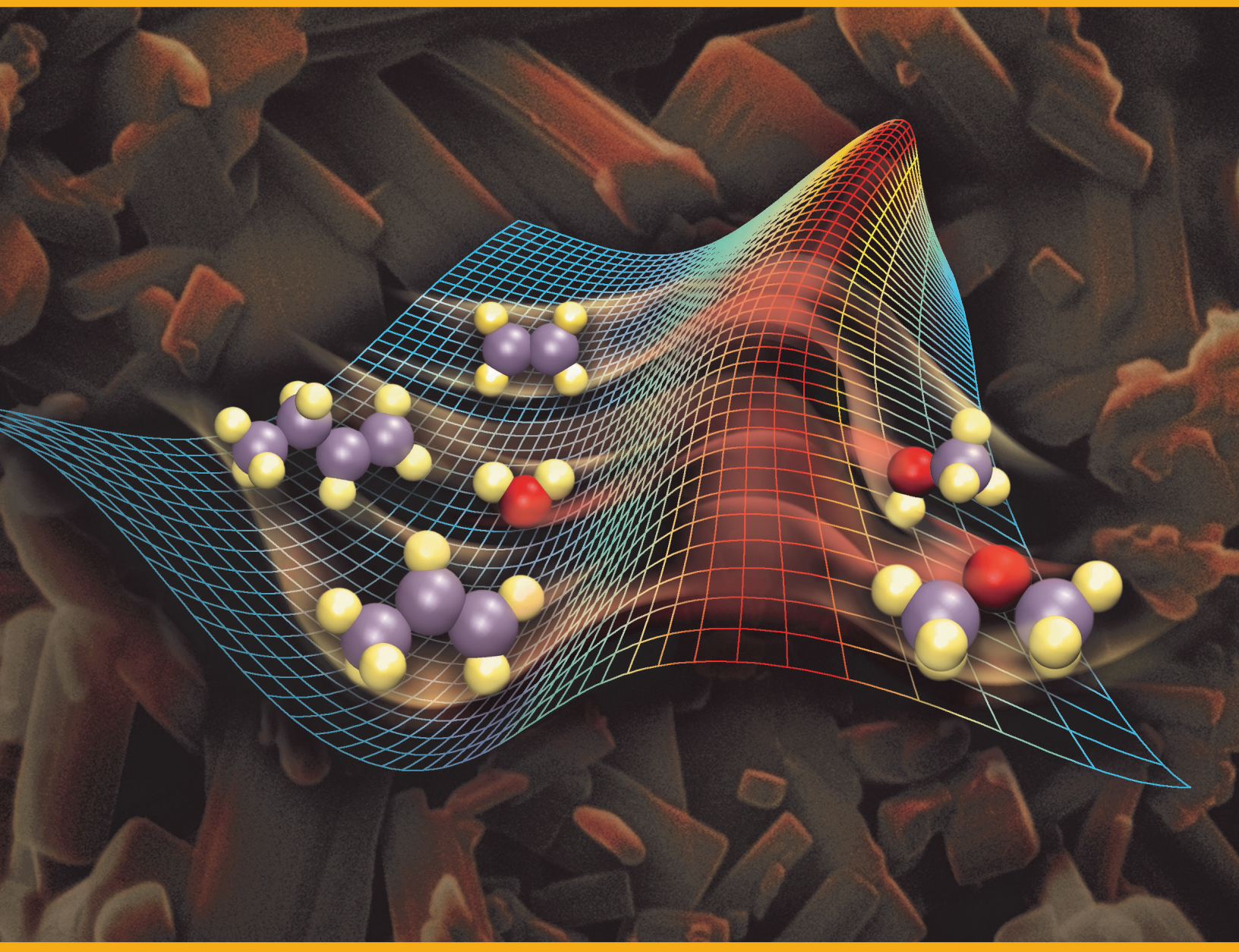
Basic Research Needs for

Catalysis Science



Factual Document for the Basic Energy Sciences Workshop on

Basic Research Needs for Catalysis Science to Transform Energy Technologies

May 8–10, 2017

Image courtesy of Argonne National Laboratory.

DISCLAIMER

This report was prepared as an account of a workshop sponsored by the U.S. Department of Energy. Neither the United States Government nor any agency thereof, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Copyrights to portions of this report (including graphics) are reserved by original copyright holders or their assignees, and are used by the Government's license and by permission. Requests to use any images must be made to the provider identified in the image credits.

This report is available in pdf format at
https://science.energy.gov/bes/community-resources/reports/

Technical Perspectives Factual Document

RESOURCE DOCUMENT FOR THE BASIC ENERGY SCIENCES WORKSHOP ON BASIC RESEARCH NEEDS FOR CATALYSIS SCIENCE TO TRANSFORM ENERGY TECHNOLOGIES MAY 8–10, 2017

Table of Contents

List of Figures

List of Tables

Abbreviations, Acronyms, and Initialisms

AEM	alkaline exchange membrane
ATJ	alcohol-to-jet
BETO	(Department of Energy) Bioenergy Technologies Office
BOP	balance of plant
BTX	benzene, toluene, and p-xylene
CBP	consolidated bioprocessing
CCR	continuous catalyst regeneration
CFP	catalytic fast pyrolysis
CMR	catalyst membrane reactor
CNT	carbon nanotube
CSP	concentrated solar power
DHA	dehydroaromatization
DMA	dimethyl ether
DOE	Department of Energy
EERE	(Office of) Energy Efficiency and Renewable Energy
EPA	(U.S.) Environmental Protection Agency
FAA	Federal Aviation Administration
FBMR	fluidized bed membrane reactor
FCC	fluid catalytic cracking
FT	Fischer-Tropsch
GTL	gas-to-liquids
HCP	hydrocarbon pool
HGM	heat generating material
HTFT	high temperature Fischer-Tropsch
HTGR	high temperature gas-cooled reactor
HTL	hydrothermal liquefaction
LHV	low heating value
LLNL	Lawrence Livermore National Laboratory
LNG	liquefied natural gas
LPG	liquefied petroleum gas
LTFT	low temperature Fischer-Tropsch
MEA	membrane electrode assembly
MMR	micro-membrane reactor
MSW	municipal solid waste
MTO	methanol-to-olefins
NGL	natural gas liquids

NMOG	non-methane organic gas
NREL	National Renewable Energy Laboratory
NSTF	nanostructured thin film
OCM	oxidative coupling of methane
OER	oxygen evolution reaction
OMX	organic matrix combustion
PBMR	packed bed membrane reactor
PV	photovoltaic
SAE	Society of Automotive Engineers
SHC	selective hydrogen combustion
SMR	steam methane reforming
SSF	simultaneous saccharification and fermentation
STH	solar-to-hydrogen
TRL	technology readiness level
TWh	terawatt hours
WHSV	weight hourly space velocity

Topic 1: Diversified Energy Feedstocks and Carriers

Topic 1 focuses on catalysis research challenges associated with greater use of emerging and under-utilized energy feedstocks (NASEM 2016) such as natural gas, biomass, discarded food and materials, and industrial by-products, exhausts, and waste streams.

