00	0.00		
Iso-Propanol	0.00	0.00	0.00	0.00		
THF	0.00	1.45	3.84	10.43		
1-Butanol	0.00	0.00	0.00	5.30		
Methyl Butyrate	0.00	0.00	0.00	0.00		
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00		
1-Hexanol	0.00	0.00	0.00	0.00		
GBL	0.90	10.45	16.82	18.53		
1,4-Butanediol	0.00	46.49	84.53	46.11		
1-Heptanol	0.00	0.00	1.43	0.36		
Others	0.00	0.00	0.00	0.00		
Selectivity(%)						
1-Propanol	0.00	0.00	0.00	0.00		
iso-Propanol	0.00	0.00	0.00	0.00		
THF	0.00	2.48	3.60	12.92		
1-Butanol	0.00	0.00	0.00	6.57		
Methyl Butyrate	0.00	0.00	0.00	0.00		
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00		
1-Hexanol	0.00	0.00	0.00	0.00		
GBL	100.00	17.90	15.78	22.95		
1,4-Butanediol	0.00	79.62	79.28	57.12		
1-Heptanoi	0.00	0.00	1.34	0.45		

REPORT Experiment Date 6/19/96 7/10 200.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00		Catalyst	A14						
Experiment Date 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/19/96 6/22/96 7/23 1200.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00 1201.00	REPORT								
Entry Date 6/22/96 6/22/96 6/22/96 6/22/96 P (psig) 1200.00 1200.00 1200.00 1200.00 1200.00 T(C) 230.00 250.00 270.00 290.00 RT(s) 15.85 14.87 14.55 13.88 Err(%C) -12.00 -16.37 -10.29 -21.18 Conv(BOF) 29.15 53.57 91.08 98.41 Conv(adi) 17.15 37.20 80.79 75.23 H2 : DMS (molar) 238.94 155.13 200.40 204.64 Yield BOF(%)	Experiment Date	6/19/96	6/19/96	6/19/96	6/19/96				
P (psig) 1200.00 1200.00 1200.00 1200.00 T(C) 230.00 250.00 270.00 290.00 RT(s) 15.85 14.87 14.55 13.88 Err(%C) -12.00 -16.37 -10.29 -21.18 Conv(BOF) 29.15 53.57 91.08 96.41 Conv(adj) 17.15 37.20 80.79 75.23 H2 : DMS (molar) 238.94 155.13 200.40 204.64 Yield BOF(%) - - - - 1-Propanol 0.00 0.00 0.00 0.00 1so-Propanol 0.00 0.00 0.00 0.00 1-Butanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 4-Methyl, 1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 1.38 1-Heytanol 0.00 0.00 0.00	Entry Date	6/22/96	6/22/96	6/22/96	6/22/96				
P (psig) 1200.00 1200.00 1200.00 1200.00 T(C) 230.00 250.00 270.00 290.00 RT(s) 15.85 14.87 14.55 13.88 Err(%C) -12.00 -18.37 -10.29 -21.18 Conv(BOF) 29.15 53.57 91.08 96.41 Conv(adj) 17.15 37.20 80.79 75.23 H2 : DMS (molar) 238.94 155.13 200.40 204.64 Yield BOF(%)									
T(C) 230.00 250.00 270.00 290.00 RT(s) 15.85 14.87 14.55 13.88 Err(%C) -12.00 -16.37 -10.29 -21.18 Conv(BOF) 29.15 53.57 91.06 96.41 Conv(adj) 17.15 37.20 80.79 75.23 H2 : DMS (molar) 238.94 155.13 200.40 204.64 Yield BOF(%) 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 1.58 Methyl Butyrate 0.00 0.00 0.00 0.00 Hexanol 0.00 0.00 0.00 0.00 Hexanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1.4-Butanediol 5.62 20.36 60.97 47.91 1.4-Hexanol 0.00 0.00 0.00 0.00 0.00 Selectivity(%) 1 1 1 1.7	P (psig)	1200.00	1200.00	1200.00	1200.00				
RT(s) 15.85 14.87 14.55 13.88 Err(%C) -12.00 -16.37 -10.29 -21.18 Conv(BOF) 29.15 53.57 91.08 96.41 Conv(adj) 17.15 37.20 80.79 75.23 H2 : DMS (molar) 238.94 155.13 200.40 204.84 Yield BOF(%)	T(C)	230.00	250.00	270.00	290.00				
