THE CATALYST GROUP RESOURCESTM

AMMONIA PRODUCTION: CATALYST AND PROCESS TECHNOLOGY Advances Yielding Cost Efficiencies and CO₂ Reductions

MULTI-CLIENT STUDY PROPOSAL

July 2016



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AMMONIA PRODUCTION: CATALYST AND PROCESS TECHNOLOGY ADVANCES YIELDING COST EFFICIENCIES AND CO₂ REDUCTIONS

I. ABSTRACT

Due to the drive towards increasing energy efficiency, optimizing resource utilization (including feedstocks) and meeting ever-growing product volume demands, there is a need to go beyond incremental process technology improvements in ammonia production to yield disruptive, and even breakthrough, advancements. Such gains are particularly important and urgent for the petrochemical/chemical industries, where the volumes of product are large and the energy utilization is high. At the peak among these is ammonia, whose output on a global basis tops 145 MMT annually with 2-4.5 times that volume of CO_2 produced depending on the feedstock and process used (see **Figure 1**).



Clearly there is a role to be played for improving efficiencies and reducing emissions by process and catalyst technology advances, be they through novel catalytic routes, enhanced process integration/intensification and low- or non-CO₂ generating feedstocks (e.g., bio- or photo/electrochemically produced hydrogen) and/or energy sources (e.g., bio-derived or hydropowered fuels).



In this assessment, TCGR will document the current benchmark or "best practice" technologies (BPTs) for ammonia production and highlight the major areas where technology development has, can, or will result in both emerging/evolutionary or breakthrough/"game changer" progress towards cost efficiency gains and CO₂ reductions. Comparisons will be made between current and developmental technologies, including assessments of technology readiness levels (TRLs), timing of potential impacts at commercial scale, and the critical participants in success, whether they be licensors, producers or affiliated consortia/academia/governmental agencies on a global scale. Due to the size of ammonia production and its importance in application, notably as a critical component in fertilizers with implications on the ability to address world food needs, this topic merits detailed attention by and for the benefit of industrial players.

In recognizing the gap between current technologies (best practices or BPTs) and the developments towards both 'emerging' and disruptive 'game changer' technologies, TCGR will conduct its assessment addressing both technical and competitive/strategic information, designed to identify competitive opportunities for industrial participants and affiliated organizations/institutes.

II. BACKGROUND

A schematic for ammonia production depicts the numerous steps in which energy is consumed and CO₂ is generated (see **Figure 2**):



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In documenting the challenges and opportunities for technology development in addressing energy efficiency gains and CO₂ reductions, the International Energy Agency (IEA), the International Council of Chemical Associations (ICCA) and DECHEMA Society for Chemical Engineering and Biotechnology (DECHEMA) issued a document entitled **"Technology Roadmap: Energy and GHG Reductions in the Chemical Industry via Catalytic Processes."** This provides depictions of the CO₂ emissions intensity of the chemical industry's top large volume chemicals, including ammonia as the #1 among them, as represented in **Figure 3** below:



The document (see: <u>http://www.dechema.de/industrialcatalysis</u>) also includes among its numerous and well-referenced findings:

- The manufacture of 18 products (among thousands) from the chemical industry account for 80% of energy demand in the chemical industry and 75% of GHG emissions.
- Catalyst and related process improvements could reduce energy intensity for these products by 20% to 40% as a whole by 2050.
- Achieving the deepest energy and emissions cuts will require development and deployment of emerging technologies that exceed the capacity of current best practice technologies (BPT).
- A step change in the sector's energy consumption and GHG emissions would require the development of "game changer" technologies.
- Therefore, long-term investment and support for research and development (R&D) to enable innovation is warranted to continue advances in new technologies.



III. THE NEED FOR THE STUDY

There are numerous characteristics of the ammonia production train that make it attractive as a target for cost efficiency gains and CO_2 emissions reductions, as follows:

- The market size for ammonia is enormous at over 145 MMT/yr annually on a global basis, with energy consumption and resource utilization (e.g., feedstocks, energy and H₂) the largest in the chemical industry.
- The size of the CO₂/GHG footprint is equally substantial, highlighting the potential impacts of any/all gains in process improvements (integration, product yield, etc.); notably, ammonia is included among products in the top 18 (actually, it is #1) chemicals produced with 2.5 EJ of energy and 350 MT CO₂/eq.
- The technology for ammonia production is mature and well-established, with only limited noteworthy recent gains beyond the original (Haber-Bosch) approach; these improvements have been incremental at best, highlighting the challenges in needed gains as well as potential pay-offs for success.
- There have, however, been supporting/enabling advances, notably in process efficiencies, resulting in CO₂ reductions, predominantly based on developing/optimizing and implementing alternative energy sources (i.e., non-CO₂ generating power, alternative H₂ generation via photo- and electro-catalytic routes).
- The market opportunity is large, but the efforts to date have been focused on, with limited success, by the traditional ammonia producers, technology developers and catalyst suppliers (e.g., Haldor-Topsoe, Uhde/ThyssenKrupp, Linde, KBR, Ammonia Casale, Clariant, Johnson Matthey, among others), highlighting the fact that the challenge remains substantial.

The opportunities for improvements appear across the ammonia production process steps and energy/feedstock sources. Although the most common feedstock in ammonia production globally is natural gas, other feeds include coal (predominantly in China) and oil/petroleum. When natural gas is used, the reforming step in the steam reforming process ranges between 28 and 35.5 GJ/t, of which about 20-22 GJ/t of natural gas is used as feedstock, 7.2-9.0 GJ/t is fuel consumed in the primary reformer, and the remaining 0.5-4.2 GJ/t is used in auxiliary boilers and others (Source: <u>http://ietd.iipnetwork.org/content/ammonia</u>).

The focus of development has been on processes which consume/convert the largest amount of energy, notably the primary steam reforming step. Along those lines, the leading process technology developers and licensors have pursued advances in steam reforming configurations, including the following:

• Advanced conventional primary reforming with high duty primary reforming and stoichiometric process air in the secondary reformer.



- Steam reforming with mild condition in the primary reformer and use of excess air in the secondary reformer.
- Heat exchange autothermal reforming with a process gas heat exchange reformer and a separate secondary reformer, or in combination with an autothermal reformer that uses excess or enriched air.

There are also a number of processes in which there is no use of a secondary reformer in which the nitrogen is supplied by an air separation unit (ASU). An example is the Linde LAC process. A selection of claimed energy use values of the different processes is provided in **Table 1** below.

 Table 1

 Energy Use in a Selection of Advanced Steam Reforming Configurations

Process Name	Energy Use (GJ/t NH ₃)	
Advanced conventional primary reforming		
Kellogg Low-Energy Ammonia Process	27.9 (27.01)	
Haldor Topsoe Process	27.9	
Uhde Process	28.0 (27.0)	
Lummus Process	29.6-33.5	
Processes with reduced primary refiner firing		
Foster Wheeler AM2 Process	29.3	
Processes without a primary reformer		
ICI LCA Process	29.3	
Kellogg Brown and Root (KBR KAAPplus Process	27.2	
Processes without a secondary reformer		
Linde LAC Process	28.5 (29.3 ²)	

¹Energy use when steam is exported

²Energy use when CO_2 is recovered.

Source: Ullmann's, 2011 (http://www.wiley.com/WileyCDA/WileyTitle/productCd-3527329439.html)

The following are a selection of noteworthy advances in technology which reflect recent progress for: (1) syngas shift catalysts; (2) ammonia synthesis catalysts; and (3) so-called catalyst accelerators:



• Clariant's Shiftmax 820s Presulfided Sour Gas Shift Catalyst, Process Optimization with Siemens...

Clariant has started-up its pre-sulfided ShiftMax® 820S Sour Gas Shift (SGS) catalyst at a commercial methanol production facility of Shanghai Huayi Energy Chemical Co. Ltd. - the first industrial application of the newly introduced ShiftMax® 820S catalyst in China. The catalyst employs a proprietary pre-sulfiding process which offers higher activity, reducing syngas and energy requirements and allowing more economical, efficient and simplified operations.

Another recent introduction is a new SGS process, jointly developed by Clariant and Siemens, which reduces capital expenditure for the shift system by up to 20% and optimizes operating costs with up to 30% lower catalyst volume. The technique can handle different steam-to-gas ratios and high carbon monoxide (CO) content without adjustment of the feed gas, resulting in improved availability and reliability of the whole process. (Source: <u>Clariant</u>, 10/8/2015).

Haldor Topsoe's Commercial Iron-Free HTS and KM111 Ammonia Synthesis Catalysts...

