ADVANCES IN SYNGAS PRODUCTION: CATALYST AND PROCESS DEVELOPMENTS UPDATE-2018

MULTI-CLIENT STUDY PRESENTATION
(Study Completed November 2018)

December 2018
ADVANCES IN SYNGAS PRODUCTION: CATALYST AND PROCESS DEVELOPMENTS UPDATE-2018

STUDY COMPLETED!

This TCGR multi-client study was completed in November 2018. The study’s scope, and specific contents (as depicted in the ToC on pages 10-20 of this presentation) reflect the inputs from a group of “charter” subscribers who have indicated their priorities for coverage, areas to be expanded/deepened and focal points for emphasis in opportunity identification. These are leading developers of technology for syngas production as well as the large volume syngas producers and users.

I. INTRODUCTION

Every few years, The Catalyst Group Resources (TCGR) provides an updated multi-client report on the status of syngas production developments to the benefit of process developers, users for revamp/maintenance and catalyst developers/suppliers covering commercial, economic, as well as R&D highlights and insights. In this 2018 update report, we focus on syngas production (as opposed to syngas conversion/utilization) advances as follows: SMR, ATR, dry reforming, tri-reforming, chemical looping and CPO, along with including life cycle assessments (LCA). This study specifically excludes direct C1/methane to olefins, aromatics and/or chemicals as they do not proceed through the syngas step.

There have been a number of newer developments that have been highlighted in this updated report which are important enough to be more closely benchmarked from a variety of perspectives, including: process; yield; economics; and environmental footprint (life cycle) standpoints. The following advancements are noteworthy and have been addressed (although they are not listed in any particular order):

- New dry reforming technology to be licensed from BASF/Linde
- New syngas reactor technology being introduced from Haldor Topsoe – SynCor – to eventually produce ammonia or methanol
- The potential use of a new rotary reactor in pilot, being pursued and supported by Dow Chemical
- Further developments with membrane reforming (e.g., Praxair, CoorsTek)
- Johnson Matthey’s (J-M’s) introduction and expansion Catacel SSR, metal substrates
- Zoneflow engineered packing
- New reactors and heat integration (e.g., J-M HER; H-T HTCR, HTER, TBR, etc.)
- Other material development (e.g., tube materials, dusting, etc.)
- Hybrid solutions (e.g., green syngas) and waste/waste plastics to syngas
- Advances in AGHR (J-M) and KRES (KBR)
- Advances in Chemical Looping Reforming/CLR and CPO

More detail on the processes evaluated are contained in the actual Table-of-Contents (TOC) depicted on pages 10-20, which has been modified by the “charter” subscribers which ordered TCGR’s report update prior to launch. This process allowed TCGR to focus the study to more closely meet customer’s needs. The report, thus, becomes an industry sponsored effort - by the industry, for the industry result.
II. BACKGROUND

The production of syngas (CO + H₂ in various ratios) via reforming (SMR, ATR, other) are well reviewed subjects, with significant installed industrial capacity. Those for chemical looping reforming (CLR) and catalytic partial oxidation (CPO) are well into pilot. Therefore, the intention of TCGR’s report is to highlight advances that can be used to gain commercial advantage and/or show R&D areas in pilot or beyond that can be more quickly adopted. The objective is to document the commercial progress each of the technologies has made over the last four years (since TCGR’s 2014 benchmarking report) and update both the technical/patent and economic realities, with an indication of life cycle assessment and implications.

Tubular reformers for steam reforming have not changed that much over the years. Methanol plants demand higher CO/H₂ ratio in the syngas. This has pushed the reformer syngas outlet temperature to 950 °C (1742 °F) or above. Catalyst developments have resulted in reduced sintering and maintained reasonable catalyst life. Many different formulations, shapes, and sizes of reforming catalyst have been used. Recent developments use Structured Reforming Catalysts such as thin metal foils shaped into modules provide enhanced performance. The most advanced efforts in developing structured reforming catalysts have been by Johnson Matthey Process Technologies and Zone Flow LLC.

Johnson Matthey (JM) offers a coated, foil based reforming catalyst, Catacel SSR. The catalyst was originally developed and commercialized by the Catacel Corporation which was acquired by JM in 2014. Catacel SSR is an engineered coated, thin-foil based catalyst. It is produced by forming alloy strip into engineered foil supports called fans (Figure 1, left). The fans are coated with a promoted nickel-based steam reforming catalyst using a proprietary coating process. As they are quite flexible, the fans can be pulled or pushed into the tubes. The fans are stacked one upon the other, separated by thin metal washers, inside the reforming tube (Figure 1, center). The outer edges of the fans are located close to, but not touching the internal surface of the tube. The gas flow pattern (Figure 1, right) through a Catacel SSR Stack starts with gas flowing down the tube encounters the fan but not move through it due to both central hole being blocked and the washers between fans. Johnson Matthey claims that the stacked fans deliver about 20-30% more heat transfer for the same (or lower) pressure drop when compared to traditional catalyst pellets.

