

TECHNOLOGY & COSTS

Biorenewable Insights

Glycerin as a Platform Chemical

Table of Contents

A Report by **Nexant, Inc.**

Published Date: October 2018

www.nexantsubscriptions.com

Contents

1	Executive Summary	1
1.1	Introduction.....	1
1.1.1	Overview.....	1
1.1.2	Oleochemical Industry.....	1
1.2	Technology.....	3
1.2.1	Industry Sector Patent Activity	3
1.3	Economics.....	8
1.4	Capacity Analysis	12
1.4.1	Announced Projects Summary	12
1.4.2	Project Analysis.....	13
1.5	Implications for Conventional Industry	14
1.5.1	Market Penetration.....	14
1.5.2	Prices.....	14
2	Introduction	16
2.1	Overview	16
2.1.1	Oleochemical Industry.....	16
2.1.2	Chemistry.....	17
2.2	Biodiesel Industry	19
2.3	Glycerin Grades.....	20
2.3.1	Crude Glycerin	20
2.3.2	Refined Glycerin.....	20
2.4	Recent Developments.....	21
3	Technology	22
3.1	Introduction.....	22
3.2	Industry Sector Patent Activity	22
3.3	Propylene	27
3.3.1	Process Chemistry	27
3.3.2	Process Description	28
3.4	1,2-Propanediol (Propylene Glycol).....	32

3.4.1	Process Description	33
3.5	1,3-Propanediol (PDO)	47
3.5.1	Process Chemistry	47
3.5.2	Process Description	48
3.6	Acrylic Acid.....	52
3.6.1	Process Chemistry	54
3.6.2	Process Description	55
3.7	Epichlorohydrin.....	61
3.7.1	Process Chemistry	61
3.7.2	Process Description	63
3.7.3	Other Developments	77
3.8	Methanol / Dimethyl Ether (DME).....	78
3.8.1	Process Chemistry	79
3.8.2	Process Description	82
3.9	Glycerin Carbonate.....	83
3.9.1	Process Chemistry	83
3.9.2	Process Description	83
3.9.3	Patent Activity	86
3.10	Glycidol	88
3.10.1	Process Chemistry	88
3.10.2	Process Description	89
3.10.3	Patent Activity	91
3.10.4	Process Chemistry	93
3.10.5	Process Description	98
3.10.6	Bio-on	99
3.10.7	Patent Activity	102
3.11	Closing Remarks	106
4	Economics	108
4.1	Glycerin Basis of Economics.....	108
4.2	Methodology	109
4.2.1	Capital Cost Elements.....	109
4.2.2	Operating Cost Elements	112
4.3	Production Technologies	116
4.3.1	1,2-Propanediol (Propylene Glycol)	116
4.3.2	1,3-Propanediol.....	119
4.3.3	Acrylic Acid	122
4.3.4	Epichlorohydrin	128
4.3.5	Glycerin Carbonate	131
4.3.6	Glycidol.....	134
4.3.7	PHA	137
5	Capacity Analysis.....	140
5.1	Methodology Overview	140

5.2	Existing Industry	143
5.2.1	Propylene.....	143
5.2.2	1,2-Propanediol (Propylene Glycol).....	144
5.2.3	1,3-Propanediol (1,3-PDO).....	144
5.2.4	Acrylic Acid	145
5.2.5	Epichlorohydrin	146
5.2.6	Methanol.....	147
5.2.7	Glycerin Carbonate	148
5.2.8	Glycidol.....	148
5.2.9	PHA	148
5.3	Announced Projects Summary.....	149
5.3.1	Project Analysis.....	151
6	Implications for Conventional Industry	152
6.1	Scale and Market Penetration	152
6.1.1	Market Penetration.....	152
6.1.2	Scale.....	152
6.1.3	Applications	153
6.2	Prices	161
A	References	163

