ADVANCES IN OLEFIN CO-MONOMER AND POLYOLEFIN PRODUCTION

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

Client Private
October 2016
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).
## CONTENTS

### EXECUTIVE SUMMARY


### 1. INTRODUCTION


### 2. ADVANCES IN OLEFIN CO-MONOMER PRODUCTION

#### 2.1 INTRODUCTION

- 2.1.1 The Global Alpha Olefins Market
- 2.1.2 Sources and Applications Review
- 2.1.3 Criteria for Co-monomer Selection

#### 2.2 ADVANCES IN CATALYSTS AND TECHNOLOGY FOR COMMERCIAL APPLICATIONS

- 2.2.1 Full Range Linear Alpha Olefins Processes
- 2.2.2 Extractive Sources
- 2.2.3 On-Purpose 1-Butene Processes
- 2.2.4 On-Purpose 1-Hexene Processes
- 2.2.5 On-Purpose 1-Octene Processes

#### 2.3 CURRENT R&D AND FUTURE DEVELOPMENT - NEW CATALYSTS AND PROCESSES UNDER DEVELOPMENT

- 2.3.1 Catalyst Development Activity
- 2.3.2 Process Developments

#### 2.4 CONCLUSIONS, RECOMMENDATIONS & HURDLES

- 2.4.1 Changing Supply Structures
- 2.4.2 Full-Range Alpha Olefin Technologies
- 2.4.3 Highly Selective On-Purpose Technologies
- 2.4.4 Recommendations & Hurdles – Alpha Olefin Technologies

#### 2.5 REFERENCES


### 3. ADVANCES IN POLYOLEFIN PRODUCTION

#### 3.1 INTRODUCTION

- 3.1.1 Global Capacity for Production of Polyethylene
- 3.1.2 Global Capacity for Production of Polypropylene
- 3.1.3 Global Demand for Polyolefins

#### 3.2 EVOLUTION & CURRENT STATUS OF POLYOLEFIN TECHNOLOGIES

- 3.2.1 Review of Industry Evolution & Trends
- 3.2.2 Polyethylene Catalyst & Process Technologies
3.2.3 Polypropylene Catalyst & Process Technologies ...................................................... 70

3.3 CURRENT R&D AND FUTURE DEVELOPMENT - NEW CATALYSTS AND PROCESSES UNDER DEVELOPMENT ................................................................. 76

3.3.1 Polyethylene Technologies .................................................................................... 76

3.3.2 Polypropylene Technologies .................................................................................. 116

3.4 SUMMARY & CONCLUSIONS ..................................................................................... 132

3.4.1 Research into New Processes for PE & PP .............................................................. 132

3.4.2 Research into PE Catalyst & Product Technologies ............................................... 133

3.4.3 Research into PP Catalyst & Product Technologies ............................................... 134

3.5 REFERENCES ............................................................................................................. 135

4. INDEX .......................................................................................................................... 139

FIGURES

Figure 2.1 Global Demand for LAOs by End-Use .............................................................. 4

Figure 2.2 Global LAO Demand by Chain Length ............................................................ 5

Figure 2.3 Example of Schulz-Flory Product Distributions ............................................. 9

Figure 2.4 The Shell SHOP Process for Detergent Range α-olefins ................................... 12

Figure 2.5 Idemitsu Full Range Alpha Olefin Process ......................................................... 15

Figure 2.6 The α-SABLIN Reactor .................................................................................... 16

Figure 2.7 The α-SABLIN Process – Outline Flow Diagram ............................................. 17

Figure 2.8 The IFP/Axens AlphaButol Process for 1-Butene ............................................. 21

Figure 2.9 IFP/University of Amsterdam Dimerization Catalyst ........................................ 22

Figure 2.10 The CB&I 1-Hexene Process from Mixed C4’s ............................................... 24

Figure 2.11 Dow Telomerization Reaction Scheme .......................................................... 25

Figure 2.12 Dow’s Alkoxymonomerization Catalyst Ligand ............................................. 26

Figure 2.13 Shell Basic Bisarylimino Pyridine Catalysts ................................................... 28

Figure 2.14 Shell High Selectivity Bisarylimino Pyridine Catalysts .................................... 29

Figure 2.15 CP Chem Bi-Centered Bisarylimine Pyridine Complexes ............................... 30

Figure 2.16 Sinopec Imino-pyridyl Tridentate Iron Complex .............................................. 30

Figure 2.17 DuPont Diimine Fe Complexes ...................................................................... 31

Figure 2.18 Mitsui’s Single-Site Oligomerization Catalysts .............................................. 35

Figure 2.19 Mitsui’s Hexene-Selective Single-Site Catalyst Complex ................................ 36