Figure 1
Catacel™ SSR Views

Left: CatacelJM SSR Fan  Center: CatacelJM SSR Stack  Right: CatacelJM SSR Fan Flow Pattern
Other companies are looking to make chemicals by reacting CO with hydrogen acquired from water electrolysis. But multi-million-metric-ton use of CO₂ as a chemical reagent is relegated mostly to old-school production of urea and sodium bicarbonate. The German industrial gas and engineering giant Linde is looking to change that. Company officials claim to have made a breakthrough in dry reforming, a process that reacts CO₂, instead of steam or oxygen, with methane to yield the mixture of CO and H₂ known as synthesis gas.

Dry reforming may be the way to introduce CO₂ into the manufacture of large-scale chemicals such as methanol, acetic acid, and the diesel substitute dimethyl ether (DME), according to Nicole Schoedel, head of chemical development and services at Linde Engineering. “It is one of the few options where you can use CO₂ without an additional H₂ source,” she says. She says that tapping into methane’s hydrogen simplifies the incorporation of CO₂ in a large-scale chemical manufacturing process. Linde’s process isn’t pure dry reforming. The company does use some steam in the reaction to boost the amount of H₂ in the final syngas. However, dry reforming can reduce the carbon footprint of an integrated process, Schoedel claims.

Figure 2
Dry Reforming Test Results

In addition to dry reforming (DRM) more intense interest has arisen in tri-reforming (TRM). Much of this progress has surrounded Ni (0) promoted, with a variety of base and rare earth combinations. Of greater specific interest has been the more recent developments by Debek in which hydrotalcites (double layered hydroxides LDHs) contain Ni, Mg and Al in their structures, thus fulfilling the requirements for appropriate redox and basic properties. High CO₂ conversions may be obtained even at relatively low temperatures (around 600°C) with appropriate tailoring by the addition of other structural elements such as Zr, Ce and the application of La as a promoter was proven advantageous.
Among three main tri-reforming reactions only the steam reforming of natural gas is the process on industrial scale. This reformation is focused on hydrogen production, and operates in the 700–1000°C, in the presence of nickel catalyst supported on alumina. Dry methane reforming has not yet been implemented.

ENI and Haldor Topsoe have been collaborating on the development of SCT-CPO for some time. They built their first syngas pilot plant in Houston in 2001 and a second one in Sicily in 2006. The Houston unit was used to study air-blown SCT-CPO. The Sicilian unit was designed to test multiple feeds – from natural gas to HC liquids and to use oxidants ranging for pure oxygen to air. Their initial focus was on Pt group metals supported on a metal mesh or other inorganic support. A mixing system and reactor design was developed to allow processing of a relatively heavy HC stream, along with guidance for design to avoid heat transfer from the hot oxidation zone into the mixing zone. The catalyst is not "poisoned" by the presence of sulphur compounds, unlike the traditional ones used for hydrogen production.

![Figure 3](ENI SCT-CPO Reactor Design)

Eni’s proprietary SCT-CPO technology makes two orders of magnitude reduction in plant size and amount of catalyst needed compared with the traditional industrial process of steam reforming.

For chemical looping reforming (CLR), another 3-bed approach is being developed by Alstom with the intention of applying the CL concept to solid fuels. Their concept includes:

- A reducer, where the hydrocarbon fuel is oxidized by CaSO₄ – the extent (combustion vs POX) depending on the Ca/SO₄/fuel ratio. CO₂ from the fuel carbon reacts with CaO to form CaCO₃
- An oxidizer, where CaS from the reducer is oxidized by air back to CaSO₄
- A calciner, where CaCO₃ is heated to form CaO and drive off CO₂. If syngas is desired, the carbonate/CaO loop is not included
This concept has been steadily developed with significant funding from US DOE. The primary thrust has been to apply CLC to solid fuels. To this end, a 1 MW prototype has been built and operated at Darmstadt and 3 MW prototype was retrofit at Alstom’s test facility in Windsor, Conn. Integrated testing has only been carried out for the CLC process, wherein excess CaSO₄ is used to ensure that the product gas from the reducer is CO₂.

In this completed study, TCGR revisits the concepts above and updates the latest technical and pilot plant data as well as progress toward commercialization.

III. THE NEED FOR THE STUDY

TCGR provides independent professional process engineering and technical benchmarking undertaken periodically to ensure our industrial clients get both the latest but also most qualified information, so they can undertake their own business and technical decisions on a daily basis. For subscribers, it is important for them to maintain safe and economically favorable plant operations while continually improving their environmental footprints.

Syngas manufacture is a large and important industrial segment that is undergoing continual improvements with new catalysts and energy integration with improving yields; however, this requires a constant producer vigilance. One way to improve the cost effectiveness of this work is to subscribe to TCGR’s multi-client studies which very effectively spreads this cost externally over several subscribing companies.

IV. SCOPE AND METHODOLOGY

The study’s scope follows the actual Table of Contents (see pages 10-20). A brief “Introduction”, providing the needed background, as well as an “Executive Summary” are followed by the report Sections:

Section III details new developments in current reforming SMR through ATR, with new catalyst and process modifications to improve current productivities and reduce footprint environmental standards. Line items like JM’s new Catacel SSR and Haldor Tospoe’s Syncor are examples, but the progress of these newer developments are benchmarked, along with newer developments on internals and heat integration steps.