Err(%C) -12.00 -16.37 -10.29 -21.18 Conv(BOF) 29.15 53.57 91.08 96.41 Conv(adj) 17.15 37.20 80.79 75.23 H2 : DMS (molar) 238.94 155.13 200.40 204.64 Yield BOF(%) 0.00 0.00 0.00 0.00 1-Propanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 THF 0.47 0.86 2.32 3.46 1-Butanol 0.00 0.00 0.00 0.00 4-Methyl I-Pentanol 0.00 0.00 0.00 0.00 4-Methyl, 1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1.4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.00 0.00 0.00 Selectivity(%) 1 1.79 2.31 2.87	RT(s)	15.85	14.87	14.55	13.88				
Conv(BOF) 29.15 53.57 91.08 96.41 Conv(adj) 17.15 37.20 80.79 75.23 H2 : DMS (molar) 238.94 155.13 200.40 204.64 Yield BOF(%)	Еп(%С)	-12.00	-16.37	-10.29	-21.18				
Conv(adj) 17.15 37.20 80.79 75.23 H2 : DMS (molar) 238.94 155.13 200.40 204.64 Yield BOF(%) 0 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 1.58 Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00	Conv(BOF)	29.15	53.57	91.08	96.41				
H2 : DMS (molar) 238.94 155.13 200.40 204.64 Yield BOF(%) 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 THF 0.47 0.86 2.32 3.46 1-Butanol 0.00 0.00 0.00 0.00 4-Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1.4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1.4-Botanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00	Conv(adj)	17.15	37.20	80.79	75.23				
Yield BOF(%) 0.00 0.00 0.00 0.00 0.00 1-Propanol 0.00 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 0.00 1-Butanol 0.00 0.00 0.00 1.58 Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.00 0.00 0.00 Selectivity(%)	H2 : DMS (molar)	238.94	155.13	200.40	204.64				
1-Propanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 THF 0.47 0.86 2.32 3.46 1-Butanol 0.00 0.00 0.00 1.58 Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl, 1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1.4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.00 0.00 0.00 Selectivity(%)	Yield BOF(%)								
Iso-Propanol 0.00 0.00 0.00 0.00 THF 0.47 0.86 2.32 3.46 1-Butanol 0.00 0.00 0.00 1.58 Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.53 1.38 1.79 Others 0.00 0.00 0.00 0.00 Selectivity(%)	1-Propanol	0.00	0.00	0.00	0.00				
THF 0.47 0.86 2.32 3.46 1-Butanol 0.00 0.00 0.00 1.58 Methyl Butyrate 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.53 1.38 1.79 Others 0.00 0.00 0.00 0.00 Selectivity(%)	Iso-Propanol	0.00	0.00	0.00	0.00				
1-Butanol 0.00 0.00 0.00 1.58 Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.00 0.00 0.00 Others 0.00 0.00 0.00 0.00 Selectivity(%)	THF	0.47	0.86	2.32	3.46				
Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.53 1.38 1.79 Others 0.00 0.00 0.00 0.00 Selectivity(%)	1-Butanol	0.00	0.00	0.00	1.58				
4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.53 1.38 1.79 Others 0.00 0.00 0.00 0.00 Selectivity(%)	Methyl Butyrate	0.00	0.00	0.00	0.00				
1-Hexanol 0.00 0.00 0.00 GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.53 1.38 1.79 Others 0.00 0.00 0.00 0.00 Selectivity(%)	4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00				
GBL 11.06 15.45 16.13 20.49 1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.53 1.38 1.79 Others 0.00 0.00 0.00 0.00 Selectivity(%)	1-Hex a nol	0.00	0.00	0.00	0.00				