Appendices

A	References	163
---	------------------	-----

Figures

Figure 1	Chemical Synthesis Reactions of Fats and Oils.....	2
Figure 2	Identified Patents Relating to Chemicals of Interest.....	3
Figure 3	Granted Patents Relating to Chemicals of Interest	4
Figure 4	Top 10 Patent Holders	4
Figure 5	Patent versus Crude Glycerin Prices and Petrochemical Profitability	5
Figure 6	Biodiesel Supply by Region.....	6
Figure 7	All Patents by Region.....	7
Figure 8	Granted Patents by Region.....	7
Figure 9	Granted Patents in East Asia for Select Products.....	8
Figure 10	Propylene Glycol Economics – Cash Cost.....	8
Figure 11	1,3 Propanediol Economics – Cash Cost.....	9
Figure 12	Crude Acrylic Acid Economics - Cash Cost	10
Figure 13	Epichlorohydrin Economics - Cash Cost.....	10
Figure 14	PHA Economics - Cash Cost.....	11
Figure 15	Glycerin Carbonate and Glycidol Economics - Cash Cost.....	11
Figure 16	Estimated Bio-Based Penetration for Methanol	14
Figure 17	Comparison of Feedstock Prices.....	15
Figure 18	Chemical Synthesis Reactions of Fats and Oils.....	17
Figure 19	Chemical Structure of Triglyceride in Natural Oil or Animal Fat.....	17
Figure 20	Hydrolysis of Triglyceride (Oils and Fats)	18
Figure 21	Identified Patents Relating to Chemicals of Interest.....	22
Figure 22	Granted Patents Relating to Chemicals of Interest	23
Figure 23	Top Ten Patent Holders	23
Figure 24	Patent versus Crude Glycerin Prices and Petrochemical Profitability	24
Figure 25	Biodiesel Supply by Region.....	25
Figure 26	All Patents by Region.....	26
Figure 27	Granted Patents by Region	26
Figure 28	Granted Patents in East Asia for Select Products.....	27
Figure 29	Reactor Effluent Hydrocarbon Composition.....	28
Figure 30	Block Flow Diagram for the Production of Propylene from Glycerin.....	31
Figure 31	GBT Glycerin to Propylene Glycol Process Flow Diagram	35
Figure 32	UOP PG Process Block Flow Diagram	37
Figure 33	BASF Process Block Flow Diagram	39
Figure 34	Suppes Proposed Mechanism via Acetol Intermediate	41
Figure 35	Suppes Proposed Mechanism via Lactaldehyde Intermediate	41
Figure 36	Suppes/Senergy Process Block Diagram	42
Figure 37	DPT Process Summary Block Diagram	44
Figure 38	DPT Process Flow Diagram	45
Figure 39	Metabolic Pathway to 1,3-Propanediol – Glycerin.....	48
Figure 40	DuPont Bio-based PDO Process, Fermentation	50
Figure 41	DuPont Bio-based PDO Process, Downstream Purification	53

Figure 42	Bio-Based Routes to Acrylic Acid	54
Figure 43	Acrylic Acid from Glycerin via Acrolein (Two-Step, Arkema)	58
Figure 44	Conser SPA Process: Glycerin to Epichlorohydrin.....	65
Figure 45	DOW Process: Recycle Glycerin to Epichlorohydrin	68
Figure 46	Solvay Process: Glycerin to Dichloropropanol Process.....	72
Figure 47	Solvay Process: Dichloropropanol to ECH Process	75
Figure 48	Solvay Process: ECH Purification Process	76
Figure 49	Primary Bio-based Routes to Methanol and DME Production	78
Figure 50	BioMCN Bio-Methanol from Glycerin Process	82
Figure 51	Glycerin to Glycerin Carbonate with DMC	83
Figure 52	Propylene Carbonate Reacting With Glycerin.....	84
Figure 53	Glycerin Carbonate Patents – Top 10.....	86
Figure 54	Glycerin Carbonate Patents – Top 10 and Others	86
Figure 55	Glycerin Carbonate Decomposition to Glycidol.....	88
Figure 56	Glycidol Patents –Top 10	91
Figure 57	Glycidol Patents –Top 10 and Others	92
Figure 58	General Structure of Polyhydroxyalkanoate (PHA) Homopolymer.....	93
Figure 59	General Structure of PHA Copolymers	93
Figure 60	Glycerin Pathway to P3HB Illustration	96
Figure 61	Glycerin Pathway to mcl-PHA Illustration.....	97
Figure 62	PHA Production Process.....	98
Figure 63	Bio-on PHA Yield and Cell Density from Sucrose	102
Figure 64	PHA Patents – Top 10	103
Figure 65	PHA Patents – Top 10 and Others	103
Figure 66	Estimated Bio-Based Penetration for Methanol	152
Figure 67	Global Propylene Demand, 2016-e	155
Figure 68	Acrylic Acid Derivatives.....	156
Figure 69	Acrylic Acid Consumption.....	157
Figure 70	Methanol Demand Drivers.....	159
Figure 71	Comparison of Feedstock Prices.....	162

