

## CO<sub>2</sub> UTILIZATION IN REFORMING

A techno-economic investigation  
commissioned by the members of the  
**Carbon Dioxide Capture & Conversion (CO<sub>2</sub>CC) Program**

Client Private  
December 2017



### The Carbon Dioxide Capture & Conversion (CO<sub>2</sub>CC) Program

The **CO<sub>2</sub>CC Program** is a membership-directed consortium whose members are involved in the development, monitoring and utilization of the “state-of-the-art” in technological progress and commercial implementation of carbon dioxide capture/clean-up and conversion. 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 document technically and commercially viable options for CO<sub>2</sub> capture/clean-up as well as its conversion into useful products which meaningfully address the challenges posed by CO<sub>2</sub> life-cycle and overall sustainability issues.

Members receive three in-depth **CO<sub>2</sub>CC Techno-economic Reports** which are written by leading scientists and experienced industry professionals in areas selected by the membership (via ballot); weekly *CO<sub>2</sub>CC Communiqués* (delivered via e-mail) which provide the latest updates on technical breakthroughs, commercial events and exclusive development opportunities; and attendance at the CO<sub>2</sub>CC Program **Annual Meeting**.

The **Carbon Dioxide Capture & Conversion (CO<sub>2</sub>CC) Program** is available on a membership basis from The Catalyst Group Resources (TCGR). For further details, please contact John J. Murphy at [John.J.Murphy@catalystgrp.com](mailto:John.J.Murphy@catalystgrp.com) or +1.215.628.4447 (x1121).



P.O. Box 680  
Spring House, PA 19477 U.S.A.  
ph: +1.215.628.4447

## CONTENTS

<b>EXECUTIVE SUMMARY.....</b>	<b>xix</b>
<b>1. INTRODUCTION.....</b>	<b>1</b>
1.1 REPORT CONTRIBUTORS .....	2
<b>2. CO<sub>2</sub> CONVERSION TO SYNGAS .....</b>	<b>5</b>
2.1 INTRODUCTION .....	5
2.2 STATE OF THE ART OF SYNGAS PRODUCTION.....	6
2.2.1 Water Gas Shift Reaction (WGS) .....	6
2.2.2 Gasification .....	8
2.2.3 Partial Oxidation of Methane (POX) .....	11
2.2.4 Steam Methane Reforming (SMR) .....	12
2.2.5 Auto-thermal reforming process (ATR).....	15
2.2.6 Outlook.....	16
2.3 CO <sub>2</sub> AS FEEDSTOCK FOR SYNGAS PRODUCTION .....	17
2.3.1 Dry Reforming of Methane (DRM) .....	17
2.3.2 DRM in the presence of steam (bi-reforming).....	26
2.3.3 DRM in the presence of oxygen (oxy-reforming).....	30
2.3.4 DRM in the presence of steam & oxygen (tri-reforming).....	32
2.3.5 Outlook.....	37
2.4 CO <sub>2</sub> TO SYNGAS ENABLING TECHNOLOGIES .....	37
2.4.1 CALCOR® dry reforming technology .....	38
2.4.2 Shell-SARI dry reforming technology .....	39
2.4.3 Carnol technology .....	39
2.4.4 BASF two-stage dry reforming technology .....	39
2.4.5 Haldor Topsøe A/S bi-reforming technology .....	40
2.4.6 Chiyoda bi-reforming technology .....	41
2.4.7 KOGAS tri-reforming technology .....	41
2.4.8 Oberon Fuels process .....	42
2.4.9 Outlook.....	42
2.5 CO <sub>2</sub> TO SYNGAS VIA OTHER DEVELOPMENT ROUTES .....	42
2.5.1 Solar-based thermochemical technology .....	43

**PROPRIETARY -- Do Not Reproduce or Redistribute!**

This message is in red ink. If not, you have an unauthorized copy.

