

CHEMSYSTEMS PERP PROGRAM

"Green" Acetyls

08/09S7

July 2010

Dr Riccardo M Ambrosini



www.chemsystems.com

44 South Broadway, White Plains, New York 10601, USA
Tel: +1 914 609 0300 Fax: +1 914 609 0399

This Report was prepared by Nexant, Inc ("Nexant") and is part of the ChemSystems Online® suite. Except where specifically stated otherwise in this Report, the information contained herein is prepared on the basis of information that is publicly available, and contains no confidential third party technical information to the best knowledge of Nexant. Aforesaid information has not been independently verified or otherwise examined to determine its accuracy, completeness, or financial feasibility. Neither NEXANT, Subscriber nor any person acting on behalf of either assumes any liabilities with respect to the use of or for damages resulting from the use of any information contained in this Report. Nexant does not represent or warrant that any assumed conditions will come to pass.

The Report is submitted on the understanding that the Subscriber will maintain the contents confidential except for the Subscriber's internal use. The Report should not be reproduced, distributed, or used without first obtaining prior written consent by Nexant. Each Subscriber agrees to use reasonable effort to protect the confidential nature of the Report.

Copyright © by Nexant Inc. 2010. All rights reserved.

Contents

Section	Page
1 Executive Summary	1
1.1 SYNOPSIS.....	1
1.2 PRODUCTION TECHNOLOGY.....	2
1.2.1 Routes to “Green Acetlys”	3
1.2.2 Fermentation Platform	3
1.2.3 Thermochemical Platform.....	3
1.3 PROCESS TECHNO-ECONOMICS	6
1.3.1 Comparative Economics for Ethanol Production.....	6
1.3.2 Comparative Economics for Green Acetic Acid Production	7
1.4 COMMERCIAL STATUS.....	8
1.4.1 Global Demand	11
1.5 SUPPLY	12
1.5.1 Major Producers.....	12
1.6 SUPPLY/DEMAND OUTLOOK.....	14
2 Introduction.....	16
2.1 OVERVIEW	16
2.1.1 Fermentation Platform	16
2.1.2 Thermochemical Platform.....	16
3 Technology Analysis - Fermentation Routes	19
3.1 INTRODUCTION.....	19
3.2 FERMENTATION ROUTES FOR ETHANOL/BUTANOL PRODUCTION.....	21
3.2.1 Ethanol via First Generation Fermentation	21
3.2.2 Ethanol via Second Generation Fermentation.....	25
3.2.3 Bio-Butanol Production	34
3.3 ETHYLENE VIA DEHYDRATION OF ETHANOL.....	36
3.3.1 Chemistry	36
3.3.2 Process Description.....	36
3.4 ETHYLENE OXIDATION TO ACETIC ACID VIA ACETALDEHYDE.....	41
3.4.1 Why Acetaldehyde?	41
3.4.2 Acetaldehyde from Ethylene.....	41
3.4.3 Acetaldehyde Conversion to Acetic Acid	44
3.5 DIRECT ETHYLENE VAPOR PHASE OXIDATION TO ACETIC ACID.....	48

3.5.1	Showa Denko Process	48
3.6	DIRECT PROCESS TO ACETIC ACID FROM ETHANOL	54
4	Technology Analysis - Gasification Routes	56
4.1	INTRODUCTION.....	56
4.2	BIOMASS GASIFICATION	56
4.2.1	CHOREN Carbo-V ® – Staged Gasification	57
4.3	CARBON MONOXIDE SEPARATION FROM SYNGAS	59
4.4	SYNGAS TO METHANOL	59
4.4.1	Methanol Synthesis	59
4.4.2	Recovery	60
4.4.3	Distillation.....	60
4.5	METHANOL CARBONYLATION TO ACETIC ACID.....	60
4.5.1	Monsanto/BP Process - Chemistry.....	61
4.6	SYNGAS FERMENTATION TO ETHANOL.....	66
4.6.1	Biosyngas Fermentation with Carbon Monoxide Utilization, H ₂ Byproduct.....	66
5	Acetyl Integration Opportunities	70
5.1	INTRODUCTION.....	70
5.2	ACETIC ANHYDRIDE.....	71
5.2.1	Ketene-based Process from Acetic Acid	71
5.2.2	Liquid Phase Oxidation of Acetaldehyde	73
5.2.3	Methyl Acetate Carbonylation	74
5.3	ACETATE ESTERS	77
5.3.1	Esterification	78
5.3.2	Tishchenko Route for Ethyl Acetate Production.....	82
5.3.3	Ethyl Acetate from Ethanol.....	85
5.4	VAM PRODUCTION VIA ETHYLENE ACETOXYLATION	87
5.4.1	Process Chemistry	87
6	Economic Analysis	92
6.1	INTRODUCTION.....	92
6.1.1	Fermentation Approach.....	92
6.1.2	Thermochemical Approach.....	92
6.2	PRICING BASIS	93
6.2.1	Variable Costs and Manpower Assumptions	93