Section IV documents advances in both dry reforming and well as tri-reforming which has taken up renewed interest during the last five (5) years. In addition, the idea of renewables like solar for photocatalytic reactions has also made advances, along with the idea of electrochemical routes based on similar chemistries to try and green the use of alternative energies, are explored in this section.

Section V explores advances in CPO. There is considerable advanced work being undertaken in the pilot with Gas Technology Institute (GTI) in Illinois, U.S., as well as in Korea, KAIST. Updates on TurboPOX and others are certainly warranted. Chiyoda and JGC have also progressed since our last look into these processes since 2014.
**Section VI** examines chemical looping, which needs further consideration. The main issue here is the scale up challenges, which has historically defaulted to the EPC power providers Alstom and Stone and Webster. But there are other ongoing developments in Korea, Australia and Europe which have been benchmarked again after four (4) years to see what progress has been made.

**Section VII** addresses numerous unconventional and/or breakthrough approaches to syngas generation including electrically heated reforming, the use of waste/waste plastics as feedstocks, and hybrid solutions such as “green” syngas. These are assessed relative to current approaches, including their impacts on CO₂ footprints.

All of this updating required considerable field work. However, assembling this, as always, is extremely valuable to the commercial, as well as R&D/technical, processes of companies looking to decide their own research programs or in looking into venture capital investments. Thus TCGR’s report becomes a valuable resource in the senior management decision-making process. As usual TCGR’s insight into pipeline technology and developments provides a tool that is not available from other sources, which are more focused on market supply/demand or benchmarking just the top three (3) licensed processes in manufacturing technologies.

TCGR uses in-house and external resources, as well as expertise from within industry, academia, as well as our highly-regarded DIALOG GROUP® in order to complete:
- Technology evaluations
- Patent reviews and analyses
- Representative economics
- Market needs/drivers
- Competitive implications (developers and users)

The contents/scope are global in content, so we review all important sources/regions including developments within Russia and China using local consultants, as well as patent analyses.

All TCGR studies are characterized by competitive and strategic insights for industrial and financial investment companies to evaluate. These include key trends, concerns, and conclusions on the best return on investment (ROI) actions, competitive expectations and strategic SWOT’s on the players. TCGR is noted for its sound strategic advice in over 35 years of experience.

**TCGR’s unique background and established global Dialog Group® ensures expert capability and skill level in this study area.** TCGR has utilized numerous deeply experienced experts in syngas production to assist us to provide insights beyond what other sources that do not have the reach and industrial experience can provide.

As it does in each of its industrially-focused multi-client studies, TCGR has sought input from “charter” subscribers to help shape the report’s scope/ToF so that it covers and emphasizes the most pertinent content due to the large volume of research and the numerous areas that might be of interest.
V. QUALIFICATIONS

The Catalyst Group Resources, a member of The Catalyst Group, works with clients to develop sustainable competitive advantage in technology-driven industries such as chemicals, refining, petrochemicals, polymers, specialty/fine chemicals, biotechnology, pharmaceuticals, and environmental protection. We provide concrete proven solutions based on our understanding of how technology impacts business.

Using our in-depth knowledge of molecular structures, process systems, and commercial applications, we offer a unique combination of business solutions and technology skills through a range of client-focused services. Often working as a member of our clients' planning teams, we combine our knowledge of cutting-edge technology with commercial expertise to:

- Define the business and commercial impacts of leading-edge technologies
- Develop technology strategies that support business objectives.
- Assess technology options through strategy development, including:
  - Independent appraisals and valuations of technology/potential
  - Acquisition consulting, planning and due diligence
- Provide leading-edge financial methodology for shareholder value creation
- Lead and/or manage client-sponsored R&D programs targeted through our opportunity identification process.
- Provide leading information and knowledge through:
  - World-class seminars, conferences and courses
  - Timely technical publications

The client-confidential assignments conducted by The Catalyst Group include projects in:

- Reinventing R&D pipelines
- Technology alliances
- Technology acquisition
- Market strategy

We have built our consulting practice on long-term client relationships, dedication, and integrity. Our philosophy is clear and focused:

We Provide the "Catalysts" for Business Growth by Linking Technology and Leading-Edge Business Practices to Market Opportunities
VI. DELIVERABLES AND PRICING

This report is timely and strategically important to those industry participants and observers both monitoring and investing in the development and implementation of new technology in syngas production. TCGR’s report, based on technology evaluations, commercial/market assessments and interviews with key players goes beyond public domain information. As a result, subscribers are requested to complete and sign the “Order Form and Secrecy Agreement” on the following page.

The study, “Advances in Syngas Production: Catalyst and Process Developments Update-2018” was completed in November 2018 and is immediately available.

Post-production subscribers  
Advances in Syngas Production: Catalyst and Process Developments Update-2018  
Report in PDF format, in addition to subscription price  

US$22,500  
US$1,000

*Charter subscribers (those who signed up for the study prior to launch) had the opportunity to work with TCGR to further refine the scope of the report by delineating areas of particular interest for inclusion in the assessment.

