

un
DVORSCAK
Patented
8

8-27-97

**DEVELOPMENT OF A CATALYST FOR CONVERSION OF
SYNGAS-DERIVED MATERIALS TO ISOBUTYLENE**

DOE/PC/90042--T20
FINAL

prepared for
**The U. S. Department of Energy
Pittsburgh Energy Technology Center**

under
Contract No. DE-AC22-91PC90042

We have no objection from a patent
standpoint to the publication or
dissemination of this material.

M. Dvorscak Aug 27, 1997
Office of Intellectual Date
Property Counsel
DOE Field Office, Chicago

prepared by
P. T. Barger, B. C. Spehlmann and G. J. Gajda
UOP
Des Plaines, Illinois

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

October 1996

**CLEARED BY
PATENT COUNSEL**

97 AUG 26 8:22

RECEIVED

U. S. DEPARTMENT OF ENERGY
I.P.C.

MASTER

15 OCT 29 AM 10:54

RECEIVED
1500E/PETC

U. S. ASSISTANCE DIV.

AD
Zim

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

TABLE OF CONTENTS

TABLE OF CONTENTS	i
LIST OF TABLES	iv
LIST OF FIGURES	vii
EXECUTIVE SUMMARY	viii
1 OBJECTIVES	1
2 INTRODUCTION	3
2.1 Utilization of Higher Branched Alcohols (Isobutanol)	3
2.1.1 Current Production and Utilization of Isobutanol	4
2.1.2 Isobutanol Dehydration to Isobutylene	4
2.1.3 Isobutyraldehyde Hydrogenation to Isobutanol	5
2.2 Formation of Higher Branched Alcohols from Synthesis Gas	5
2.2.1 Alkali Modified Methanol Synthesis Catalysts	6
2.2.2 Noble Metal on Zn/Mn/Zr Oxide Catalysts	7
2.2.3 Proposed Reaction Mechanisms	8
2.3 Formation of Higher Branched Alcohols from Light Alcohols	9
2.3.1 Condensation of Mixtures of Methanol, Ethanol and Propanol	9
2.3.2 Condensation of Methanol Only	10
2.4 Basic Metal Oxides	10
2.5 Direct Conversion of Synthesis Gas to Isobutylene (Isosynthesis)	11
3 EXPERIMENTAL SUMMARY	13
3.1 Catalyst Identification and Reaction Mechanism (Task 1)	14
3.1.1 Pilot Plant Descriptions	15
3.1.1.1 Pilot Plant for CO/H ₂ Conversion to Higher Alcohols	15
3.1.1.2 Blank Runs with CO/H ₂ Feed	16
3.1.1.3 Pilot Plant for Conversion of Methanol and Methanol/Ethanol to Higher Alcohols	16
3.1.1.4 Blank Runs with Methanol and Methanol/Ethanol Feeds	17

3.3.4	H ₂ , CO and CO ₂ Co-Feeds	35
3.4	Pilot Plant Demonstrations (Task 3)	36
3.4.1	Methanol-Only Conversion over Pt on Zn/Mn/Zr Oxide Catalysts	36
3.4.2	Demonstration of Optimum Conditions for Methanol/Ethanol Conversion to Higher Alcohols with 2% Pt on Zn/Mn/Zr Oxide Catalyst	38
3.4.3	Methanol/Ethanol Conversion with High H ₂ Co-feed	39
3.5	Economic Evaluation (Task 5)	40
3.5.1	Summary of Process Variable Studies/Optimum Conditions Obtained Experimentally	40
3.5.2	Modeling of a Commercial Isobutanol Synthesis Plant	40
3.5.3	Basis for Capital Cost Estimate	41
3.5.4	Process Simulation Results	42
3.5.5	Vent Loss Study	43
3.5.6	Economic Analysis	44
3.5.6.1	Overview of Methodology	44
3.5.6.2	Utility and Other Operating Costs	44
3.5.6.3	Base Case Economic Study and Other Cases Considered	45
3.5.6.4	Conclusions of the Economic Analysis	46
3.6	Direct Conversion of Synthesis Gas to Isobutylene (Isosynthesis)	46
4	CONCLUSIONS AND RECOMMENDATIONS	49
5	TABLES	53
6	FIGURES	113
7	APPENDIX	139
8	REFERENCES	143

LIST OF TABLES (con't.)