1.1 THE EVOLVING ROLE OF FOSSIL RESOURCES: IMPACT ON U.S. ECONOMY

Coal, oil, and natural gas (Figure 1), the three major forms of fossil fuels, are the basis for the world's chemical industry. From generating heat to run the energy intensive chemical processes, to providing the source of carbon and hydrogen to produce transportation fuels and all the raw materials required for manufacturing, we rely on fossil fuels for the advancement of society.

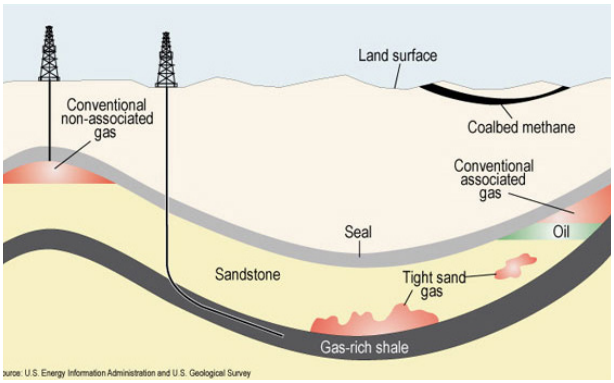


Figure 1. Natural gas reserves. Source: U.S. Energy Information Administration (February 2011).

The chemical industry usually determines the raw material based on whatever feedstocks are most cost-effective. China has responded to the changing feedstock accessibility by increasing availability of coal-to-chemical facilities—85 chemical- or ammonia-producing plants came online from 2004 to 2014 (DOE, National Energy Technology Laboratory 2018). However, China has recently announced reduced use of coal for energy and chemical production.

The United States, a long-time producer of chemicals from coal through gasification, has a deeply established share of the chemicals market (DOE, National Energy Technology Laboratory 2018). Because feedstocks derived from natural gas and petroleum can make, in general, the same number of chemical products produced via coal gasification, the chemical industry has been agnostic regarding the use of any particular feedstock. Thus, natural gas can bridge the gap between dependence on fossil fuels to reliance on renewable, carbon-neutral forms of energy, while moving in the direction of reducing carbon emissions.

The abundance of natural gas brought by the development of new fracking technologies for its extraction from shale formation (fine-grained sedimentary rocks with relatively low permeability) has triggered a remarkable renaissance of the U.S. chemical manufacturing industry (Figure 2). Natural gas availability has made the United States the lowest-cost chemical producer outside of the Middle East, attracting billions of dollars in investments and transforming the United States from an energy importer to an energy exporter. The global landscape is changing not only how countries interact, but how supply chains, manufacturing operations, and processes work together.

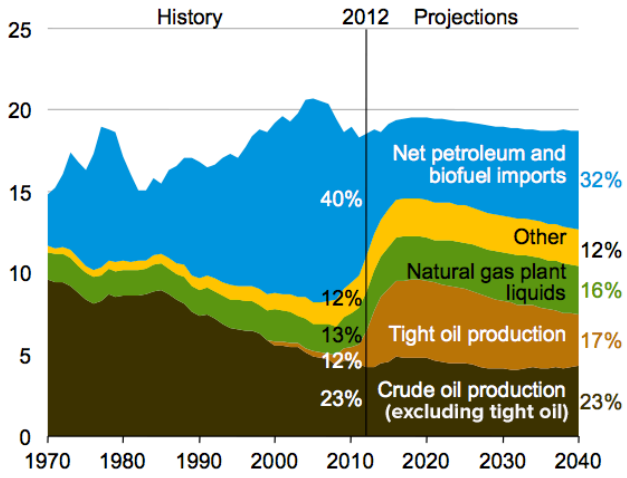


Figure 2. Projections of U.S. fossil fuel resources. Source: U.S. Energy Information Administration, AEO2014 Early Release Overview (2014).

Natural gas has been the preferred source of heat for U.S. chemical manufacturers, but historically high natural gas prices have precluded industry from taking full advantage of its use in manufacturing processes. The relatively low price of natural gas gives U.S. chemical manufacturers an advantage over many global competitors who rely on naphtha, a more costly, oil-based feedstock. New and progressive methods for use of natural gas products by industry segments other than fuel could have considerable commercial impact since fine and other commodity chemicals carry a comparatively high economic potential.

Widespread adoption of hydraulic fracturing changed the chemical production landscape in the United States and stands ready to impact chemical production globally. U.S. natural gas production was dropping in the 1990s, leading to several key changes in the industry. Natural gas-fed processes were shutdown and moved. Both ammonia and methanol production were impacted. Ethylene production in units with the capacity to use heavy feedstocks shifted away from ethane and propane. The world changed quickly with the coming of shale resources. Shale resources increased production of natural gas, but natural gas liquid production grew even more owing to its high liquid content. Exports of liquefied petroleum gas (LPG) increased dramatically due to the world market for those materials. Cryogenic transport is required for ethane and the lack of infrastructure created an ethane glut in the United States. Ethane pricing, long pegged to naphtha equivalent pricing, diverged. Ethane became a significantly advantaged feedstock. It became so advantaged that naphtha cracking was curtailed, as all assets that could swing lighter did.

The current cost and availability of natural gas products and liquid fuels encourage investigations into catalysts and methods with a lower carbon footprint to enable the direct conversion (i.e., without first converting to syngas) of these feedstocks to chemicals (Figure 3).

Although methane is the largest component in natural gas,[1] the availability of ethane and propane is considerable, opening an economic opportunity to generate olefins on purpose for the synthesis of plastics. (Olefins, such as ethylene, propylene, and butadiene, are traditionally produced as a by-product of the naphtha cracking processes). Honeywell UOP LLC developed the C3 Oleflex™ process to produce polymer grade propylene from a propane feedstock. The C3 Oleflex™ process uses catalytic dehydrogenation with a new, fully recyclable, platinum alumina-based catalyst system to convert propane to propylene.

Powerful economic and environmental reasons, including near-depletion of domestic fossil fuel reserves in the last century, have driven deep development of shifting feedstock sources and has caused changes in the world's chemical industry—the starting point for transportation fuels and all the raw materials required for manufacturing. New fracking technologies in the last decade have made natural gas from shale abundantly available domestically, revitalized the U.S. chemical manufacturing industry, and triggered interest in ways to use natural gas products for non-fuel applications. The focus is turning to development of low-carbon footprint catalysts and methods to directly convert liquid natural gas to chemicals, and biomass-to-fuel technologies as a longer-term solution for production of gaseous and liquid fuels.