6.2.2	Capital Investment Basis.....	94
6.2.3	Cost of Production Basis.....	94
6.3	ECONOMICS FOR FERMENTATION ROUTES TO ETHANOL.....	95
6.3.1	Ethanol from Corn	95
6.3.2	Ethanol from Sugarcane	97
6.3.3	Ethanol from Wheat (Western Europe).....	98
6.3.4	Ethanol from Biomass (Western Europe)	98
6.3.5	Comparative Economics for Ethanol Production.....	104
6.4	ECONOMICS FOR GREEN ACETIC ACID PRODUCTION	105
6.4.1	Economics for the Direct Process of Ethanol to Acetic Acid	105
6.4.2	Economics for the Ethylene Routes to Acetic Acid.....	108
6.4.3	Economics for Biomass Gasification Routes to Acetic Acid.....	113
6.4.4	Comparative Economics for Green Acetic Acid Production	119
6.5	DOWNSTREAM GREEN ACETYLS PRODUCTION	120
6.5.1	Economics for Acetic Anhydride via Acetic Acid.....	120
6.5.2	VAM Costs of Production.....	123
6.5.3	Economics for Ethyl Acetate Production.....	127
6.5.4	Economics for Butyl Acetate Production.....	132
7	Commercial Analysis	135
7.1	DEMAND	135
7.1.1	VAM	137
7.1.2	PTA	138
7.1.3	Ethyl and Butyl Acetates.....	139
7.1.4	Acetic Anhydride	139
7.1.5	Other Uses	139
7.1.6	Global Demand	139
7.2	SUPPLY	140
7.3	SUPPLY/DEMAND OUTLOOK.....	147
8	References	150
8.1	NEXANT CHEMSYSTEMS PERP REPORTS.....	150
8.2	CITED REFERENCES	150

Appendix	Page
A Nexant's Capital Cost Estimates.....	A-1
B PERP Program Title Index (2000/2001 – 2009/2010).....	B-1

Figure	Page
1.1 Feedstock Choices and Process Routes for Acetic Acid Production	2
1.2 Block Flow Diagram – Fermentation Route Options of Green Acetyls Production.....	4
1.3 Block Flow Diagram – Conceptual Acetic Acid Production from Biomass Gasification	4
1.4 Block Flow Diagram – Possible Hybrid Thermochemical/Fermentation Based Plant	5
1.5 Comparison of Ethanol Cost of Production	6
1.6 Comparison of Acetic Acid Cost of Production, by Process	7
1.7 Main Acetic Acid Derivatives and End-Use Applications.....	9
1.8 Global Acetic Demand by End-Use, 2009	9
1.9 Main Vinyl Acetate Applications Derivatives and End-Use Applications	10
1.10 Global VAM Demand by End-Use, 2009	10
1.11 Global Acetic Acid Demand by Region, 2009	12
1.12 Global Virgin Acetic Acid Capacity by Producers, 2009	13
1.13 Global Acetic Acid Supply/Demand Balance	14
1.14 Regional Acetic Acid Demand.....	15
2.1 Block Flow Diagram – Fermentation Route Options of Green Acetyls Production.....	17
2.2 Block Flow Diagram – Conceptual Acetic Acid Production from Biomass Gasification	17
2.3 Block Flow Diagram – Possible Hybrid Thermochemical/Fermentation Based Plant	18
3.1 Block Flow Diagram – Fermentation Route Options of Green Acetyls Production	20
3.2 Block Flow Diagram – Ethanol Production from Sugarcane.....	22
3.3 Material Balance of Ethanol Production from Sugarcane and Bagasse	23
3.4 Wet Milling versus Dry Milling of Corn	24
3.5 Conceptual Structure of Cellulose in Plants(1)	26
3.6 NREL Lignocellulosic Biomass to Ethanol Process	31
3.7 Simplified Schematic Flowsheet of Batch <i>C. Beijerinckii</i> BA101 Butanol Process.....	35
3.8 Ethylene from Ethanol Chematur Fixed Bed Process	38
3.9 Ethylene from Ethanol Lummus Fluid Bed Process	40
3.10 Acetaldehyde via Ethylene Oxidation Single Stage Process.....	43
3.11 Acetaldehyde via Ethylene Oxidation Two-Stage Process	45
3.12 Acetic Acid via Acetaldehyde Oxidation.....	47
3.13 Acetic Acid via Direct Ethylene Oxidation – Showa Denko Process	50
3.14 Wacker Ethanol to Acetic Acid.....	55
4.1 Block Flow Diagram – Conceptual Acetic Acid Production from Biomass Gasification	56