Figure 2.20 CP Chem Highly Selective Pyrrole Substituents ............................................. 37

Figure 2.21 CP Chem Phosphilnyl Amidine Chromium Complexes – General Form .......... 37
Figure 2.22  Examples of CP Chem Phosphilnyl Amidine Chromium Complexes ........................................... 38
Figure 2.23  SABIC Preferred PNPN-H Ligands .................................................................................. 39
Figure 2.24  SABIC PNPO and PNPS Ligands .................................................................................. 40
Figure 2.25  Sasol’s DMP-PNP Ligand ............................................................................................ 41
Figure 2.26  ExxonMobil’s Heteroaryl Thiazole Amine Ligands ....................................................... 42
Figure 3.1  Ethylene Polymer Capacity by Product Type ................................................................. 52
Figure 3.2  Polypropylene Capacity by Process Type ...................................................................... 53
Figure 3.3  Global Demand for Polyethylene & Polypropylene ..................................................... 54
Figure 3.4  Share of Tubular Reactor Plants in World LDPE Capacity ........................................... 64
Figure 3.5  World PP Capacity by Process - 2016 ......................................................................... 70
Figure 3.6  Lyondellbasell Tubular Extrusion Coating Grade Process with Bifunctional Co-
monomer ........................................................................................................................................ 82
Figure 3.7  LyondellBasell Bifunctional Co-Monomer .................................................................... 83
Figure 3.8  Comparative Results of LyondellBasell Bifunctional Co-Monomer Technology ......... 83
Figure 3.9  LyondellBasell Tubular Flow Scheme with Segregated Feed ......................................... 84
Figure 3.10 LyondellBasell Segregated Feed Reactor Profile ........................................................ 85
Figure 3.11 LyondellBasell Segregated Feed Tubular Reactor Product Mw Profile .................... 85
Figure 3.12 Celanese Phenolate Ether Complex Example ............................................................. 94
Figure 3.13 Dow’s Group 4 Metal Complex of a Bis(Hydroxyarylaryloxy) Ligand ..................... 96
Figure 3.14 Dow’s Zirconium Centered, Bridged and Substituted Polyvalent Aryloxyethers .... 97
Figure 3.15 LyondellBasell’s Monocyclopentadienyl Chromium Complexes ............................... 98
Figure 3.16 LyondellBasell Tridentate Iron Catalytic Complexes .................................................. 100
Figure 3.17 Sinopec’s Non-Metallocene Catalysts for Ultra-Linear PE ........................................ 101
Figure 3.18 Total’s Bidentate Iminonaphthol Ligands for High Mw PE ........................................ 102
Figure 3.19 Single-Site Catalysts for Single-Reactor Trimodal High Mw PE .............................. 103
Figure 3.20 Schematic of Self-Reinforced PE Production ............................................................... 103
Figure 3.21 Performance of Self-Reinforced HDPE/UHMW-PE Reactor Blends ....................... 104
Figure 3.22 Univation’s High Mw PE Catalyst Species ................................................................. 105
Figure 3.23 Calculation of Dow’s Co-monomer Distribution Constant ........................................ 107
Figure 3.24 Co-Monomer Distribution Constants of Selected PE Resins ..................................... 108
Figure 3.25 Conceptual Depiction of the Hyperzone™ Process ..................................................... 114
Figure 3.26 Molecular Weight Distributions from LyondellBasell’s New Process ...................... 116
Figure 3.27 Sinopec Non-Phthalate Internal Donors ................................................................. 117
Figure 3.28 LyondellBasell Diol Ester Internal Donors ............................................................... 118
Figure 3.29  Candidates for Grace’s 6th Generation Internal Donors ................................. 120
Figure 3.30  Borealis’ Asymmetric Bis-Indenyl Metallocenes ........................................ 122
Figure 3.31  Aryloxyether SSCs for Solution Polymerization of Isotactic PP ...................... 123
Figure 3.32  Dow’s Stereoselective Catalysts for Propylene Polymerizations .................... 125
Figure 3.33  Dow’s Chain Straightening Chromium-Based Catalysts for Propylene  
Polymerization .............................................................................................................. 125
Figure 3.34  Borealis Gas Phase Polyolefin Process .......................................................... 127

**TABLES**

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 2.1</td>
<td>LAO End-Use by Chain Length ....................................................................</td>
<td>4</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>LyondellBasell Segregated Feed Tubular Reactor Product Branching ........</td>
<td>86</td>
</tr>
<tr>
<td>Table 3.2</td>
<td>Borealis High-Initiator Product Compared to Conventional Extrusion Coating Grade</td>
<td>87</td>
</tr>
</tbody>
</table>