*****

Notice to Subscribers of TCGR’s 2014 “Natural Gas Conversion vs. Syngas Routes” Two Volume Multi-Client Study Series

Due to the complementary nature of this study to the 2014 two volume study series, we are offering a discounted price to subscribers of those reports. Subscribers are requested to contact John J. Murphy at +1.215.628.4447, or John.J.Murphy@catalystgrp.com for further details. When completing the order form, please make sure to indicate your company’s subscription to either/both of the “Natural Gas Conversion vs. Syngas Routes” study series.
ORDER FORM AND SECRECY AGREEMENT
The Catalyst Group Resources, Inc. Tel: +1.215.628.4447
Gwynedd Office Park Fax: +1.215.628.2267
P.O. Box 680 e-mail: tcgr@catalystgrp.com
Spring House, PA 19477 - USA - website: www.catalystgrp.com

Please enter our order for “Advances in Syngas Production: Catalyst and Process Developments Update-2018,” completed in November 2018, as follows:

____ Advances in Syngas Production: Catalyst and Process Developments Update-2018 for US$22,500 (post-production)

____ Please enter our order for the study to be delivered in PDF (Adobe Acrobat) format for use across our sites/locations (i.e., site license) for an additional $1,000.

____ Please send us _____ additional printed copies @ $250 each.

____ * * * We are subscribers to either/both of TCGR’s 2014 two-volume study series addressing “Natural Gas Conversion vs. Syngas Routes” and are therefore entitled to the discounted subscription rate. * * *

In signing this order form, our company agrees to hold this report confidential and not make it available to subsidiaries unless a controlling interest (>50%) exists.

Signature: _______________________________ Date: _______________________________
Name: _______________________________ Title: _______________________________
Company: _______________________________
Billing Address: _______________________________
Shipping Address (no P.O. Boxes): _______________________________

Express delivery services will not deliver to P.O. Boxes
City: _______________________________ State/Country: _______________________________
Zip/Postal Code: _______________________________ Phone: _______________________________
E-mail: _______________________________ Fax: _______________________________

This report and our study findings are sold for the exclusive use of the client companies and their employees only. No other use, duplication, or publication of this report or any part contained herein is permitted without the expressed written consent of The Catalyst Group Resources.
# CONTENTS

SECTION I. EXECUTIVE SUMMARY ................................................................. 1

SECTION II. INTRODUCTION/BACKGROUND ........................................ 7
   A. INTRODUCTION ............................................................................... 7
   B. BACKGROUND .............................................................................. 8
   C. THE NEED FOR THE STUDY ......................................................... 11
   D. STUDY TEAM .............................................................................. 11
   E. REFERENCES .............................................................................. 13

SECTION III. ADVANCED SYNGAS ROUTES AND BENCHMARKING .... 15
   A. BACKGROUND .............................................................................. 15
   B. HALDOR TOPSOE SYNCOR™ ..................................................... 16
      1. Brief History ............................................................................ 16
      2. Technology Description ........................................................ 16
      3. Technology Advantages and Challenges ................................ 18
      5. Commentary .......................................................................... 21
   C. JOHNSON MATTHEY CATACEL SSR™ ........................................ 21
      1. Brief History ............................................................................ 21
      2. Technology Description ........................................................ 21
      3. Technology Advantages and Challenges ................................ 23
      5. Commentary .......................................................................... 25
   D. ZONEFLOW TECHNOLOGY ............................................................. 25
      1. Brief History ............................................................................ 25
      2. Technology Description ........................................................ 26
      3. Technology Advantages and Challenges (Ratan, April 2018) .... 27
      5. Commentary .......................................................................... 29
   E. NEW REACTORS AND HEAT INTEGRATION .................................. 29
      1. Haldor Topsoe Convective Reformers: HTCR, HTER, TBR ......... 29
         a. Technology Description of HTCR (Convective Reformer) ........ 29
b. Technology Advantages and Challenges of HTCR .................................... 31
c. Technology Description of HTER (Exchanger Reformer) ....................... 32
d. Technology Advantages and Challenges of HTER .................................... 34
e. Technology Description of TBR (Tubular Bayonet Reformer) .................. 35
f. Technology Advantages and Challenges of TBR ....................................... 36

2. Johnson Matthey: GHR, CR ........................................................................... 36
   a. Technology Description of GHR (Gas Heated Reformer) ..................... 36
   b. Technology Advantages and Challenges of GHR ................................. 38
c. Technology Description of CR (Compact Reformer) ............................. 39
d. Technology Advantages and Challenges of CR ........................................ 41
e. Current Commercial Status and Economic Comparison of Convective Reformer Technologies .......................................................... 42
   i. Current Commercial Status ............................................................... 42
   ii. Economic Comparison ................................................................. 42
f. Commentary on Convective Reformers ..................................................... 43

3. Praxair Membrane Reforming ........................................................................ 44
   a. Technology Description ..................................................................... 44
   i. Background ...................................................................................... 44
   ii. CO and H$_2$S Resistance ............................................................... 45
   iii. Membrane Manufacturing ............................................................... 46
   iv. Tube Bundle Design and Manufacturing ........................................... 46
   v. Membrane Test Performance ............................................................. 48
   vi. Other Pd Membrane Technologies .................................................. 49
b. Technology Advantages and Challenges ................................................ 49
c. Current Commercial Status and Commentary ........................................ 50