4.2	Process Schematic - CHOREN Syngas Production from Biomass.....	57
4.3	Mitsubishi Superconverter	60
4.4	The Reaction Mechanism for the Monsanto/BP Rhodium-Catalyzed Carbonylation of Methanol to Acetic Acid	62
4.5	Acetic Acid via Methanol Carbonylation Monsanto/BP Process	65
4.6	Biosyngas Fermentation Process Schematic	68
5.1	Block Flow Diagram – Possible Hybrid Thermochemical/Fermentation Based Plant	70
5.2	Ketene Process: Acetic Anhydride from Acetic Acid.....	72
5.3	Acetic Anhydride by Carbonylation of Methyl Acetate: Esterification Section.....	75
5.4	Acetic Anhydride by Carbonylation of Methyl Acetate Halcon/Eastman Process	76
5.5	Routes to Ethyl Acetate.....	77
5.6	Ethyl Acetate via Ethyl Alcohol and Acetic Acid.....	79
5.7	Butyl Acetate via <i>n</i> -Butanol and Acetic Acid	81
5.8	Tishchenko Process for Ethyl Acetate via Acedelhyde.....	84
5.9	Davy Process Technology Ethanol to Ethyl Acetate.....	86
5.10	Vapor Phase, Fixed-Bed Vinyl Acetate from Ethylene Process	89
6.1	Sensitivity of Ethanol from Corn Cost of Production to Corn/DDGS Price	96
6.2	Comparison of Ethanol Cost of Production	105
6.3	ACEO® Process – Sensitivity of Acetic Acid Cost of Production to Ethanol Price	107
6.4	ACEO® Process – Sensitivity of Cost of Production to Investment Capital	108
6.5	Ethylene Cost of Production via Ethanol Dehydration – Sensitivity to Investment Capital ..	109
6.6	Sensitivity of Acetic Acid Produced via the Gasification Route to Biomass Cost	114
6.7	Comparison of Acetic Acid Cost of Production, by Process	119
6.8	Mass Balance for the VAM Plant Based on the Showa Denko Process	123
6.9	Mass Balance for the VAM Plant Based on the Wacker Chemie ACEO® Process	125
6.10	Mass Balance for a Hybrid VAM Plant Based on the Monsanto/BP Process and an Integrated Ethanol Dehydration Unit	125
6.11	Comparison of Vinyl Acetate Costs of Production, by Upstream Processes	126
6.12	Comparison of Ethyl Acetate Cost of Production, by Process	128
7.1	Main Acetic Acid Derivatives and End-Use Applications.....	136
7.2	Global Acetic Demand by End-Use, 2009	136
7.3	Main Vinyl Acetate Applications Derivatives and End-Use Applications	137
7.4	Global VAM Demand by End-Use, 2009	138
7.5	Global Acetic Acid Demand by Region, 2009	140

7.6	Global Virgin Acetic Acid Capacity by Producers, 2009	141
7.7	Global Acetic Acid Supply/Demand Balance	147
7.8	Regional Acetic Acid Demand.....	148

