

ADVANCES IN CATALYSIS FOR OXIDATION INTERMEDIATES AND DERIVATIVES

A technical investigation
commissioned by the members of the
Catalytic Advances Program

Client Private
December 2013



The Catalytic Advances Program (CAP)

The Catalytic Advances Program (CAP) is an information resource for research and development organizations in the petroleum, chemical, and polymer industries. By the direction of the member companies (through balloting and other interactive means), the program delivers a range of timely and insightful information and analyses which are accessible exclusively to members and protected by confidentiality agreements. The objective is to provide a technical update on commercially viable advances in catalysis as well as benchmark commercial advances in catalysis and process technology.

Members receive three in-depth **CAP Technical Reports** which are written and peer reviewed by leading scientists and experienced industry professionals in areas selected by the membership (via ballot); weekly *CAP Communications* (delivered via e-mail) which provide the latest updates on technical breakthroughs, commercial events and exclusive development opportunities; and attendance at the **CAP Annual Meeting**.

The **Catalytic Advances Program (CAP)** is available on a membership basis from The Catalyst Group Resources (TCGR). For further details, please contact Matthew A. Colquitt at Matthew.A.Colquitt@catalystgrp.com or +1.215.628.4447 (x1130).



P.O. Box 680
Spring House, PA 19477 U.S.A
ph: +1.215.628.4447
fax: +1.215.628.2267
website: www.catalystgrp.com

CONTENTS

EXECUTIVE SUMMARY	xxv
1. INTRODUCTION	1
2. ADVANCES IN ETHYLENE OXIDE AND DERIVATIVES	5
2.1 CATALYST AND TECHNOLOGY ADVANCES	5
2.1.1 Ethylene Oxide	5
2.1.1.1 Technology	5
2.1.1.2 Catalyst.....	7
2.1.1.3 Significance of Carriers.....	10
2.1.2 Ethylene Glycol.....	10
2.1.2.1 Technology	11
2.1.2.2 Catalyst.....	14
2.1.3 Ethylene Glycol Ethers.....	15
2.1.3.1 Technology	15
2.1.3.2 Catalyst.....	16
2.1.4 Ethoxylates	16
2.1.4.1 Technology	17
2.1.4.2 Catalyst.....	19
2.1.5 Ethanolamines	19
2.1.5.1 Technology	19
2.1.5.2 Catalyst.....	20
2.2 CURRENT R&D.....	21
2.2.1 Ethylene Oxide	21
2.2.2 Ethylene Glycol.....	23
2.2.3 Ethylene Glycol Ethers.....	24
2.2.4 Ethoxylates	24
2.2.5 Ethanolamines	25
2.3 REACTION TECHNOLOGY AND PRODUCT DEVELOPMENT	25
2.3.1 Ethylene Oxide	25
2.3.2 Ethanolamines	26
2.3.3 1,3-Propanediol	27

2.4	TECHNICAL HURDLES.....	27
2.5	CONCLUSIONS AND RECOMMENDATIONS	29
2.6	REFERENCES.....	29
3.	ADVANCES IN PROPYLENE OXIDE AND DERIVATIVES	33
3.1	CATALYST ADVANCES	33
3.1.1	Propylene Oxide	33
3.1.1.1	Co-Product Processes	36
3.1.1.2	Direct Production.....	44
3.1.1.3	Renewable Processes.....	52
3.1.2	Propylene Glycol	52
3.1.2.1	Conventional Process.....	52
3.1.2.2	Renewable Processes.....	53
3.1.3	Propylene Glycol Ethers.....	55
3.1.3.1	Conventional Process.....	55
3.1.3.2	Potential Improvements.....	55
3.1.4	Polyether Polyols.....	56
3.1.4.1	Polyurethane Polyether Polyols Process.....	56
3.1.4.2	Potential Improvements.....	58
3.2	CURRENT R&D	59
3.2.1	Focus on Sustainability.....	59
3.3	REACTOR TECHNOLOGY AND PRODUCT DEVELOPMENT	60
3.4	TECHNICAL HURDLES.....	61
3.5	CONCLUSIONS AND RECOMMENDATIONS	62
3.6	REFERENCES	63
4.	ADVANCES IN OTHER OXIDATION CHEMICAL INTERMEDIATES AND DERIVATIVES.....	65
4.1	CATALYST AND TECHNOLOGY ADVANCES.....	65
4.1.1	Acrolein	65
4.1.1.1	Technology	66
4.1.1.2	Catalyst	66
4.1.2	Acrylic Acid.....	68
4.1.2.1	Technology	68
4.1.2.2	Catalyst	69
4.1.3	Phenol	71