Topsoe introduced SK-501 Flex[™] – a high temperature shift (HTS) catalyst with the unique ability to operate at any steam-to-carbon ratio, allowing producers to achieve record plant efficiency in ammonia, hydrogen and syngas production. For a large-scale ammonia plant, the improvement in revenue is approximately \$11 million per year or \$57 million over a typical catalyst lifetime. The SK-501 Flex[™] formulation is based on zinc oxide and zinc aluminum spinel. The iron-free formulation prevents formation of unwanted iron carbides that reduce the catalyst strength of conventional iron-based HTS catalysts. (Source: <u>Haldor Topsoe</u>, 3/1/2016).

In 2014, the company also unveiled an ammonia synthesis catalyst: KM 111 - a magnetite-based catalyst developed for optimal performance in the lower beds of the ammonia converter. Produced with a new manufacturing method, the KM 111 catalyst possesses an activity that surpasses the market-leading activity of KM1. The increase in activity improves the kinetics of the synthesis reaction, which allows for reductions in temperature. At existing plants, energy consumption can be reduced by operating at lower loop pressures and lower converter inlet flows with no compromise to production levels. (Source: Haldor Topsøe, 2/25/2014).

QuantumSphere's New Ammonia Production Technology, Collaboration with Casale...

Catalyst producer QuantumSphere has received patent approval for its advanced FeNIX nanocatalyst accelerator technology for ammonia production. The next-generation ammonia production technology involves application of iron nanocatalysts, applied as a coating onto existing commercial ammonia catalysts, to increase catalytic activity and production efficiency in ammonia synthesis (see **Figure 4**).





During the test by QuantumSphere and a partner in early 2015, the technology increased the catalytic activity and production output by 10% to 15%, without requiring any modifications to the ammonia production facilities. The company is now collaborating with Casale for commercialization of FeNIX technology, which is expected in the second half of this year. It had signed a joint development deal with Casale in May 2015 for pre-commercialization of the technology in the ammonia industry and QSI-Nano catalysts for end-use applications. (Source: <u>QuantumSphere</u>, 1/29/2016).

Beyond these areas targeted for catalyst and process improvement for ammonia production, a more critical, and potentially breakthrough or "game changer" area of focus is the generation of H_2 from non-CO₂ generating routes. This process, as one of the largest energy-consuming steps in ammonia production, has begun to receive increased attention, notably for its potential as a means to utilize renewable energy sources, offsetting fossil-fuel consumption and lowering the GHG/CO₂ footprint of the process. In particular, areas such as photocatalysis or photovoltaic-assisted water electrolysis (using solar energy to help split water) are being addressed. These options are worthy of further investigation as they allow: (1) production of H_2 from electrolytic water cleavage using electricity from renewable sources; (2) ammonia synthesis from H_2 and nitrogen gas (N₂), omitting steam reforming and/or water-gas shift from gas or coal.

A selection of the more noteworthy developmental areas along these lines includes:

Photochemical/catalysis

Photoelectrochemical (PEC) devices

- including semiconductor, nanostructured, doped metal oxides, etc. Others – photobiological (e.g., cyanobacteria, algae, etc.)



PV-assisted electrolysis

Thin film solar cells Dye sensitized solar cells (DSSCs) Surface plasmon polaritons Others - organic solar concentrators/waveguides

Electrochemical/catalysis
 Electrolyzers

including alkaline, mono-/bi-polar
 Solid Polymer Electrolytes (SPEs)/Polymer Electrolytic Membranes (PEMs)
 Solid Oxide Electrolyzers (SOEs)

Direct routes to ammonia (N₂ reduction via nanosheets) Central China Normal University's layered BiOBr catalyst with oxygen vacancies Others

Despite the R&D/technology interest, it is well-understood that these non-CO₂ generating H₂ production approaches face significant challenges related to both scientific hurdles (e.g., efficiencies) as well as economic viability (e.g., costs). In fact, even at production costs which are multiples of 2-5 times that of current H₂ generation (at best, with some more than 50 times), these must be considered long(er) term opportunities. Progress towards lower multiples, making the option more appealing (and economically viable) is the objective, but not necessarily assured, especially for competitiveness without subsidies or other forms of economic support. As a result, TCGR will assess the most promising of these options and provide an indication of likely "winners" based on potential for success and timing, noting the hurdles to be overcome and the techno-economic factors involved in reducing the cost multiples.

IV. SCOPE AND METHODOLOGY

Following a brief **Introduction** section providing the needed background, as well as an **Executive Summary** section, the report will provide (**Section III**) a benchmarking of the current leading ammonia production processes considered as "best practices" (BPTs). A delineation of the processes and comparisons between them and the others also in use will be provided. An indication of areas where energy, feedstock or other inputs are being pursued for improvement will be noted, including the H_2 -generating step.