Tables

Table 1	Announced Projects for Glycerin Derivatives	12
Table 2	Glycerin-Based Projects.....	13
Table 3	Material Balance: Glycerin to Propylene Process	30
Table 4	ADM Nickel-on-Alumina Catalyst Composition	33
Table 5	UOP PG Process Conditions	37
Table 6	BASF PG Process Conditions	39
Table 7	BASF Catalyst Compositions	39
Table 8	BASF Process Results.....	40
Table 9	Suppes/Senergy Reactor Conditions.....	42
Table 10	DPT Process Conditions	43
Table 11	DPT Feed Analysis	44
Table 12	DPT Process Results'	44
Table 13	Composition of Commercial Methanol Catalysts.....	80
Table 14	Glycerin Carbonate Granted Patents.....	87
Table 15	Glycidol Yield at Varying Operating Conditions.....	90
Table 16	Glycidol Granted Patents	92
Table 17	PHA Types	94
Table 18	Select PHA Pathways from Varying Feedstocks.....	95
Table 19	PHA Properties versus Conventional Plastics.....	97
Table 20	PHA Granted Patents	104
Table 21	Cost of Production Estimate for: Propylene Glycol.....	116
Table 22	Cost of Production Estimate for: Propylene Glycol Process: Glycerin Hydrogenolysis; Western Europe	117
Table 23	Cost of Production Estimate for: Propylene Glycol Process: Glycerin Hydrogenolysis; China	118
Table 24	Cost of Production Estimate for: 1,3-Propanediol Process: Glycerin Hydrogenolysis; USGC	119
Table 25	Cost of Production Estimate for: 1,3-Propanediol Process: Glycerin Hydrogenolysis; Western Europe	120
Table 26	Cost of Production Estimate for: 1,3-Propanediol Process: Glycerin Hydrogenolysis; China	121
Table 27	Cost of Production Estimate for: Crude Acrylic Acid Process: via Acrolein from Dehydration of Glycerin; USGC	122
Table 28	Cost of Production Estimate for: Crude Acrylic Acid Process: via Acrolein from Dehydration of Glycerin; Western Europe	123
Table 29	Cost of Production Estimate for: Crude Acrylic Acid Process: via Acrolein from Dehydration of Glycerin; China	124
Table 30	Cost of Production Estimate for: Glacial Acrylic Acid Process: Additive Enhanced Distillation of Crude Acrylic Acid; USGC.....	125
Table 31	Cost of Production Estimate for: Glacial Acrylic Acid Process: Additive Enhanced Distillation of Crude Acrylic Acid; Western Europe	126
Table 32	Cost of Production Estimate for: Glacial Acrylic Acid Process: Additive Enhanced Distillation of Crude Acrylic Acid; China.....	127

Table 33	Cost of Production Estimate for: Epichlorohydrin Process: Glycerin Hydrochlorination, Dichlorohydrin Epoxidation; USGC.....	128
Table 34	Cost of Production Estimate for: Epichlorohydrin Process: Glycerin Hydrochlorination, Dichlorohydrin Epoxidation; Western Europe	129
Table 35	Cost of Production Estimate for: Epichlorohydrin Process: Glycerin Hydrochlorination, Dichlorohydrin Epoxidation; China	130
Table 36	Cost of Production Estimate for: Glycerin Carbonate Process: Glycerin Carbonylation; USGC	131
Table 37	Cost of Production Estimate for: Glycerin Carbonate Process: Glycerin Carbonylation; Western Europe	132
Table 38	Cost of Production Estimate for: Glycerin Carbonate Process: Glycerin Carbonylation; China	133
Table 39	Cost of Production Estimate for: Glycidol Process: Glycerin Carbonate Decomposition; USGC.....	134
Table 40	Cost of Production Estimate for: Glycidol Process: Glycerin Carbonate Decomposition; Western Europe.....	135
Table 41	Cost of Production Estimate for: Glycidol Process: Glycerin Carbonate Decomposition; China.....	136
Table 42	Cost of Production Estimate for: PHA (P3HB-co-3HV); 20mol% 3HV Content Process: Glycerin Fermentation; USGC	137
Table 43	Cost of Production Estimate for: PHA (P3HB-co-3HV); 20mol% 3HV Content Process: Glycerin Fermentation; Western Europe	138
Table 44	Cost of Production Estimate for: PHA (P3HB-co-3HV); 20mol% 3HV Content Process: Glycerin Fermentation; China	139
Table 45	Project Scoring Methodology	140
Table 46	Synthetic Routes – Petrochemicals	143
Table 47	Announced Projects for Glycerin Derivatives	150
Table 48	Glycerin-Based Projects.....	151
Table 49	U.S. FDA Approved Use of Propylene Glycol in Foods	155
Table 50	Alkyl Carbonates Applications	160

Nexant Inc.

TECHNOLOGY & COSTS

Biorenewable Insights Glycerin as a Platform Chemical

The Nexant Subscriptions' Biorenewable Insights program is recognized globally as the industry standard source for information relevant to the chemical process and refining industries. Biorenewable Insights reports are available as a subscription program or on a single report basis.

Contact Details:

Americas:

Marcos Nogueira Cesar, Vice President, Global Products, E&CA: Nexant Subscriptions
Phone: + 1-914-609-0324, e-mail: mcesar@nexant.com

Erica Hill, Client Services Coordinator, E&CA-Products
Phone: + 1-914-609-0386, e-mail: ehill@nexant.com

EMEA:

Anna Ibbotson, Director, Nexant Subscriptions
Phone: +44-207-950-1528, aibbotson@nexant.com

Asia:

Chommanad Thammanayakatip, Managing Consultant, Energy & Chemicals Advisory
Phone: +66-2793-4606, email: chommanadt@nexant.com

Nexant, Inc. (www.nexant.com) is a leading management consultancy to the global energy, chemical, and related industries. For over 38 years, Nexant has helped clients increase business value through assistance in all aspects of business strategy, including business intelligence, project feasibility and implementation, operational improvement, portfolio planning, and growth through M&A activities. Nexant has its main offices in San Francisco (California), White Plains (New York), and London (UK), and satellite offices worldwide.

Copyright © by Nexant Inc. 2018. All Rights Reserved.