4.1.3.1	Technology	71
4.1.3.2	Catalyst	72
4.1.4	1, 4 – Butanediol	73
4.1.4.1	Technology	74
4.1.4.2	Catalyst	75
4.1.5	1, 3 – Propanediol	76
4.1.5.1	Technology	77
4.1.5.2	Catalyst	77
4.2	CURRENT R&D	78
4.2.1	Acrolein	78
4.2.2	Acrylic Acid	80
4.2.3	Phenol	81
4.2.4	1, 4 – Butanediol	83
4.2.5	1, 3 – Propanediol	84
4.3	REACTION TECHNOLOGY AND PRODUCT DEVELOPMENT	87
4.4	TECHNICAL HURDLES	87
4.5	CONCLUSIONS AND RECOMMENDATIONS	88
4.6	REFERENCES	89

FIGURES

Figure 2.1	Simplified EO process flow diagram	6
Figure 2.2	Simplified EG process flow diagram	11
Figure 2.3	BCT Loop Reactor Technology	17
Figure 2.4	Enhanced Loop Reactor (ELR)	18
Figure 2.5	Schemes of semibatch reactors mainly employed industrially for ethoxylation/ propoxylation processes: (a) stirred-tank reactor; (b) Venturi loop reactor; (c) spray loop reactor	18
Figure 2.6	Ethanolamine technology overview	20
Figure 2.7	Schematic of the KU-CEBC liquid phase process for the epoxidation of ethylene oxide	23
Figure 2.8	Ethanolamine (EA) product distribution (reaction 1)	26
Figure 2.9	Ethanolamine (EA) product distribution (reaction 2)	27
Figure 3.1	Global Propylene Consumption c. 70 million metric tonnes/year	33
Figure 3.2	Propylene Oxide via Chlorohydrin Process	34

Figure 3.3	Global Propylene Oxide Production by Process.....	35
Figure 3.4	Propylene Oxide via TBHP Process.....	38
Figure 3.5	Propylene Oxide via EBHP Process.....	39
Figure 3.6	Comparison of C ₃ '/CMHP epoxidation activity between TS-1 catalyst and Sumitomo Ti catalyst.....	42
Figure 3.7	Comparison of the micropore (blue) and mesopore (gray) structure between TS-1 catalyst and Sumitomo Ti catalyst.....	43
Figure 3.8	Suggested flow scheme for a propene epoxidation process by integrating an anthrahydroquinone hydrogen peroxide production process with a propene epoxidation reaction catalyzed by TS-1.....	47
Figure 3.9	Evonik/Uhde Propylene Oxide.....	48
Figure 3.10	GHG Emissions and Capital Cost LCA.....	50
Figure 3.11	Conventional vs. Impact/DMC Polyether Polyol Production Process.....	57
Figure 3.12	BASF-Dow HPPO Process.....	61
Figure 4.1	OPX Biotechnologies Acrylic Acid Production.....	69
Figure 4.2	UOP QMax™ Process for Cumene Production.....	72
Figure 4.3	Davy Process Technology BDO Process.....	75

TABLES

Table 2.1	Selected Ethylene Oxide (EO) Patents.....	8
Table 2.2	Selected Ethylene Glycol (EG) Patents.....	13
Table 2.3	Selectivity of Selected EG Catalysts.....	14
Table 3.1	Subsidiary Components for Hydroperoxide Formation for Epoxidation Reactions.....	37
Table 3.2	Co-Product/Propylene Oxide Weight Ratios.....	40
Table 3.3	Commercial and Emerging Direct PO Processes.....	44
Table 3.4	Comparison of Total Capital Investments for the Conventional PO/TBA, HPPO, and CEBC-PO Processes.....	49
Table 4.1	Yields for Acrolein Production.....	66
Table 4.2	Catalyst Systems Tested for the Direct Oxidation of Propane to Acrolein.....	67
Table 4.3	Yields for Acrylic Acid Production.....	70
Table 4.4	Selected Patents for Acrolein Production.....	78
Table 4.5	Selected Patents for Acrylic Acid Production.....	80
Table 4.6	Selected Patents For Phenol Production.....	83
Table 4.7	1,4-Butanediol Patents Filed by Davy Process Technology.....	84