[1] As reported by DOE National Energy Technology Laboratory and Office of Fossil Energy, the composition of natural gas is 70–90% methane; 0–20% ethane + propane + butane; <1% pentane; <1% hexane; 0–5% nitrogen; 0.8% carbon dioxide; 0–5% hydrogen sulfide; and traces of the rare gases Ar, He, Ne, Xe (DOE, National Energy Technology Laboratory 2013; DOE, Office of Fossil Energy 2018).

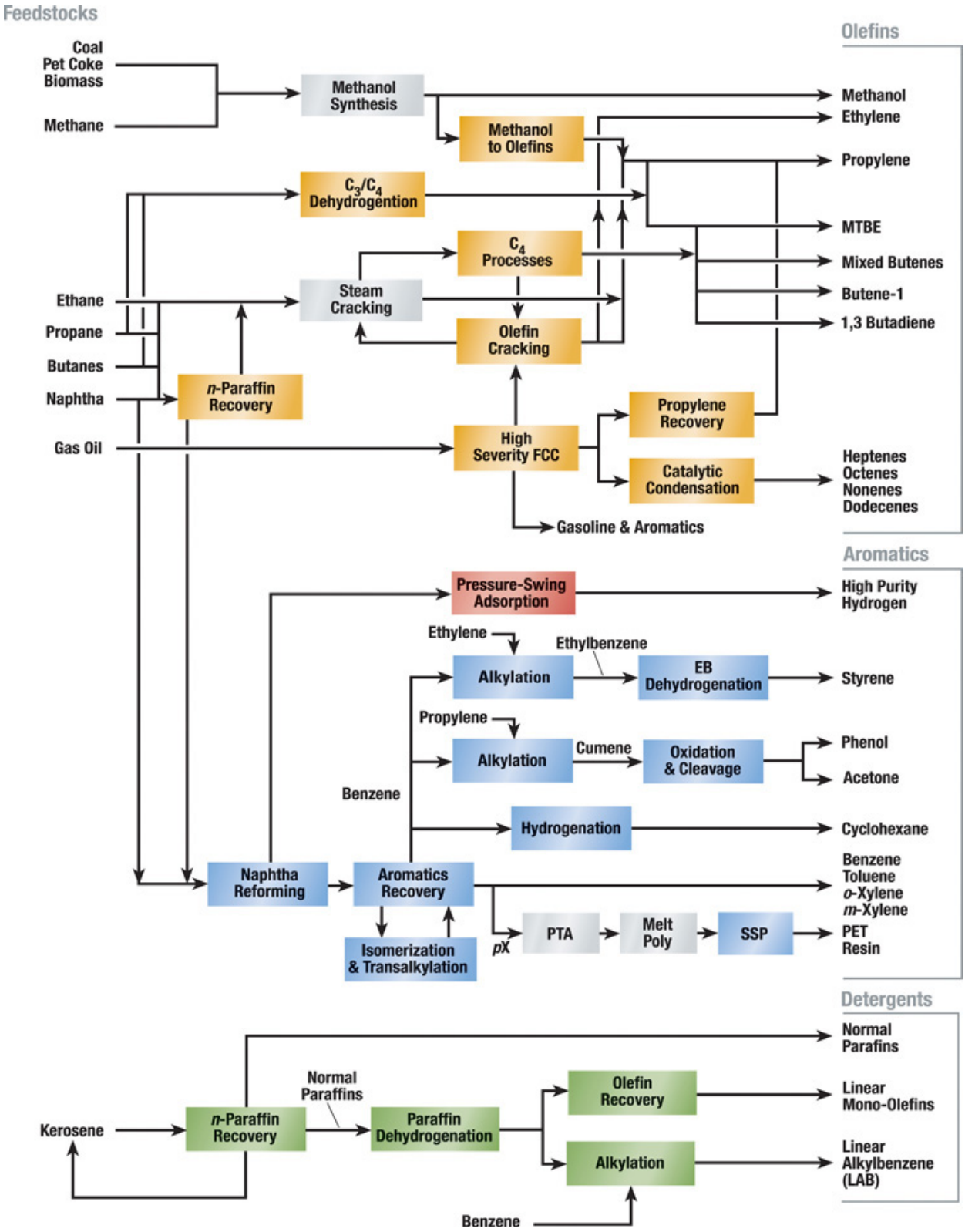


Figure 3. Varieties of feedstock, catalysts, and processes in the production of chemicals. From Honeywell UOP, "Petrochemicals Flow Scheme" (Honeywell UOP 2018a), Courtesy of Honeywell UOP.

1.2 CATALYTIC TRANSFORMATION OF SHALE GAS

1.2.1 Ethane, Propane, Butane Transformation

The U.S. production capacity of liquefied natural gas (LNG) is expected to grow to about 600 billion cubic meters by 2021, enabling a projected 15% market share of global LNG exports. The petrochemical industry now relies on steam cracking methods (Section 1.2.4) to manufacture ethylene and propylene from natural gas and liquid fuel products. The non-catalytic steam cracking process is also non-selective and the wide ranging output requires further treatment. Unwanted by-products must be extracted to maintain the value of hydrogenation to mono-olefins or alkanes (Maffia et al. 2016). Currently, clean "on purpose" conversion of ethane, propane, and butane to olefins or aromatic liquids, such as benzene, toluene, and p-xylene (BTX), is possible via catalytic non-oxidative dehydrogenation or a dehydrocyclization process.

Olefin on purpose (non-oxidative and oxidative dehydrogenation). Non-oxidative dehydrogenation of light alkanes converts ethane, propane, and butane to the corresponding olefin and hydrogen. The reaction is highly endothermic and thermodynamically limited.

$$C_2H_{6(g)} \rightarrow C_2H_{4(g)} + H_{2(g)} \qquad \Delta H_{298K} = 137.0\ kJ/mol$$

$$C_3H_{8(g)} \rightarrow C_3H_{6(g)} + H_{2(g)} \qquad \Delta H_{298K} = 124.3\ kJ/mol$$

$$C_4H_{10(g)} \rightarrow C_4H_{8(g)} + H_{2(g)} \qquad \Delta H_{298K} = 117.6\ kJ/mol$$

A reaction temperature between 825 K and 1025 K and/or a lower alkane partial pressure are required to obtain substantial conversion (Figure 4). Removing the hydrogen produced via selective hydrogen combustion (SHC) using CO_2 as a mild oxidant can shift reaction equilibrium to a higher conversion (see Section 3.4.2 for membrane reactors). The heat generated is used to promote the endothermic, non-oxidative alkane dehydrogenation.