F. OTHER MATERIALS DEVELOPMENTS ..................................................... 50
1. Tube Materials ......................................................................................... 50
   a. Background ...................................................................................... 50
   b. Creep Resistant Alloys ....................................................................... 51
   c. Stronger Alloys and Thinner Tubes ................................................... 51
d. Longer Tube Life and Economic Assessment .......................................... 52
2. Material Resistant to Metal Dusting ........................................................ 52
   a. Background ...................................................................................... 52
   i. Metal Dusting Resistant Alloys ......................................................... 55
ii. Gas Phase Inhibitors ................................................................. 55
iii. Diffusion Coatings ................................................................. 56

b. Technology Status and Challenges ....................................... 56
c. Current Commercial Status and Economic Assessment ........... 57
   i. Current Commercial Status .................................................. 57
   ii. Economic Assessment ......................................................... 58

   a. Technology Status and Challenges ........................................ 59

G. ECONOMIC COMPARISON & LIFE CYCLE ASSESSMENT .......... 60

H. CONCLUSIONS ........................................................................ 63

I. REFERENCES ........................................................................... 65

SECTION IV. DRY REFORMING, TRI-REFORMING AND SOLAR-ASSISTED REFORMING: ADVANCES AND BENCHMARKING .......... 69

A. BACKGROUND ........................................................................... 69

B. LINDE/BASF DRYREF PROJECT ................................................ 70
   1. Economics ........................................................................... 73
   2. Summary/Conclusion ............................................................ 74

C. CHIYODA CT-CO₂AR™ DRY REFORMING PROJECT ................. 74
   1. Background ........................................................................ 74
   2. CT-CO₂AR™ Dry Reforming ............................................... 74
   3. Economics ........................................................................... 75
   4. Conclusions ........................................................................ 75

D. TRI-REFORMING ...................................................................... 75
   1. Background ........................................................................ 75
   2. Development Status ............................................................ 77
   3. Economics ........................................................................... 78
   4. Conclusions – Tri-Reforming ................................................. 79

E. SOLAR-ASSISTED REFORMING ............................................... 79
   1. Background ........................................................................ 79
   2. Solar-thermal ........................................................................ 80
   3. Economics of Solar Thermal Reforming .................................. 81

F. PHOTOCATALYSIS ................................................................ 82
   1. Background ........................................................................ 82
   2. Economics of Photocatalysis .................................................. 83
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. History &amp; Background</td>
<td>123</td>
</tr>
<tr>
<td>2. Technology Description</td>
<td>124</td>
</tr>
<tr>
<td>3. Technology Advantages and Challenges</td>
<td>125</td>
</tr>
<tr>
<td>4. Commercial Status</td>
<td>126</td>
</tr>
<tr>
<td>5. Economic Analysis</td>
<td>127</td>
</tr>
<tr>
<td>6. Summary Assessment</td>
<td>127</td>
</tr>
<tr>
<td>D. WASTE AND WASTE PLASTIC TO SYNGAS</td>
<td>128</td>
</tr>
<tr>
<td>1. Municipal Solid Waste</td>
<td>128</td>
</tr>
<tr>
<td>2. Introduction to Municipal Solid Waste Conversion</td>
<td>130</td>
</tr>
<tr>
<td>a. Cutting Costs, Increasing Energy</td>
<td>130</td>
</tr>
<tr>
<td>3. Gasification of Non-recycled Plastic and MSW</td>
<td>131</td>
</tr>
<tr>
<td>4. Specific MSW Conversion Examples</td>
<td>134</td>
</tr>
<tr>
<td>a. ThermoChem Recovery International (TRI)</td>
<td>134</td>
</tr>
<tr>
<td>i. History and Background</td>
<td>134</td>
</tr>
<tr>
<td>ii. Technology Description</td>
<td>135</td>
</tr>
<tr>
<td>iii. Technology Advantages and Challenges</td>
<td>136</td>
</tr>
<tr>
<td>iv. Status of the technology</td>
<td>136</td>
</tr>
<tr>
<td>v. Economic Analysis</td>
<td>136</td>
</tr>
<tr>
<td>vi. Summary Assessment</td>
<td>137</td>
</tr>
<tr>
<td>b. Enerkem</td>
<td>138</td>
</tr>
<tr>
<td>i. History and Background</td>
<td>138</td>
</tr>
<tr>
<td>ii. Technology Description</td>
<td>138</td>
</tr>
<tr>
<td>iii. Technology Advantages and Challenges</td>
<td>139</td>
</tr>
<tr>
<td>iv. Status of the Enerkem Technology</td>
<td>140</td>
</tr>
<tr>
<td>v. Economic Analysis</td>
<td>140</td>
</tr>
<tr>
<td>vi. Summary Assessment</td>
<td>141</td>
</tr>
<tr>
<td>c. BTG Supercritical Water Gasification</td>
<td>141</td>
</tr>
<tr>
<td>i. History and Background</td>
<td>141</td>
</tr>
<tr>
<td>ii. Technology Description</td>
<td>141</td>
</tr>
<tr>
<td>iii. Technology Advantages and Challenges</td>
<td>144</td>
</tr>
<tr>
<td>iv. Status of the Technology</td>
<td>144</td>
</tr>
<tr>
<td>v. Economic Analysis</td>
<td>144</td>
</tr>
<tr>
<td>vi. Summary Assessment</td>
<td>144</td>
</tr>
</tbody>
</table>
E. DISTRIBUTED SYNGAS PRODUCTION: NEW TECHNOLOGIES FOR H₂ AND OTHER TRENDS .......................................................... 144
   1. History & Background .................................................................................................................. 144
   2. Technology Description ............................................................................................................. 147
   3. Commercial Status .................................................................................................................. 152
   4. Economic Analysis .................................................................................................................. 153
   5. Future Outlook ......................................................................................................................... 154
F. ELECTROLYSIS AND PLASMA REFORMING ADVANCES .............. 156
   1. Plasma reforming of MSW ........................................................................................................ 156
      a. Introduction to Plasma Technology ......................................................................................... 156
      b. Specific Plasma Technology Examples .................................................................................. 157
         i. AlterNRG Plasma Gasification technology ................................................................................. 157
         ii. InEnTec ................................................................................................................................. 161
         iii. Aemetis ............................................................................................................................... 166
   2. Electrolysis for Generation of Hydrogen .................................................................................. 168
      a. History and Background ......................................................................................................... 168
      b. Current Operating Technology and Status ............................................................................. 169
      c. Summary Assessment ............................................................................................................. 172
G. OUTLOOK FOR THE FUTURE .................................................................................. 172
H. REFERENCES ......................................................................................................................... 174