1,4-Butanediol 5.62 20.36 60.97 47.91 1-Heptanol 0.00 0.53 1.38 1.79 Others 0.00 0.00 0.00 0.00 Selectivity(%)	GBL	11.06	15.45	16.13	20.49				
1-Heptanol 0.00 0.53 1.38 1.79 Others 0.00 0.00 0.00 0.00 Selectivity(%)	1,4-Butanediol	5.62	20.36	60.97	47.91				
Others 0.00 0.00 0.00 0.00 Selectivity(%)	1-Heptanol	0.00	0.53	1.38	1.79				
Selectivity(%) I	Others .	0.00	0.00	0.00	0.00				
1-Propanol 0.00 0.00 0.00 0.00 Iso-Propanol 0.00 0.00 0.00 0.00 THF 2.73 2.31 2.87 4.61 1-Butanol 0.00 0.00 0.00 2.10 Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 64.48 41.53 19.96 27.24 1,4-Butanediol 32.79 54.74 75.47 63.68 1-Heptanol 0.00 1.42 1.70 2.38	Selectivity(%)								
Iso-Propanol 0.00 0.00 0.00 0.00 THF 2.73 2.31 2.87 4.61 1-Butanol 0.00 0.00 0.00 2.10 Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 64.48 41.53 19.96 27.24 1,4-Butanediol 32.79 54.74 75.47 63.68 1-Heptanol 0.00 1.42 1.70 2.38	1-Propanol	0.00	0.00	0.00	0.00				
THF2.732.312.874.611-Butanol0.000.000.002.10Methyl Butyrate0.000.000.000.004-Methyl,1-Pentanol0.000.000.000.001-Hexanol0.000.000.000.00GBL64.4841.5319.9627.241,4-Butanediol32.7954.7475.4763.681-Heptanol0.001.421.702.38	iso-Propanol	0.00	0.00	0.00	0.00				
1-Butanol 0.00 0.00 0.00 2.10 Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 64.48 41.53 19.96 27.24 1,4-Butanediol 32.79 54.74 75.47 63.68 1-Heptanol 0.00 1.42 1.70 2.38	THF	2.73	2.31	2.87	4.61				
Methyl Butyrate 0.00 0.00 0.00 0.00 4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 0.00 GBL 64.48 41.53 19.96 27.24 1,4-Butanediol 32.79 54.74 75.47 63.68 1-Heptanol 0.00 1.42 1.70 2.38	1-Butanol	0.00	0.00	0.00	2.10				
4-Methyl,1-Pentanol 0.00 0.00 0.00 0.00 1-Hexanol 0.00 0.00 0.00 0.00 GBL 64.48 41.53 19.96 27.24 1,4-Butanediol 32.79 54.74 75.47 63.68 1-Heptanol 0.00 1.42 1.70 2.38	Methyl Butyrate	0.00	0.00	0.00	0.00				
1-Hexanol0.000.000.000.00GBL64.4841.5319.9627.241,4-Butanediol32.7954.7475.4763.681-Heptanol0.001.421.702.38	4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00				
GBL64.4841.5319.9627.241,4-Butanediol32.7954.7475.4763.681-Heptanol0.001.421.702.38	1-Hex a nol	0.00	0.00	0.00	0.00				
1,4-Butanediol32.7954.7475.4763.681-Heptanol0.001.421.702.38	GBL	64.48	41.53	19.96	27.24				
1-Heptanol 0.00 1.42 1.70 2.38	1,4-Butanediol	32.79	54.74	75.47	63.68				
	1-Heptanol	0.00	1. 42	1.70	2.38				
Catalyst A15									
---------------------	----------------	---------	---------------	---------------------------------------	--	--	--	--	--
REPORT	R60.1	R60.2	R60.3	R60.4					
Experiment Date	7/1/96	7/1/96	7/1/96	7/1/96					
Entry Date	7/3/96	7/3/96	7/3/96	7/3/96					
-									
P (psig)	1200.00	1200.00	1200.00	1200.00					
T(C)	230.00	250.00	270.00	290.00					
RT(s)	15. 6 0	15.34	14.45	13.8 9					
Еп(%С)	-1.55	-11.87	-7.35	-4.42					
Conv(BOF)	1.96	23.82	60.68	83.23					
Conv(adj)	0.42	11.95	53.32	78.81					
H2 : DMS (molar)	216.92	209.96	219.84	202.27					
Yield BOF(%)				· · · · · · · · · · · · · · · · · · ·					
1-Propanol	0.00	0.00	0.00	0.00					
Iso-Propanol	0.00	0.00	0.00	0.00					
THF	0.42	0.37	1.28	2.41					
1-Butanol	0.00	0.00	0.00	0.00					
Methyl Butyrate	0.00	0.00	0.00	0.00					
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00					