Table	Page
1.1 Business Market Value of Major Acetyls	8
3.1 Comparison of Lignocellulosic Pretreatment Technologies	27
3.2 General Design Parameters of NREL Bioethanol Process.....	28
3.3 Corn and Stover Compositions	29
3.4 Major Unit Operations of NREL's Bioethanol Process	30
3.5 Chematur Ethanol Dehydration Process – Selectivity Breakdown at 99 Percent Conversion	39
3.6 Showa Denko Patent Data (EP0620205B1).....	52
4.1 Catalyst Systems for Methanol Carbonylation.....	61
4.2 Ethanol Yields from Microbial Conversion of Syngas	69
5.1 Typical Ethyl Acetate Specifications(1)	80
5.2 Typical <i>n</i> -Butyl Acetate Specifications(1).....	82
5.3 Typical Product Quality from the Davy Process Technology Ethanol-Based Ethyl Acetate Process	85
6.1 Price and Utility Basis.....	93
6.2 Cost of Production Estimate for: Ethanol Process: Corn Dry Milling	100
6.3 Cost of Production Estimate for: Ethanol Process: Sugarcane Fermentation.....	101
6.4 Cost of Production Estimate for: Ethanol Process: Wheat Fermentation with Co-production of DDGS	102
6.5 Cost of Production Estimate for: Ethanol Process: 2nd Generation Biomass Fermentation.....	103
6.6 Feedstock Requirements for Various Ethanol Production Technologies.....	104
6.7 Cost of Production Estimate for: Acetic Acid Process: Wacker Chemie's ACEO® from Ethanol.....	106
6.8 Cost of Production Estimate for: Ethylene Process: Ethanol Dehydration – Fixed Bed.....	110
6.9 Cost of Production Estimate for: Acetic Acid Process: Showa Denko Ethylene Oxidation.....	111
6.10 Cost of Production Estimate for: Acetic Acid Process: Wacker Two-Stage Ethylene Oxidation via Acetaldehyde.....	112
6.11 Cost of Production Estimate for Syngas Process: Gasification Biomass (Purchased Oxygen).....	115
6.12 Cost of Production for: Carbon Monoxide Process: Cryogenic Separation from Syngas (1.7:1 H ₂ :CO)	116

6.13	Cost of Production for: Methanol Process: Syngas (2:1 H ₂ :CO)	117
6.14	Cost of Production Estimate for: Acetic Acid Process: Monsanto/BP Methanol Carbonylation	118
6.15	Cost of Production for: Acetic Anhydride Process: Ketene Route.....	121
6.16	Cost of Production for: Acetic Anhydride Process: Methyl Acetate Carbonylation.....	122
6.17	Cost of Production Estimate for: Vinyl Acetate Process: Conventional Fixed-Bed, Vapor-Phase Ethylene Acetoxylation.....	124
6.18	Cost of Production Estimate for: Ethyl Acetate Process: Davy.....	129
6.19	Cost of Production Estimate for: Ethyl Acetate Process: Esterification	130
6.20	Cost of Production Estimate for: Ethyl Acetate Process: Wacker / Tishchenko via Acetaldehyde.....	131
6.21	Cost of Production Estimate for: Butanol Process: Blashek et al. Advanced Continuous ABE - C Beijerinckii BA 101	133
6.22	Cost of Production Estimate for: Butyl Acetate Process: Esterification	134
7.1	Business Market Value of Major Acetyls	135
7.2	Acetic Acid Production Capacity in North America, 2009	142
7.3	Acetic Acid Production Capacity in Central and South Americas, 2009	142
7.4	Acetic Acid Production Capacity in Western Europe, 2009	143
7.5	Acetic Acid Production Capacity in East Asia, 2009.....	144
7.6	Acetic Acid Production Capacity in India, 2009.....	146
7.7	Virgin Acetic Acid Production Capacity in the Middle East, 2009	146
7.8	North American Acetic Acid Supply/Demand Balance, 2007-2018.....	148
7.9	West European Acetic Acid Supply/Demand Balance, 2007-2018	149
7.10	East Asian Acetic Acid Supply/Demand Balance, 2007-2018	149
7.11	Global Acetic Acid Supply/Demand Balance, 2007-2018.....	149