SECTION VIII. SUMMARY, ANALYSIS AND RECOMMENDATIONS ...... 179

FIGURES

Figure I-1  Future Hydrogen Production Scheme ......................................................... 2
Figure I-2  Renewable and Zero-Carbon Gas Pathways ............................................. 2
Figure I-3  Scale Dependence of Unit Cost ................................................................. 3
Figure II-B-1 Catacel™ SSR Views ............................................................................... 9
Figure II-B-2 Dry Reforming Test Results ................................................................. 9
Figure II-B-3 ENI SCT-CPO Reactor Design ............................................................ 10
Figure III-B-1 Topsoe SynCor™ Process ................................................................. 17
Figure III-B-2 SynCOR™ATR ..................................................................................... 18
Figure III-B-3  Front End CAPEX SynCOR Ammonia vs SMR ......................... 20
Figure III-C-1  Catacel™ SSR Fan .............................................................. 22
Figure III-C-2  Catacel™ SSR Stack ............................................................ 22
Figure III-C-3  Catacel™ SSR Stack Installation ......................................... 22
Figure III-C-4  Catacel™ SSR Fan Flow Pattern ........................................ 23
Figure III-D-1  ZoneFlow Reactor Stack ....................................................... 26
Figure III-D-2  ZoneFlow Reactor Nested Modules ...................................... 26
Figure III-D-3  ZoneFlow Reactor Installation ............................................. 27
Figure III-E-1  HTCR Steam Reformer ........................................................ 30
Figure III-E-2  Topsoe Convection Reformer Process (HTCR) ..................... 30
Figure III-E-3  HTCR Convection Reformer ............................................... 31
Figure III-E-4  HTER Exchange Reformer .................................................. 33
Figure III-E-5  HTER Configurations .......................................................... 33
Figure III-E-6  TBR Bayonet Reformer ........................................................ 35
Figure III-E-7  Johnson Matthey GHR Process .......................................... 37
Figure III-E-8  Comparison of GHR with AGHR ...................................... 38
Figure III-E-9  Compact Reformer .............................................................. 40
Figure III-E-10 Compact Reformer Demonstration unit at Nikiski, Alaska .... 40
Figure III-E-11 Compact Reformer Module at Nikiski .................................. 41
Figure III-E-12 Impact of alloy composition on H₂ permeability ................ 45
Figure III-E-13 Porous Gen 3 substrate (bottom), activated for electroless plating (2nd from bottom), coated with a thin film of Pd (3rd from bottom), coated with Au (4th from bottom), and annealed (top)... 46
Figure III-E-14 Layered structure of Pd-Au membrane fabrication ............ 46
Figure III-E-15 Flux decreases along the length of the membrane because the surface concentration of the permeate species (green) decreases... 47
Figure III-E-16 Praxair Demonstration unit separator design ...................... 47
Figure III-F-1  Temperature dependence of the metal dusting corrosion rate of iron in 50CO:50H₂ gas mixture ......................................................... 53
Figure III-F-2  Calculations of the carbon activity as function of temperature for a particular gas ................................................................. 54
Figure III-F-3  Weight loss as function of temperature of Alloy 600, 601 and 602CA under metal dusting conditions at 650 °C. The lowest weight loss is observed in the alloy with the largest Cr-content ... 55
Figure III-F-4  Maximum pit depth measurements for samples exposed to CO-20%H₂ at 621°C ................................................................. 57
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>III-G-1</td>
<td>Processes in natural gas extraction and processing for Marcellus Shale gas</td>
</tr>
<tr>
<td>III-G-2</td>
<td>Syngas generation LCA model</td>
</tr>
<tr>
<td>III-G-3</td>
<td>Syngas LCA emissions for ATR</td>
</tr>
<tr>
<td>IV-B-1</td>
<td>DryRef Process for H\textsubscript{2} and CO Production</td>
</tr>
<tr>
<td>IV-B-2</td>
<td>Range of H\textsubscript{2}/CO ratio of various syngas production technologies</td>
</tr>
<tr>
<td>IV-B-3</td>
<td>Type I (G1-110T) - Stable operation at 20 bar for &gt;1,000h @ S/C ~0.9 w/o coke formation</td>
</tr>
<tr>
<td>IV-B-4</td>
<td>Type II (G2-120T) - Stable operation at 20 bar for &gt;500h @ S/C ~0.4 w/o coke formation</td>
</tr>
<tr>
<td>IV-B-5</td>
<td>Screening Test Rig at hte</td>
</tr>
<tr>
<td>IV-B-6</td>
<td>Linde single tube Test Stand</td>
</tr>
<tr>
<td>IV-B-7</td>
<td>Linde Mono-tube Reformer Test Rig at Pullach, Germany</td>
</tr>
<tr>
<td>IV-C-1</td>
<td>Chiyoda DryRef Catalyst</td>
</tr>
<tr>
<td>IV-D-1</td>
<td>TriReforming Concept</td>
</tr>
<tr>
<td>IV-D-2</td>
<td>Schematic of the TCTDR</td>
</tr>
<tr>
<td>IV-E-1</td>
<td>Solar Concentrator Tower and Heliostats at Crescent Dunes, Nevada Facility</td>
</tr>
<tr>
<td>IV-E-2</td>
<td>Solar methane reforming reactor</td>
</tr>
<tr>
<td>V-A-1</td>
<td>Flow scheme for CPO</td>
</tr>
<tr>
<td>V-A-2</td>
<td>CPO applied to Urea Production</td>
</tr>
<tr>
<td>V-A-3</td>
<td>CPO applied to Methanol Production</td>
</tr>
<tr>
<td>V-B-1</td>
<td>Catalyst Stability as a function of Reynolds Number</td>
</tr>
<tr>
<td>V-C-1</td>
<td>ENI CPO Pilot Plant in Sicily</td>
</tr>
<tr>
<td>V-D-1</td>
<td>JGC AATG®</td>
</tr>
<tr>
<td>VI-A-1</td>
<td>Chemical Looping Combustion General Process Schematic</td>
</tr>
<tr>
<td>VI-A-2</td>
<td>General Chemical Looping Reforming Process Schematic</td>
</tr>
<tr>
<td>VI-A-3</td>
<td>Chemical Looping Reforming - Variant 1</td>
</tr>
<tr>
<td>VI-A-4</td>
<td>Chemical Looping Reforming - Variant 2</td>
</tr>
<tr>
<td>VI-A-5</td>
<td>Packed Bed CLR for H\textsubscript{2} and CH\textsubscript{3}OH Production</td>
</tr>
<tr>
<td>VI-A-6</td>
<td>Catalyst tested in PBR-CLR Scheme</td>
</tr>
<tr>
<td>VI-D-1</td>
<td>CLR Facilities with interconnected fluidized beds</td>
</tr>
<tr>
<td>VI-E-1</td>
<td>Process block diagram for hydrogen production based on CLR</td>
</tr>
</tbody>
</table>
Figure VII-A-1 Levelized cost of H₂ for small (1500 kg/day) and large (100,000 tonne/year) plants in conventional, membrane-based and solar-integrated configurations, at current and future (50% of current) membrane costs .............................................. 113