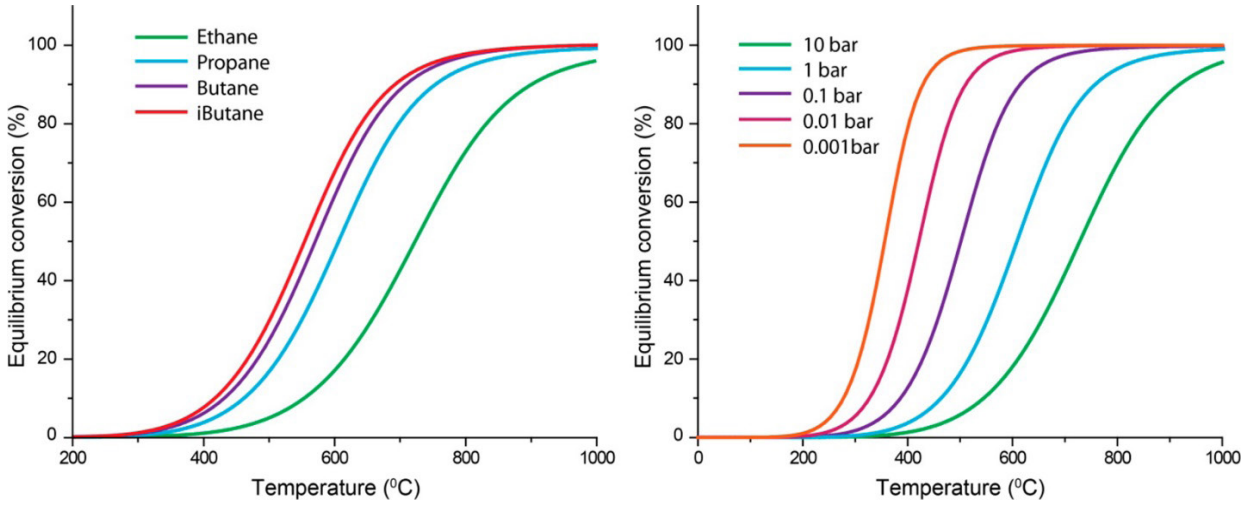


Figure 4. Equilibrium conversion of C2–C4 light alkanes to olefins as a function of temperature at 1 bar (left), and pressure dependence of the dehydrogenation of propane as a function of temperature (right). Reprinted with permission from *Chemical Reviews,* Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides, Sattler et al. Copyright © 2014, American Chemical Society.

The high temperatures necessary to achieve high olefin yields also favor side-reactions such as hydrogenolysis, cracking, and isomerization and are optimal for formation of coke. Coke formation, along with metal catalyst sintering, causes a progressive decrease in catalyst activity and selectivity, which induces frequent regeneration of the catalyst.

Two technologies typically used for the non-oxidative dehydrogenation of light alkanes, in particular for propane to propylene, are a promoted platinum-based catalyst (the Oleflex™ process, Honeywell UOP) and a CrO_x-based catalyst (the Catofin® process, CB&I Lummus). The majority of these processes are present in the United States, China, and the Middle East. The Oleflex process runs at temperatures between 800 K and 980 K and pressures ranging from 1 to 3 bar, using a Pt-Sn/Al_2O_3 catalyst in three or four adiabatic radial flow reactors. The solid catalyst flows through the reactors, and a Continuous Catalyst Regeneration (CCR) unit continuously regenerates

the catalyst by first burning the deposited coke and then redispersing the platinum nanoparticles on the metal oxide support using a burning chlorine-air mixture. The overall selectivity of propane to propylene is around 89% by weight (wt%), with on-stream conversion of approximately 98 wt%. The average catalyst life is between one and three years.

High surface area alumina is typically used to support platinum nanoparticle dehydrogenation catalysts because of its thermal stability and mechanical strength. The reaction rate depends only on the number of active sites and is independent of the structure, size, and exposed crystallographic planes of the platinum nanoparticles. Alkali metals such as lithium, sodium, and potassium are added to suppress the formation of coke. The addition of a tin promoter to form a Pt-Sn alloy is needed to (1) suppress hydrogenolysis and isomerization side reactions, (2) minimize metal sintering, (3) neutralize acid sites, and (4) partially prevent the deposition of carbon.

In the Catofin technology, the non-oxidative dehydrogenation reaction is performed at temperatures around 850 K and a partial pressure from 0.2 atm to 0.5 atm in the presence of a CrO_x/Al_2O_3 catalyst in five to eight parallel, adiabatic fixed-bed reactors. The continuous cyclic process proceeds through a controlled sequence of dehydrogenation, catalyst regeneration, and purge. Clariant introduced Heat Generating Material (HGM) in the propane dehydrogenation plant at Ningbo Haiyue (Figure 5). Heat from the HGM drives the dehydrogenation reaction and enhances selectivity and yield in the already efficient Catofin process (Clariant 2016).

Figure 5. CATOFIN® propane dehydrogenation plant using Heat Generating Material at Ningbo Haiyue, China, Ningbo City, Zhejiang Province. (Photo courtesy of Clariant).

The reactor temperature drops during the reaction step owing to the endothermic reactions, and the reaction temperature requires constant incremental adjustment. During the regeneration step, any carbon deposited on the catalyst is burned off. The overall selectivity of propane to propylene is greater than 86 wt%, with on-stream conversion of approximately 98 wt%. The average catalyst life of 2–3 years is characterized, as time on-stream accumulates, by increasing loss in activity. To compensate and obtain constant dehydrogenation activity throughout the life of the catalyst life, temperatures are gradually increased (Sattler et al. 2014).

Aromatic on purpose (dehydrocyclodimerization). The dehydrocyclodimerization of propane and butane (natural gas liquids [NGL]) yields petrochemical grade aromatics, such as BTX, and hydrogen in a single unit. The catalyst is usually a H-ZSM-5 zeolite containing transition metals such as platinum, zinc, gallium, and molybdenum. In this bifunctional catalyst, the active metal, after carburization, provides a dehydrogenation function (a rate determining step), and zeolite acidity catalyzes the subsequent dehydroaromatization (DHA)

of olefinic intermediates to produce C_6–C_{10} aromatic ring compounds. The zeolite channel system provides shape selectivity, preventing the formation and diffusion out of larger molecules such as highly methylated and condensed aromatics. Coke build-up compromises the stability of the catalyst over time.

