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

## MULTI-CLIENT STUDY PRESENTATION
**(Study Completed November 2018)**

**December 2018**

TCGR THE CATALYST GROUP RESOURCES™

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# 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 TofC 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 $C_1$/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.



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## II. BACKGROUND

The production of syngas (CO + $H_2$ 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/$H_2$ 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: CatecelJM SSR Fan* *Center: CatacelJM SSR Stack* *Right: CatacelJM SSR Fan Flow Pattern*



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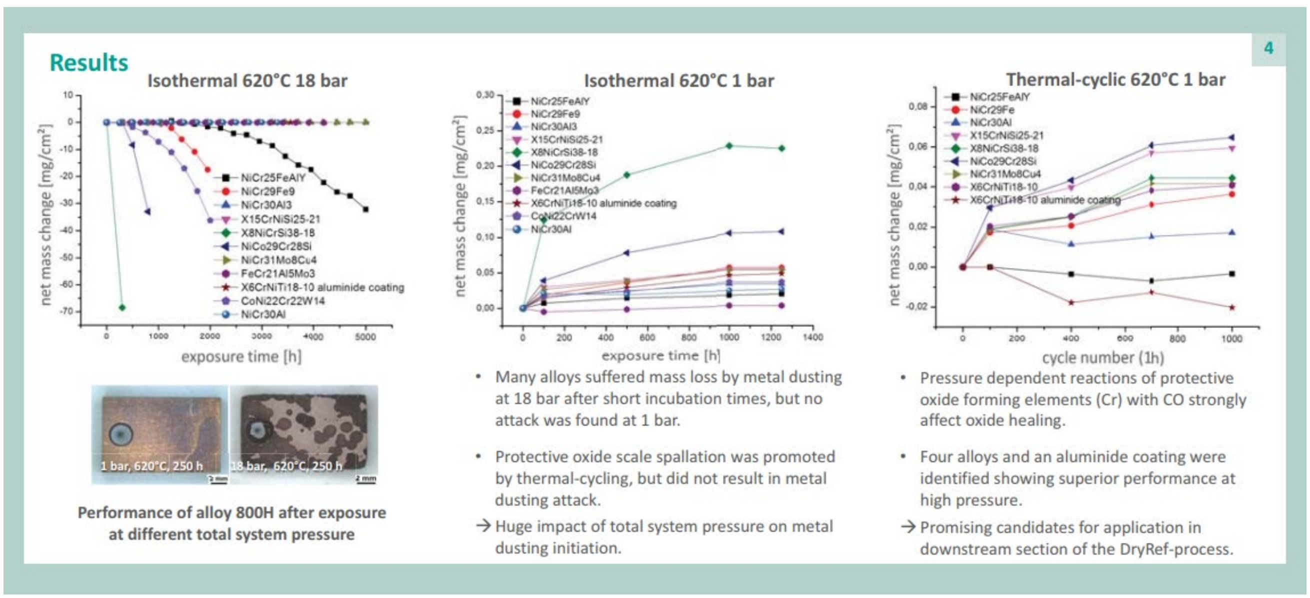
Other companies are looking to make chemicals by reacting CO with hydrogen acquired from water electrolysis. But multi-million-metric-ton use of $CO_2$ as a chemical reagent is relegated mostly to old-school production of urea and sodium bicarbonate. The German industrial gas and engineering giant Linde is looking to change that. Company officials claim to have made a breakthrough in dry reforming, a process that reacts $CO_2$, instead of steam or oxygen, with methane to yield the mixture of CO and $H_2$ known as synthesis gas.

Dry reforming may be the way to introduce $CO_2$ 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 $CO_2$ without an additional $H_2$ source,” she says. She says that tapping into methane’s hydrogen simplifies the incorporation of $CO_2$ 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 $H_2$ 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 $CO_2$ 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.



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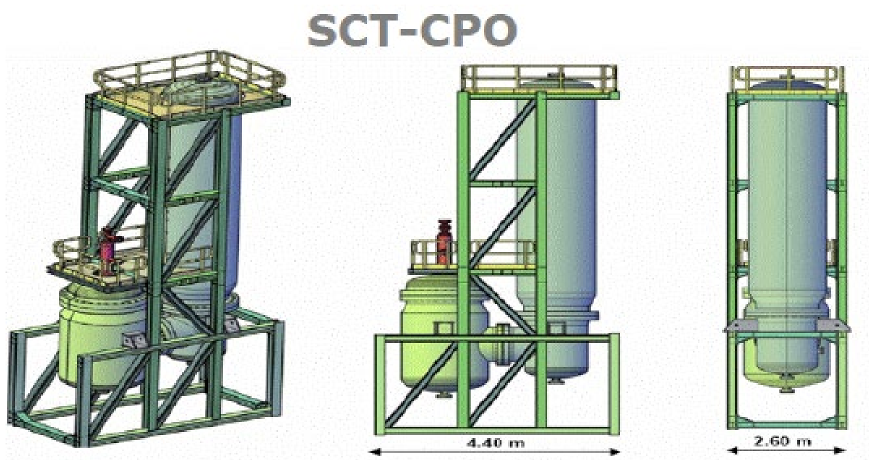
Among three main tri-reforming reactions only the steam reforming of natural gas is the process on industrial scale. This reformation is focused on hydrogen production, and operates in the 700–1000° C, in the presence of nickel catalyst supported on alumina. Dry methane reforming has not yet been implemented.

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 $CaSO_4$ – the extent (combustion vs POX) depending on the $Ca/SO_4$/fuel ratio. $CO_2$ from the fuel carbon reacts with CaO to form $CaCO_3$
- An oxidizer, where CaS from the reducer is oxidized by air back to $CaSO_4$
- A calciner, where $CaCO_3$ is heated to form CaO and drive off $CO_2$. If syngas is desired, the carbonate/CaO loop is not included



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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 $CaSO_4$ is used to ensure that the product gas from the reducer is $CO_2$.

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.



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**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 $CO_2$ 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/TofC 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.*



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## 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:
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  - 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***



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## 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 | US$22,500 |

**Advances in Syngas Production: Catalyst and Process Developments Update-2018**

| | |
|---|---|
| Report in PDF format, in addition to subscription price | 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.*

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