Figure VII-B-1 Principles of hysteresis heating proposed for SMR .................. 115
Figure VII-B-2 Comparing heating systems in a SMR unit .................................. 116
Figure VII-B-3 Preparation of catalytic Co-Ni nanoparticles ............................. 117
Figure VII-B-4 Methane conversion testing electrical heated SMR .................. 118
Figure VII-B-5 Projected USA electricity distribution by 2020 .......................... 120
Figure VII-B-6 Projected industrial electricity costs in USA and Germany by 2020 ................................................................................................................. 121
Figure VII-B-7 Tentative economics for methanol production ............................ 122
Figure VII-B-8 Methanol production cost against electricity cost ...................... 122
Figure VII-C-1 Comparison of methane conversion for traditional SMR reactors (TR) and membrane reactors (MR). The temperature of the reactors is set at 723 K with a steam/methane inlet ratio of 3:1. A reactor length of 70 cm with membrane thickness of 50 μm was studied. Co-current vs. counter-current MR configurations specify the direction of the sweep gas flow .......................................................... 123

Figure VII-C-2 Schematic of CoorsTek membrane reformer. Methane and steam are fed (1:2.5 molar ratio) on the reaction side. The methane is almost completely reacted along the length of the electrode. Hydrogen is transported across the electrolyte by applying a potential across the reactor. The heat evolved at the membrane for 1) the separation and 2) compression of hydrogen is coupled with the SMR reaction .............................................................. 125

Figure VII-C-3 PMR longevity assessment with separate direct natural gas and direct ethanol feed. Natural gas consists of 19.5 ppm H₂S. Operating temperatures and current densities are given ..................................... 126