The net reaction is endothermic and requires high temperatures to achieve high per-pass conversions, while maintaining high selectivity to aromatics, with an overall aromatics (BTX) selectivity of 58–60 wt% and hydrogen selectivity of approximately 5 wt%. Honeywell UOP and BP jointly developed the Cyclar™ process (Ga-ZSM-G catalyst, Figure 6), which uses UOP's CCR technology. The CCR technology removes coke, a reaction by-product, from the catalyst and regenerates the catalyst (Foley 2018). The process operates at temperatures between 895 K and 1025 K and at pressures below 7 bar in a series of vertically stacked reactors, in which the catalyst flows down under gravity in the form of a dense medium, and reactants flow through the catalyst bed in a radial direction. This technology was successfully commercialized in the Middle East from 1999 to 2013 producing circa 45,000 barrels/day of aromatics. SINOPEC Luoyang and Mitsubishi-Chiyoda also independently commercialized a dehydrocyclization process using a bifunctional catalyst consisting of a Zn-ZSM-5 base material with BTX yields of up to 55–60 wt%. The adiabatic, fixed-bed reactor runs at temperatures between 730 K and 800 K and at pressures below 7 bar.

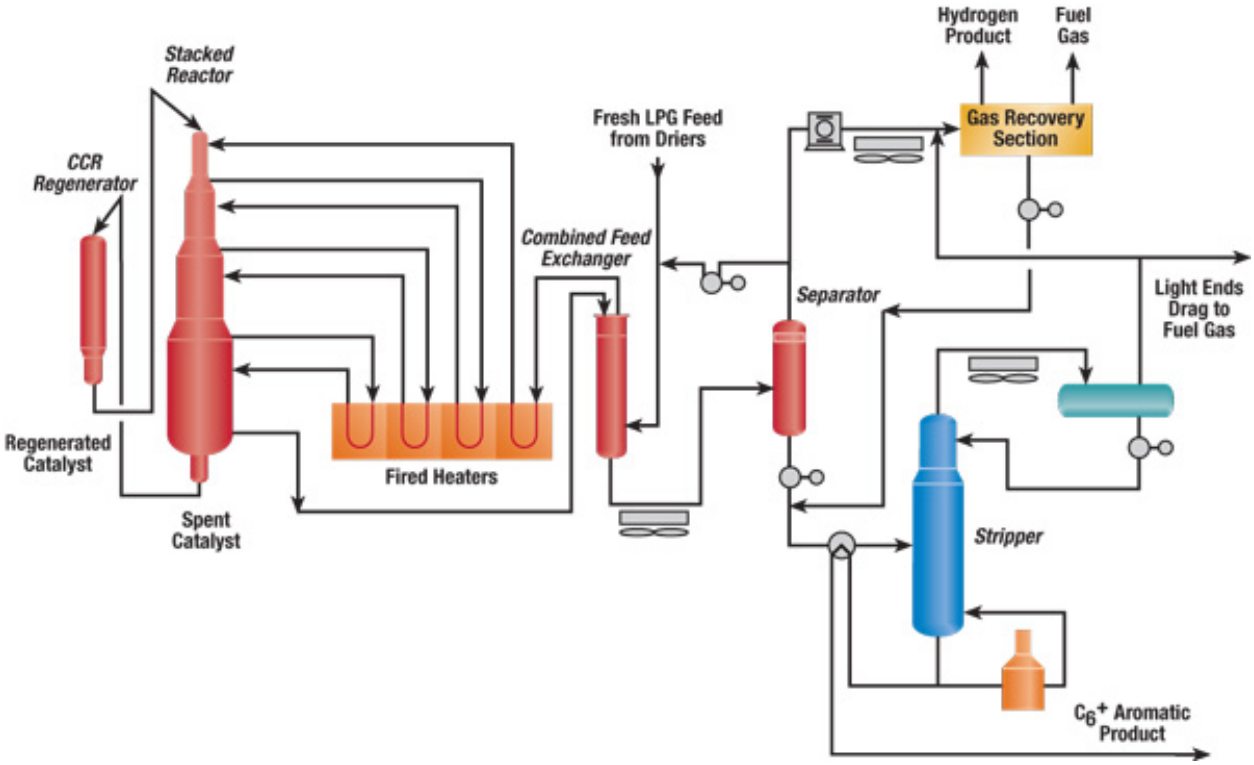


Figure 6. Honeywell UOP's Cyclar™ process layout. From Foley, "CYCLAR™ Process Produces High-Quality Aromatic Products" (Foley 2013). Courtesy of Honeywell UOP.

Recent research in the area of ethane, propane, and butane transformations has focused on:

- Improving the selectivity to olefins of the C_2–C_4 fraction using secondary metals such as Sn.
- Using mild oxidants like CO_2 to shift equilibrium toward formation of olefins.
- Reducing the rate of catalyst deactivation via coking and metal sintering.

1.2.2 Methane Coupling

The importance of methane, the largest component in natural gas from shale gas and one of the simplest building blocks for the production of chemicals, has undoubtedly changed the landscape and direction of catalysis research in the last decade. One of the most active areas of research in homogeneous and heterogeneous catalysis for the last fifty years has been the activation of methane. In particular, the direct coupling resulting in the formation of a new carbon-carbon bond has attracted much interest from the heterogenous catalysis community (Guo et al. 2014). On the other hand, the homogeneous catalysis community has been interested in pursuing direct carbon-hydrogen activation of methane for nearly fifty years (Hartwig 2016).

However, the state of the art for the conversion of methane into ethylene and larger hydrocarbons or aromatics has not changed in recent years, and still no commercial methane coupling processes have been built without first converting to CO and H_2, followed by transforming to chemicals via the Fischer-Tropsch process. The complexity of converting CO and H_2 into hydrocarbons, in contrast to the apparent simplicity of converting methane into ethane and/or ethylene, has spurred a large number of academic and industrial groups to target research to optimize the process.

Methane coupling can be performed in the absence of oxygen as it corresponds to a pyrolysis reaction, where the products usually range from C_2 to C_6 and C_{10}. Following the pioneering work of Keller and Bhasin (1982), oxidative coupling of methane (OCM) became one of the most pursued topics of research in methane activation. In a recent review covering the literature on oxidative methane coupling up to 2011, Zavyalova et al. (2011) reported more than 27,000 research articles and about 140 patents on the subject.

Despite the efforts invested to understand the chemistry of the oxidative coupling of methane, the selectivity and yields are not high enough to compete with steam cracking because of the inherent reactivity of the products toward oxygen. Incremental but significant advances have been made in oxidative coupling catalysts to the point where it is now possible to achieve 20% CH_4 conversion at 80% combined C_2H_4 and C_2H_6 selectivity, with no diluent in the reagents, but this process is still far from reaching commercial applications. Horn and Schlögl (2015) in a recent review indicated that "superficially viewed, not much progress has been made in industrial methane chemistry in decades." Siluria Technologies has focused in this area, however, and has recently described a new process utilizing nanowire-based catalysts that could result in a viable method to directly convert methane to ethylene (Galadima and Muraza 2016).