2.5.2	Non-thermal plasma technology .....	44
2.5.3	Electrochemical technology.....	47
2.5.4	Outlook .....	49
2.6	MARKETS AND OPPORTUNITIES .....	49
2.6.1	Markets .....	49
2.6.2	Opportunities.....	51
2.7	TECHNICAL/ECONOMIC HURDLES .....	52
2.8	CONCLUSIONS.....	53
2.9	REFERENCES .....	55
<b>3.</b>	<b>CO<sub>2</sub> CONVERSION TO METHANE.....</b>	<b>65</b>
3.1	INTRODUCTION .....	65
3.2	STATE OF THE ART OF SYNTHETIC METHANE PRODUCTION .....	66
3.2.1	Feedstocks.....	66
3.2.2	Process Concepts .....	66
3.2.3	Benchmarking technologies.....	69
3.2.4	Catalysts .....	71
3.3	POWER TO GAS CONCEPT (PtG) .....	73
3.3.1	Process Scheme to Methane.....	73
3.3.2	Methane vs Syngas Production.....	75
3.4	ENABLING TECHNOLOGIES .....	75
3.5	OTHER DEVELOPMENT ROUTES .....	77
3.5.1	Photochemical Route .....	77
3.5.2	Electrochemical Route .....	77
3.5.3	Thermochemical Ammonia Route .....	78
3.5.4	Biological Methanation.....	78
3.6	MARKETS AND OPPORTUNITIES .....	79
3.7	TECHNICAL/ECONOMIC HURDLES .....	80
3.8	CONCLUSIONS.....	80
3.9	REFERENCES .....	81
<b>4.</b>	<b>INDEX.....</b>	<b>85</b>

## FIGURES

Figure 2.2.2.1	Global syngas output by feedstock.....	9
Figure 2.2.2.2	The hydromethanation process developed by GreatPoint Energy.....	10
Figure 2.2.4.1	Reaction rate vs metal dispersion on $ZrO_2$ , $Al_2O_3$ and $MgAl_2O_4$ support at 500°C with steam:CH <sub>4</sub> molar ratio of 4 (adapted from Jones <i>et al.</i> , 2008)....	14
Figure 2.2.5.1	Basics of (a) multi-purpose gasification and (b) autothermal reforming reactors (adapted from Lurgi, 2003).....	16
Figure 2.3.1.1	Number of publications (blue) and patents (red) published per year since 1995 ("CO <sub>2</sub> reforming" keyword in the publications/patents titles).....	17
Figure 2.3.1.2	Effect of temperature on the equilibrium composition for DRM (CH <sub>4</sub> :CO <sub>2</sub> = 1:1, $P$ = 0.1 MPa). Adapted from Noureldin <i>et al.</i> , 2014. ....	19
Figure 2.3.2.1	CO <sub>2</sub> and CH <sub>4</sub> conversions in bi-reforming of methane (a) and natural gas (b) over 15 wt% Ni/MgO at 830°C and 0.7 MPa (adapted from Olah <i>et al.</i> , 2015) .....	29
Figure 2.3.3.1	Equilibrium carbon deposition as a function of temperature for dry reforming, oxy-reforming and by-reforming using HBC Chemistry (adapted from Kumar <i>et al.</i> , 2016b). .....	31
Figure 2.3.4.1	Carbon analysis on the catalysts by temperature-programmed oxidation after the tri-reforming reaction (adapted from Song & Pan, 2004).....	35
Figure 2.3.4.2	Effect of time-on-stream on CH <sub>4</sub> , CO <sub>2</sub> , and H <sub>2</sub> O conversion (adapted from Singha <i>et al.</i> , 2016). .....	36
Figure 2.4.1.1	Schematic flow diagram for CALCOR® Standard process (© 2001 URBAN-VERLAG Hamburg/Wien GmbH). .....	38
Figure 2.4.7.1	KOGAS tri-reformer reactor and KDN-1 catalyst (© 2017 Cho W, Yu H, Mo Y. Licensee InTech).....	41
Figure 2.5.1.1	Scheme of the two-step redox cycle for CO <sub>2</sub> and H <sub>2</sub> O splitting to CO and H <sub>2</sub> .....	43
Figure 2.5.2.1	List of possible effects of plasma on catalyst, and vice versa (adapted from Snoeckx & Bogaerts, 2017). .....	45
Figure 2.5.2.2	(a) DBD reactor scheme with the catalyst, (b) CH <sub>4</sub> and CO <sub>2</sub> conversions obtained with plasma alone, catalyst alone and plasma-catalyst combination, and (c) H <sub>2</sub> and CO selectivity. Flowrate, 60 mL/min; flowrate of Ar, 30 mL/min; CH <sub>4</sub> :CO <sub>2</sub> molar ratio = 1; discharge length, 10 cm; 60W; GHSV= 1800 h <sup>-1</sup> ; 450°C. Catalyst alone: CH <sub>4</sub> :CO <sub>2</sub> :Ar = 0.25:0.25:0.5; GHSV= 1800 h <sup>-1</sup> ; 450°C; 0.1 g. (adapted from Zhang <i>et al.</i> , 2010). .....	46
Figure 2.5.3.1	Scheme of SOEC and electrochemical reactions. ....	48
Figure 2.6.1.1	CO <sub>2</sub> emissions (%) from combustion-related activities by regions. ....	50