Section IV will address the ammonia process technology developments, by developer, towards incremental or "emerging" and then the disruptive or potentially "game changer" approaches. These will highlight the technical and/or economic opportunities being addressed (including CO₂ mitigation) as well as the impacts of the technologies on the competitive landscape and strategic opportunities.

In **Section V**, to supplement the process descriptions, catalyst usage and producer profiles in Section IV, the report will include indications of technology readiness levels (TRLs) and "scoping" economics (including CO_2 mitigation) to allow for an indication of the breadth of



potential impacts at the commercial level. An outlook for future opportunities and threats (i.e., vulnerabilities to novel technologies) will be provided. Of particular focus will be the scientific hurdles (e.g., efficiencies) and economic viability (e.g., costs) related to non-CO₂ generating H₂ production (i.e., lowering the production cost multiples vs. current H₂ generation). TCGR will assess the most promising of these options and provide an indication of likely successful approaches based on potential impact and timing.

Lastly, **Section VI** will include a strategic and competitive assessment, highlighting current and future participants affected by the changes and reactions in the marketplace, serving as the basis for indicating "winners and losers."

A preliminary Table of Contents appears on the following page.

As it does in each of its industrially-focused multi-client studies, TCGR will seek input from "charter" subscribers to help shape the report's final scope/TofC so that it covers and emphasizes the most pertinent content due to the large volume of research and the numerous areas (i.e., BPTs, incremental, emerging and disruptive technologies, etc.) that might be of interest.

In completing this assessment, TCGR will evaluate the commercial/trade press, academic literature, conference and investor presentations and patents/applications. We will also incorporate information from our proprietary multi-client studies, membership programs and monthly newsletters. Especially important among these is TCGR's catalyst/process industries forecasting model, utilized to complete our bi-annual statistical industry report series entitled *"The Intelligence Report: Business Shifts in the Global Catalytic Process Industries"* as well as technical/R&D and techno-economic reports from our **Catalytic Advances Program** (CAP) and Carbon Dioxide Capture & Conversion (CO₂CC) Program.

All TCGR studies are characterized by competitive and strategic insights for industrial and financial investment companies to evaluate. These include key trends, concerns, 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 30 years of experience.

TCGR's unique background and established global Dialog Group® ensures expert capability and skill level in this study area. TCGR will utilize numerous deeply experienced experts in membranes and separations to assist us to provide insights beyond what other sources that do not have the reach and industrial experience can provide.

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A particularly relevant TCGR multi-client study entitled "**Natural Gas Conversion vs. Syngas Routes: A Future of Convergence**" (completed as a 2-part series in 2014) addressed in detail both syngas generation and conversion to products which included substantial coverage of SMR, syngas/H₂ utilization and ammonia process technology with notable recent advances (through 2014). Due to the overlap in coverage, as well as the likely interest of those subscribers in this currently proposed study, TCGR is offering a discounted subscription fee to those who subscribed to the 2014 study series. When ordering this study, please indicate your past subscription or inquire at TCGR (via John J. Murphy at John.J.Murphy@catalystgrp.com or +1.215.628.4447) to determine your eligibility and amount (based on purchase of one of both volumes of the 2014 2-volume series).

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Preliminary Table of Contents:

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*Charter subscribers (those who sign up for the study before August 26, 2016) will have 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.



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.

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- Define the business and commercial impacts of leading-edge technologies
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 - Independent appraisals and valuations of technology/potential
 - Acquisition consulting, planning and due diligence
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- 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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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 ammonia production and related/enabling technologies with significant implications on energy efficiency and GHG/CO₂ mitigation. TCGR's report, based on technology evaluations, market assessments and interviews with key players will assess results and provide opinions beyond the 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, "*Ammonia Production: Catalyst and Process Technology Advances Yielding Cost Efficiencies and CO*₂ *Reductions*" is expected to be available in November/December, 2016.

Participation	Deadline	<u>Price</u>
"Charter" Subscribers	before August 26, 2016	\$19,500

Ammonia Production: Catalyst and Process Technology Advances Yielding Cost Efficiencies and CO₂ Reductions

Post-launch Subscribers	<u>after August 26, 2016</u>	\$21,500
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Ammonia Production: Catalyst and Process Technology Advances Yielding Cost Efficiencies and CO₂ Reductions

Report in PDF format, in addition to subscription price \$1,000

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* * * * *

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