Siluria Technologies, leveraging work done at the Massachusetts Institute of Technology, is focusing on the development of alternative catalysts for the OCM process. The startup uses genetic engineering of bacteriophages to create biological scaffolds, or substrates, for growth of inorganic materials like lithium-ion cathodes. Siluria prepares their OCM catalyst by doping transition/non-transition metals or their oxide crystals, and uses the substrates as templates for crystal growth. Their nanowire catalyst enables the OCM reaction to occur at 200–300 °C in a partially autothermal process. While still in the development stage (Kondratenko et al. 2017), the process aims to achieve direct conversion of methane to ethylene, an essential raw material used in high volumes globally for various petrochemical processes.

Methane aromatization, which produces benzene and hydrogen, has recently become another pathway to utilize cheap and abundant natural gas. Thermodynamic calculations show that benzene formation is negligible below 600 °C. However, at temperatures above 1000 °C benzene formation is favorable.

$$6CH_{4(g)} \rightarrow C_6H_{6(g)} + 9H_{2(g)} \qquad \Delta H^o_r = 531\ kJ/mol \qquad \Delta G^o_r = 433\ kJ/mol$$

A methane conversion rate of 10%—correlating with benzene selectivities of 60% to 80%—will net a benzene yield of less than 10%. Including alkanes/alkenes in the methane feed in the presence of Mo/HZSM-5 and Mo/MCM-22 catalysts will diminish the thermodynamic limitation on benzene formation. The catalyst additions will bring lower molecular weight hydrocarbons and higher molecular weight substituted aromatics. Methods to limit carbon formation, which is thermodynamically favored at all conditions of interest, include adding H_2, steam, or other oxidants (Spivey and Hutchings 2014).

The high cost of catalysts has driven advances in reactor configurations that specifically focus on designs that regenerate a catalyst deactivated by carbon deposition (Spivey and Hutchings 2014).

Recent research in the area of methane coupling has focused on:

- Improving the selectivity and yield for the formation of C–C bonds.
- Decreasing the amount of deep oxidation via the reaction of gas phase radicals.
- Formulating new catalysts that overcome the high temperature normally required for the reaction, which leads to coking and deep oxidation.

1.2.3 Thermal Decomposition of Methane (Methane Cracking) to Carbon and Hydrogen

The thermal decomposition or cracking of methane is a moderately endothermic high-temperature process for producing carbon and hydrogen as shown in equation (1).

$$CH_{4(g)} \rightarrow C_{(s)} + 2H_{2(g)} \qquad \Delta H_{298} = 75.6\ kJ/mol \qquad (1)$$

Methane cracking is one of four processes used industrially for producing carbon black, a substance used in the manufacture of tires, high-performance coatings, and plastics. About 10%–20% of the hydrogen produced is burned to provide the heat required for the reaction to proceed, and the remainder of the hydrogen is used to fuel steam boilers for other process applications. When conducted in the absence of a catalyst, reaction temperatures in excess of 1200 °C are required to achieve reasonable yields (Abbas and Daud 2010). In the presence of a catalyst, reaction temperatures as low as 700 °C can be employed. Typical catalysts are metal-supported, such as nickel, cobalt, or iron on SiO_2 or Al_2O_3 (Echegoyen et al. 2007). Nickel is generally preferred for cracking methane because of its higher activity compared to cobalt and iron (Avdeeva et al. 1999). Catalyst deactivation and regeneration as well as carbon recovery are major challenges. Carbonaceous materials can also be used as catalysts but are generally only needed during startup since the reaction itself generates carbon deposits.

Recently, interest has been growing in using the thermal decomposition reaction to produce CO_2-free hydrogen as a potentially less energy and process intensive alternative to conventional hydrogen production, which combines steam reforming of natural gas and the water-gas shift reaction (Armin et al. 2011).

Recent research in the area of thermal decomposition of methane (methane cracking) to carbon and hydrogen has focused on:

- Lowering the rate of catalyst deactivation and regeneration as well as improving carbon recovery.
- Creating more useful forms of carbon beyond simple carbon black.
- Improving the yield of hydrogen.

1.2.4 Fluid Catalytic Cracking and Ethane Steam Cracking

Ethylene is one of the most important chemicals in U.S. manufacturing and, with other petrochemicals, is a fundamental ingredient in most production supply chains. Ethylene global demand has experienced geometric growth since the early 1990s, substantially exceeding even crude oil growth rates. More than half of ethylene production goes toward polyethylene, the widely used plastic film seen in bags, trash liners, and the like. Ethylene's highly functional profile results in its manufacture in a greater proportion (by weight) than any other chemical.

Fluid catalytic cracking (FCC) has become the principal method to convert lower value, high-molecular weight petroleum hydrocarbons into gasoline, volatile olefins, and other high value products. Thermal cracking, the original method to crack petroleum hydrocarbons, has given way to FCC because of the latter's superior yield of gasoline with a higher octane rating and olefins (by-product gases with more carbon-carbon double bonds) that bring greater economic value.

FCC catalysts are composed of a crystalline zeolite structure and a matrix, binder, and filler. Zeolite, the active component, can constitute up to half the catalyst by weight. In FCC, the zeolite has a specific structure called

faujasite (zeolite Y). Catalysts may be modified to improve activity and stability, such as using rare earth metals (e.g., cerium, lanthanum) to replace the Brønsted sites (Kogel et al. 2006; Yang 2003).

An ethane steam cracker (Figure 7) uses ethane, readily available as a component of the natural gas from the Marcellus shale, and processes it into ethylene (NFIB 2016). Crackers often feed other nearby plants that create products that are refined further "downstream." Because the price of natural gas is low, companies have announced plans to build new cracker facilities in the United States.