Figure VII-C-4 Commercialization progress of the PMR. The yellow star represents the current status of production scale .............................................. 127

Figure VII-C-5 Economic comparison of centralized hydrogen production. Note that the PMR membrane cost alone would be roughly equivalent to the entire SMR installation and operation cost ..... 128

Figure VII-D-1 Project Total Urban Waste for 2025 .............................................. 129
Figure VII-D-2 Project Urban Wast per Capita for 2025 .................................... 130
Figure VII-D-3 Typical conventional gasification reactors ................................. 132
Figure VII-D-4 Tipping fees ($/T) in the USA (1992-2011) ................................. 134
Figure VII-D-5 ThermoChem Recovery International – Technology Development Timeline .......................................................... 135

Figure VII-D-6 Enerkem Technology ................................................................. 139
Figure VII-D-7  Bio-mass reforming in supercritical water................................. 142
Figure VII-D-8  Super Critical Water Gasification.............................................. 143
Figure VII-E-1  On-site HY.GEN methane reforming systems (inset trailers) ..... 145
Figure VII-E-2  Overview of gas to liquid process flow diagram. The main change on the backend is the Fischer-Tropsch unit operation, which converts syngas to long chain hydrocarbons.................. 146
Figure VII-E-3  Compact steam methane reformer. The proximity of all the tubes allows for increased heat transfer via convection, which accounts for 90% of the heat transfer. Similar, albeit slightly larger, designs exist for auto-thermal reforming. Schematic on left, actual apparatus on right.................................................. 148
Figure VII-E-4  Above- a visualization of the microchannel reactor channels and dimensions for SMR. Methane is combusted over a palladium alumina catalyst, and the heat from this reaction is transferred to adjacent channels for SMR. Below- the actual microchannel reactor schematic for F-T fuels. One can see the cross-flow channels where heat would be transferred and subsequent reactions occur .......................................................... 149
Figure VII-E-5  8L engine reformer, coupled with a generator, designed by RTI, Columbia, and MIT ............................................................. 150
Figure VII-E-6  Top - picture of Microlith® reactor. Ceramic-coated membrane mesh contains cm-length reactors with Rh catalyst. Bottom - Microlith® auto-thermal reformer (ATR) long-term performance for converting petroleum-based jet fuel (JP-8) to syngas. Reforming efficiency is maintained at 85% over 1100h for a fuel containing 70 ppm w sulfur. Image above from Precision Combustion, Inc................................................................. 151
Figure VII-E-7  GTL plant size vs. production cost. Calculated scale factor for production capacity vs. cost/bbl is 0.7.................................................. 154
Figure VII-F-1  Alter NRG Plasma Gasification Reactor ................................. 158
Figure VII-F-2  Placement of AlterNRG plasma reactor into support structure, Wuhan Kaidi Biomass Gasification plant Wuhan, China........ 162
Figure VII-F-3  InEnTec’s Plasma Enhanced Melter PEM............................... 163
Figure VII-F-4  Bio-mass to Ethanol by Aemetis ........................................... 167
Figure VII-F-5  Electrolysers of Water by Supplying Electricity ................. 170
Figure VII-F-6  Industrial Alkaline water Electrolysers................................. 170
Figure VII-F-7  Giner PEM electrolysis equipment........................................ 171
Figure VII-G-1  Future hydrogen production scheme.................................... 173
Figure VIII-1  Future hydrogen production scheme....................................... 186
TABLES

Table III-C-1  Pre-2018 Catacel™ Reference List ........................................ 24
Table III-C-2  2018 Catacel™ Deliveries ...................................................... 25
Table III-D-1  ZF Demonstration Results in Commercial SMR .................. 29
Table III-E-1  Testing Gas Composition ..................................................... 43
Table III-E-2  Other Impurities ................................................................. 48
Table III-E-3  The Test Performance at EERC as Reported by Praxair .... 48
Table III-F-1  Typical Conditions for Main Reformer & Equilibrium
Temperatures for Carbon Forming Reactions in Different
Plant Types ........................................................................................... 54
Table III-F-2  Nominal Chemical Compositions (wt. %) for Materials
Presented ............................................................................................... 56
Table III-G-1  Natural Gas Emission Factors for Various Sources .............. 61
Table V-A-1  Coking resistant Catalysts for Methane CPO ......................... 89
Table V-C-1  Normalized Values for Comparing Conventional Technology to
CPO Schemes ..................................................................................... 93
Table VI-C-1  Oxygen Carriers Tested for CLR Applications ..................... 103
Table VI-C-2  Oxygen Carriers vs. CL Processes ....................................... 104
Table VII-B-1  Conventional Methanol/SMR ............................................. 119
Table VII-B-2  Methanol with Electrical Heated SMR ............................... 120
Table VII-D-1  Current and Future Waste Generation ............................. 129
Table VII-D-2  Mixed Waste Gasification companies ............................... 131
Table VII-D-3  Economics Using MSW to Aviation Fuel ......................... 137
Table VII-D-4  Commercial Plants by Enerkem ..................................... 140
Table VII-D-5  Gasification of MSW ......................................................... 140
Table VII-F-1  Classic WRE and Plasma Gasification ............................. 160