Table 29.	Effect of Noble Metal Loading on Performance - Pt on Zn/Mn/Zr Oxide Catalysts
Table 30.	Effect of Noble Metal Loading on Performance - 0.5% and 2% Pt on Zn/Mn/Zr Oxide Catalysts
Table 31.	Pilot Plant Performance of Large-Scale Preparation of 2% Pt on Zn/Mn/Zr Oxide Catalyst
Table 32.	Effect of Process Variables on Performance of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion
Table 33.	Effect of H ₂ , CO and CO ₂ Co-Feeds on Performance of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion
Table 34.	Conversion of Methanol Only Using Pt on Zn/Mn/Zr Oxide Catalysts
Table 35.	Conversion of Methanol Only at High Temperature and Pressure
Table 36.	Evaluation of Pt on Zn/Mn/Zr Oxide Catalyst for Methanol/Ethanol Conversion at High H ₂ Partial Pressures - Plant 700, Run 326
Table 37.	Modeling of Higher Alcohols Synthesis Process
Table 38.	Isobutanol Process - Performance vs. Separator Temperature
Table 39.	Isobutanol Process - Material Balance
Table 40.	Isobutanol Process - Summary of Utility Streams
Table 41.	Calculation of Utility Requirements
Table 42.	Utility Cost Basis
Table 43.	Calculation of the Total Annual Utility Costs
Table 44.	Basis for Economic Calculations
Table 45.	Base Case Economics for Methanol to Isobutanol
Table 46.	Summary of Economic Cases
Table 47.	Basis for Economic Analysis
Table 48.	Isosynthesis Catalyst List
Table 49.	Isosynthesis Run Summary
Table 50.	Effect of Catalyst Calcination Temperature and Surface Area
Table 51.	Effect of Additives to Zirconia Catalysts on Isobutylene Yield

LIST OF TABLES (con't.)

Table 52.	Non-Zirconia Catalysts
Table 53.	Effect of Intermediate Recycle
Table 54.	Effect of Pressure
Table 55.	Effect of Temperature
Table 56.	Effect of Space Velocity
Table 57.	Effect of H ₂ /CO Ratio

LIST OF FIGURES

- Figure 1. Reaction Mechanism
- Figure 2. Reaction Mechanism
- Figure 3. Comparison of Brucite and Hydrotalcite
- Figure 4. Plant Diagram
- Figure 5. Plant Diagram
- Figure 6. Cu/Zn/Al Oxide Performance vs. Space Time
- Figure 7. Cu/Zn/Al Oxide Performance vs. Space Time
- Figure 8. Pd on Zn/Mn/Zr Oxide Performance vs. Space Time
- Figure 9. Pd on Zn/Mn/Zr Oxide Performance vs. Space Time
- Figure 10. Pt on Zn/Mn/Zr Oxide Performance vs. Space Time
- Figure 11. Pt on Zn/Mn/Zr Oxide Performance vs. Space Time
- Figure 12. Pt on Zn/Mn/Zr Oxide Performance vs. Space Time
- Figure 13. Pd on Zn/Mn/Cr Oxide Performance vs. Space Time
- Figure 14. 2% Pt on Zn/Mn/Zr Oxide - Effect of Support Composition
- Figure 15. 2% Pt on Zn/Mn/Zr Oxide - Effect of Support Composition
- Figure 16. 2% Pd on Zn/Mn/Zr Oxide - Effect of Support Composition
- Figure 17. Effect of Pt Loading on Catalyst Performance - Conversions
- Figure 18. Effect of Pt Loading on Catalyst Performance - Selectivities
- Figure 19. Comparison of MeOH/EtOH and MeOH-only Feeds
- Figure 20. Comparison of MeOH/EtOH and MeOH-only Feeds
- Figure 21. Isoalcohols Plant Schematic
- Figure 22. Vent Losses vs. Separator Temperature
- Figure 23. Liquid Purge, Vent and Total Feed and Product Losses vs. Separator Temperature
- Figure 24. Product Price Needed for 20% Rate of Return vs. Selectivity