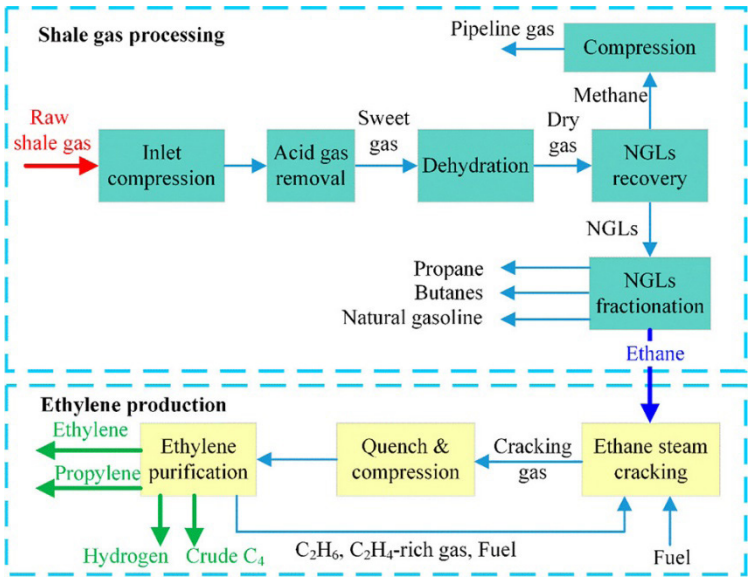


Figure 7. Flow diagram for manufacturing ethylene from ethane-rich natural gas. Reprinted with permission from Industrial & Engineering Chemistry Research, Manufacturing Ethylene from Wet Shale Gas and Biomass: Comparative Technoeconomic Analysis and Environmental Life Cycle Assessment, Yang et al. Copyright © 2018, American Chemical Society.

Many advances have taken place in the engineering of the new steam cracking plants—in particular, improving the design of the furnace where the catalytic process takes place. Sasol North American Operations is constructing a world-scale petrochemical complex near their existing site in Southwest Louisiana. The plant, which will be completed in 2018, will roughly produce 1.5 million tons of ethylene annually in the United States. Additionally, Shell Chemical Company's petrochemical complex along the Ohio River in Beaver County, Pennsylvania, will produce 250,000 tons of ethylene/year, all of which would be used internally to make polyethylene. Both new cracking plants will benefit from the extraordinary price difference between the less expensive natural gas, used by the process to extract ethane molecules, and oil.

Recent research in the area of fluid catalytic cracking (FCC) and ethane steam cracking has focused on:

- Improving the furnace design where the catalytic process takes place.
- Reducing the rate of deactivation due to the decomposition of zeolites.
- Designing crackers for raw material flexibility to process various types of feedstock, ranging from liquefied petroleum gas to heavy liquid hydrocarbons.

1.2.5 Syngas and Hydrogen Production (Steam Reforming, Dry Reforming [CH_4+CO_2], Water-gas Shift)

Synthesis gas (syngas) is a mixture of hydrogen and carbon monoxide. Syngas formation is the first elementary step in the production of liquid fuels (via Fischer-Tropsch, see Section 1.2.6) and chemicals such as ammonia (via the Haber-Bosch process) and methanol. Production of syngas can be carried out from any form of carbon or hydrocarbon source, including natural gas, petroleum naphtha, coal, and, relatively recently, from biomass and waste (see Section 1.3). The composition of syngas varies greatly with the application—from mostly H_2 for ammonia synthesis, fuel cell, and industrial hydrogen; to a syngas ratio of $H_2/CO = 1$ for aldehyde synthesis with an oxo process; or $H_2/CO = 2$ with a Fischer-Tropsch process.

Syngas and hydrogen can be synthesized using different methods:

Steam reforming. Steam reforming, the conventional method to produce syngas and hydrogen from methane and other hydrocarbons, is utilized on the industrial scale. Steam reforming is a highly endothermic reaction. At elevated temperatures (970–1370 K) and in the presence of a supported nickel on alumina (Ni/Al_2O_3) catalyst, methane (or coal) reacts with water to yield an H_2/CO mixture and a small amount of CO_2.

$$CH_{4(g)} + H_2O_{(g)} \rightarrow CO_{(g)} + 3H_{2(g)} \qquad \Delta H_{298K} = 206\ kJ/mol \qquad \Delta G_{1073K} = -24\ kJ/mol$$

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)} \qquad \Delta H_{298K} = 131\ kJ/mol \qquad \Delta G_{1073K} = -12\ kJ/mol$$

The steam reforming process suffers from fast deactivation due to coke deposition, via three main reactions: (1) hydrocarbon cracking, (2) carbon monoxide disproportionation (Boudouard reaction), and (3) carbon monoxide reduction (Snoeck et al. 2002):

$$CH_{4(g)} \rightarrow C_{(s)} + 2H_{2(g)} \qquad \Delta H_{298K} = 75\ kJ/mol$$
$$C_nH_m \rightarrow nC_{(s)} + (m/2)H_{2(g)} \qquad (1)$$

$$2CO_{(g)} \rightarrow C_{(s)} + CO_{2(g)} \qquad \Delta H_{298K} = -172\ kJ/mol \qquad (2)$$

$$CO_{(g)} + H_{2(g)} \rightarrow C_{(s)} + H_2O_{(g)} \qquad \Delta H_{298K} = -131\ kJ/mol \qquad (3)$$

Nevertheless, carbon formation on a Ni/Al_2O_3 catalyst can be minimized using using basic promoters such as MgO, Ce_2O_3, or La_2O_3. To protect downstream catalysts, the hydrocarbon feedstock should not contain any halogen-containing compounds or sulfur. Chlorides are generally removed using an alkaline doped alumina scrubber, while the sulfur is removed using the hydrodesulfurization (HDS) process.

Because of the large reserve of natural gas in the United States and nations like Qatar, steam reforming of methane is the major source of syngas and hydrogen. Syngas is made via reforming of coal in China, South Africa, and India.

Dry reforming of methane. Dry reforming of methane is an alternative method to produce syngas and hydrogen. It utilizes CH_4 and CO_2 to produce a CO/H_2 mixture. Dry reforming of methane is endothermic in nature, and, to achieve high conversion of CO_2 and minimize carbon deposition—a significant drawback in the reaction—requires temperatures as high as 970–1370 K. The reaction can be represented by:

$$CH_{4(g)} + CO_{2(g)} \rightarrow 2CO_{(g)} + 2H_{2(g)} \qquad \Delta H_{298K} = 247\ kJ/mol \qquad \Delta G_{1073K} = -10\ kJ/mol$$

Catalysts based on nickel, an abundant and inexpensive option, are most common in dry methane reforming. Nickel catalysts, however, are subject to carbon deposition, which can result in deactivation of the catalyst. Studies have shown noble metals are both active and resist carbon deposition, but they are expensive.

Non-catalytic partial oxidation. Partial oxidation of natural gas or heavy hydrocarbon fuel in the presence of a substoichiometric amount of air/O_2 yields a hydrogen-rich syngas. This process is mainly utilized for producing syngas from heavy hydrocarbons, including petroleum coke.

$$CH_{4(g)} + \tfrac{1}{2}\ O_{2(g)} \rightarrow CO_{(g)} + 2H_{2(g)} \quad \Delta H_{298K} = -36\ kJ/mol$$

The high temperature (1400 K) heat recovery in partial oxidation is not very efficient. The advantage partial oxidation technology holds over steam reforming lies in its ability to utilize feedstock containing sulfur and other compounds that would poison the steam reforming catalysts. Currently, the main utilizations of non-

catalytic partial oxidation are in the production of hydrogen for refinery applications and syngas from coal and petroleum coke.