Figure 3.2.2.1	Temperature influence on the equilibrium composition at 0.1 MPa of (a) CO methanation and water gas shift reaction, H <sub>2</sub> :CO = 3, and (b) CO <sub>2</sub> methanation and water gas shift reaction, H <sub>2</sub> :CO <sub>2</sub> = 4 .....	67
Figure 3.2.4.1	Number of publications (English language) per year since 1995 with the keyword "CO methanation" or "CO <sub>2</sub> methanation" in the publication's title (database: Web of Science). ....	71
Figure 3.2.4.2	CO <sub>2</sub> conversion with a feed of pure CO <sub>2</sub> and biogas at 350°C. ....	72
Figure 3.3.1	Discharge time vs storage capacity of flywheels, batteries, compressed air energy storage (CAES), pumped hydro storage (PHS), hydrogen (H <sub>2</sub> ) and synthetic natural gas (SNG), adapted from Specht et al., 2009.....	73
Figure 3.4.1	Audi e-gas plant maquette.....	76

## TABLES

Table 2.3.1	Ni-based DRM catalysts evaluated at time-on-stream >20 h, and 0.1 MPa pressure (unless otherwise stated).....	25
Table 2.3.2	Optimized CH <sub>4</sub> :CO <sub>2</sub> :H <sub>2</sub> O feed molar ratio and corresponding parameters of syngas (adapted from Demidov et al., 2011) .....	27
Table 2.3.3	Main reactions thermodynamically possible for tri-reforming (Song, 2004) .....	33
Table 2.4.1	Comparison of full size monotube pilot experiments (HOU) and industrial plants (referenced with country where they are constructed) of CO <sub>2</sub> -rich reforming of natural gas with different catalysts (adapted from Mortensen & Dybkjær, 2015) .....	40
Table 3.2.1	Suppliers, concepts and technology names for commercial CO and CO <sub>2</sub> methanation technologies (adapted from Rönsch et al, 2016) .....	68
Table 3.2.2	Commercial CO methanation processes (adapted from Rönsch et al, 2016 & IEA, 2014).....	70

## SCHEMES

Scheme 2.3.1.1	Schematic reaction network of carbon formation (adapted from Trimm, 1997) and TEM image of encapsulated nickel catalyst into whisker (adapted from Abild-Pedersen, 2006). .....	19
Scheme 2.3.1.2	Basics of Eley-Rideal and Langmuir-Hinshelwood mechanism in dry reforming.....	21
Scheme 2.3.1.4	Schematic representation of encapsulated particles by different coatings.....	23
Scheme 2.3.4.1	Reaction pathways for methane partial oxidation to syngas.....	33
Scheme 3.3.1	Basic concept of interconnected power and gas grids network for different markets.....	74