1-Hexanol	0.00	0.00	0.00	0.00					
GBL	0.00	11.58	19.22	25.24					
1,4-Butanediol	0.00	0.00	31.70	50.48					
1-Heptanol	0.00	0.00	1.12	0.68					
Others .	0.00	0.00	0.00	0.00					
Selectivity(%)									
1-Propanol	0.00	0.00	0.00	0.00					
Iso-Propanol	0.00	0.00	0.00	0.00					
THF	100.00	3.10	2.40	3.06					
1-Butanol	0.00	0.00	0.00	0.00					
Methyl Butyrate	0.00	0.00	0.00	0.00					
4-Methyi,1-Pentanol	0.00	0.00	0.00	0.00					
1-Hexanol	0.00	0.00	0.00	0.00					
GBL	0.00	96.90	36.05	32.03					
1,4-Butanediol	0.00	0.00	59.45	64.05					
1-Heptanol	0.00	0.00	· 2.10	0.86					

Catalyst A12									
REPORT	R60.1	R60.2	R60.3	R60.4					
Experiment Date	7/2/96	7/2/96	7/2/96	7/2/96	7/2/96				
Entry Date	7/3/96	7/3/96	7/3/96	7/3/96	7/3/96				
-									
P (psig)	600.00	600.00	600.00	600.00	600.00				
T(C)	270.00	290.00	310.00	330.00	350.00				
RT(s)	7.12	6.94	6.54	6.32	6.34				
Еп(%С)	-1.75	-7.10	-14.13	-6.77	-3.08				
Conv(BOF)	76.30	98.22	100.00	100.00	100.00				
Conv(adj)	74.55	91.13	85.87	93.23	96.92				
H2 : DMS (molar)	207.33	201.55	200.27	198.57	196.20				
Vield BOF(%)				· · · · · · · · · · · · · · · · · · · ·					
1-Propanol	0.00	0.00	0.00	0.00	0.00				
Iso-Propanol	1.80	2,10	0.00	0.00	0.00				
тнғ	29.59	52.35	77.57	84.30	85.58				
1-Butanol	1.21	2.04	5.74	8.94	11.33				
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00				
4-Methyl.1-Pentanol	0.00	0.00	0.00	0.00	0.00				
1-Hexanol	0.00	0.00	0.00	0.00	0.00				
GBL	20.64	15.81	0.00	0.00	0.00				
1.4-Butanediol	0.00	0.00	0.00	0.00	0.00				
1-Heptanol	0.00	0.00	0.00	0.00	0.00				
Others	21.31	18.83	2.56	0.00	0.00				
Selectivity(%)									
1-Propanol	0.00	0.00	0.00	0.00	0.00				
iso-Propanol	3.38	2.90	0.00	0.00	0.00				
THF	55.58	72.41	93.11	90.41	88.31				
1-Butanol	2.27	2.82	6.89	9.59	11.69				
Methyl Butyrate	0.00	0.00	0.00	0.00	0.00				
4-Methyl,1-Pentanol	0.00	0.00	0.00	0.00	0.00				
1-Hexanol	0.00	0.00	0.00	0.00	0.00				
GBL	38.77	21.87	0.00	0.00	0.00				
1,4-Butanediol	0.00	0.00	0.00	0.00	0.00				
1-Heptanol	0.00	0.00	0.00	0.00	0.00				

LIST OF REFERENCES

LIST OF REFERENCES

- 1. Ng, T.K., R.M. Busche, C.C. McDonald, R.W.F. Hardy, Science, 219, 733-740 (1983).
- 2. Datta, R., Biotech. Bioeng. Symp., No:11, 521-532, John Wiley and Sons, Inc. (1981).
- 3. Datta, R., Biotechnol. Bioeng., 23, 2167 (1981).
- 4. Levy, P.F., J.E. Sanderson, R.G. Kispert, D.L. Wise, *Enzyme Microb. Technol.*, 3, 207-215 (1981).
- 5. Zeikus, J.G., Ann. Rev. Micrbiol., 34, 423-464 (1980).
- 6. Jain, M.K., R. Datta, J.G. Zeikus, "Bioprocess Engineering, The First Generation", V, Ch. 25, 366-389, Ellis Horwood Ltd. (1989).
- 7. Arora, D.K., R.P. Elander, K.G. Mukerji, Eds., "Handbook of Applied Mycology Fungal Biotechnology", 4, Ch. 14, 357-375, Marcel Dekker, Inc. (1992).
- 8. Young, J.K., J.J. Eberhardt, E.A. Griffin, Applied Biochemistry and Biotechnology, 20/21, 339-355 (1989).
- 9. Busche, R.M., Biotechnology Progress, 1, No: 3, 165-180 (1985).
- 10. Kovały, K.A., Chemtech, August, 486-489 (1982).
- 11. Sidkar, S.K., M. Bier, P. Todd, Eds., "Frontiers in Biopreocessing", Ch. 1, 1-13, CRC Press, Inc. (1990).
- 12. Mark, H.F., D.F. Othmer, C.G., Overberger, G.T. Seaborg, Eds., *Encyclopedia of Chemical Technology*, 3rd Edn., 21, 848-864, John Wiley and Sons (1981).
- 13. Furukawa, T., (Mitsui Petrochem. Ind., Ltd.), Jpn Kokai 73 26,982 (1973).

128

- 14. Yumimoto, S., and co-workers, (Ajinomoto Co., Ltd.), Jpn Kokkai 75 63,190 (1975).
- 15. Chemical Marketing Reporter, 249, No. 9 (1996).
- 16. Zeikus, J.G., P. Elankovan, A. Grethlein, Chemical Processing, July, 71-73 (1995).
- 17. Stobbe H., Ber., 26, 2312 (1893).
- 18. Johnson, W.S., G.H. Daub, Eds., "Organic Reactions", VI, 2-73, John Wiley and Sons, N.Y. (1951).
- 19. El-Hashash, M.A., M.M. Mohammed, F.A. Sayed, O.A. Abo-Baker, Indian J. Chem, 19B, 107-111 (1980).
- 20. Neelima, A.P. Bhaduri, Indian J. Chem, 23B, 209-215 (1984).
- 21. Banerjee, S., G. Bagavant, Indian J. Chem, 20B, 362-365 (1981).
- 22. El-Khamry, A.A., M.A. El-Hashash, M.M. Habashy, Revue Roumaine de Chimie, 25, 4, 563-569 (1980).
- 23. Mark, H.F., D.F. Othmer, C.G., Overberger, G.T. Seaborg, Eds., *Encyclopedia of Chemical Technology*, 3rd Edn., 19, 510-520, John Wiley and Sons (1981).
- 24. Hollstein, E.J., W.A. Butte, (Sun Research and Development Co.), USP 3,812,148 (1974).
- 25. Hollstein, E.J., (Sun Research and Development Co.), USP 3,812,149 (1974).
- 26. Matson, M.S., (Phillips Petroleum Co.), USP 4,904,804 (1990).
- 27. Brownstein, A.M., Chemtech, August, 506-510 (1991).
- 28. Tanabe, Y., Hydrocarbon Processing, 60, No. 9, 187-190 (1981).
- 29. Mark, H.F., D.F. Othmer, C.G., Overberger, G.T. Seaborg, Eds., *Encyclopedia of Chemical Technology*, 3rd Edn., 17, 199-257, John Wiley and Sons (1981).
- 30. Sharif, M., K. Turner, (Davy Mckee (London) Ltd.) USP 4,584,419 (1986).
- 31. Suzuki, S., H. Ueno, (Tonen Corporation) USP 4,977,284 (1990).

- 32. Suzuki, S., H. Ueno, (Tonen Corporation) USP 5,037,996 (1991).
- 33. Hara, Y., H. Inagaki (Mitsubishi Kasei Corporation) USP 5,077,442 (1991).
- 34. Turner, K., and co-workers, (Davy Mckee (London) Ltd.), WO 86 03,189 (1986).
- 35. Kouba, J.K., A. Zletz, (Standard Oil Company (Indiana)), USP 4,613,707 (1986).
- 36. Narasimhan, C.S., V.M. Deshpande, K. Ramnarayan, (Iel Ltd.) IN 168,627 (1991).
- 37. Thomas, W. D., P.D. Taylor, (GAF Corporation), USP 4,797,382 (1989).
- 38. Monti, D.M., M.S. Wainwright, D.L. Trimm, Ind. Eng. Chem. Prod. Res. Dev., 24, 397-401 (1985).
- 39. Monti, D.M., N.W. Cant, D.L. Trimm, M.S. Wainwright, J. Catal., 100, 17-27 (1986).
- 40. Kohler, M.A., M.S. Wainwright, D.L. Trimm, Ind. Eng. Chem. Res., 26, 652-656 (1987).
- 41. Turek, T., D.L. Trimm, D. StC. Black, N.W. Cant, Appl. Catal., 116, 137-150 (1994).
- 42. Thomas, D.J., M.R. Stammbach, N.W. Cant, M.S. Wainwright, D.L. Trimm, Ind. Eng. Chem. Res., 29, 204-208 (1990).
- 43. Mark, H.F., D.F. Othmer, C.G., Overberger, G.T. Seaborg, Eds., *Encyclopedia of Chemical Technology*, 4th Edn., 1, 195-230, John Wiley and Sons (1993).