Autothermal reforming. Autothermal reforming combines partial oxidation (non-catalytic) and dry reforming (catalytic) of natural gas in a single reactor. In the reactor, the exothermic, partial oxidation of methane yields carbon monoxide and water. The heat produced by this reaction provides enough energy to convert CH_4 and CO_2 to a 1:1 H_2/CO mixture (an overall H_2/CO ratio of 2:3).

$$CH_{4(g)} + \tfrac{3}{2}\, O_{2(g)} \rightarrow CO_{(g)} + 2H_2O_{(g)} \quad \Delta H_{298K} = -519\ kJ/mol$$

$$CH_{4(g)} + CO_{2(g)} \rightarrow 2CO_{(g)} + 2H_{2(g)} \quad \Delta H_{298K} = 247\ kJ/mol$$

Gasification of biomass, waste, and coal. Syngas can also be produced via conversion of organic materials, such as biomass, waste, or coal at high temperature (greater than 1000 K) without combustion in the presence of a controlled amount of H_2O and/or O_2 (see Section 1.3.9).

Water-gas shift. The reaction of carbon monoxide and water yields a mixture of carbon dioxide and hydrogen. It is commonly used to produce high purity hydrogen (for ammonia synthesis) or to balance the syngas H_2/CO ratio (for the Fischer-Tropsch process).

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \qquad \begin{matrix} \Delta H_{298K} = -41\ kJ/mol \\ \Delta G_{298K} = -28\ kJ/mol \end{matrix}$$

Industrial scale water-gas shift reactions are conducted in multiple adiabatic steps involving a high temperature shift (580–720 K at a pressure of 1–83 atm) followed by a low temperature shift (470–520 K). A typical catalyst for a high temperature shift contains Fe/Cr/Mg oxides, while the low temperature shift consists of Cu/Zn oxides on alumina.

1.2.6 Fischer-Tropsch

The Fischer-Tropsch process, also known as gas-to-liquids (GTL), catalytically converts natural gas (predominantly methane), coal, or biomass/waste into liquid hydrocarbons via reforming to syngas (see Section 1.2.5). Since negligible amounts of contaminants (i.e., sulfur, nitrogen, and aromatic compounds) are present in syngas, high quality fuels can be obtained via Fischer-Tropsch such as ultra-low sulfur diesel. Because of the large natural gas reserve worldwide, the Fischer-Tropsch process has recently become a very attractive technology in the United States and other countries to turn natural gas into commodity chemicals. Also, a recent commercial technology, small-scale GTL (see Section 3.1.1), is able to convert biomass and landfill gas into liquid hydrocarbons, such as renewable diesel, jet fuel, and waxes.

The formation of methane and long chain hydrocarbons (C_2–C_{50}) from syngas is thermodynamically favorable (exothermic) since water is the other product of the reaction, along with small amounts of aromatic and oxygenate compounds. The hydrocarbons produced in the Fischer-Tropsch process are mainly linear alkanes and terminal alkenes. Hydrocarbon selectivity (alkanes vs. alkenes) can be tuned by reaction conditions (temperature and pressure) and H_2/CO ratio.

$$nCO_{(g)} + (2n+1)H_{2(g)} \rightarrow CH_3(CH_2)_{n-2}CH_{3(g)} + nH_2O_{(g)} \qquad \Delta H_{500K} = 172\ kJ/mol$$

$$nCO_{(g)} + 2nH_{2(g)} \rightarrow CH_3(CH_2)_{n-3}CH{=}CH_{2(g)} + nH_2O_{(g)} \qquad \Delta H_{500K} = -165\ kJ/mol$$

The Fischer-Tropsch process is a stepwise addition of a surface CH_x (x = 1–2) unit to a growing aliphatic chain. The polymerization distribution qualitatively follows an Anderson-Schultz-Flory statistic ($F_n = n\cdot[1-\alpha]^2\cdot\alpha^{n-1}$, where n = number of carbons atoms and α = the probability of chain growth). Controlling the probability of chain growth is the key to obtaining the desired product.

The Fischer-Tropsch reaction mechanism has been the subject of numerous studies. While there is still some controversy about the precise mechanism, the following sequence of elementary steps is plausible (Figure 8):

1. Adsorption and dissociation of CO and dissociative adsorption of H_2;

2. Surface reaction of H and O atoms to yield water, and O and CO to form CO_2;

3. Reaction of surface C and H atoms to form adsorbed CH_x species (x = 1–3);

4. Hydrogenation of surface methyl radicals to form CH_4;

5. Chain growth via addition of CH_2 to surface CH_3, CH_2CH_3, and $(CH_2)_nCH_3$ radicals.

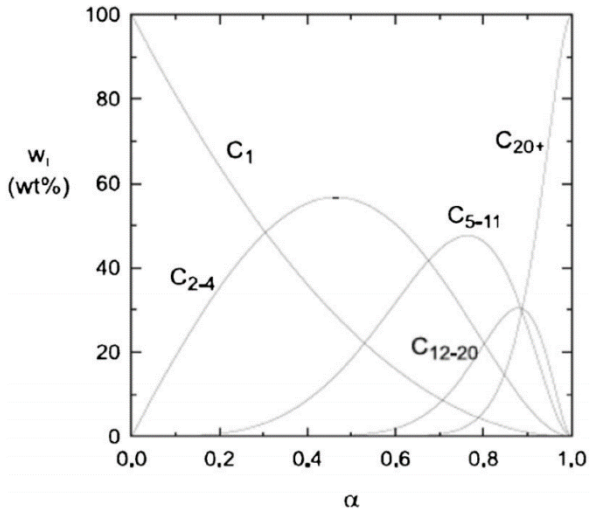


Figure 8. Weight fraction of a hydrocarbon product as a function of chain growth probability (α). From James (2012). Reproduced by permission of The Royal Society of Chemistry.

Supported iron-, nickel-, ruthenium-, and cobalt- on metal oxide (Al_2O_3, SiO_2, and TiO_2) materials are the classic Fischer-Tropsch catalysts, but a different product distribution is obtained from each type of catalyst. For example, nickel catalysts are avoided because they favor methane formation (equilibrium calculations show that methane formation is more favorable than heavier hydrocarbons). The addition of alkali promoters with iron catalysts (fused and precipitated iron catalyst on silica) is essential to obtain high basicity and to stabilize high metal surface area. On the other hand, cobalt based catalysts with promoter metals (lanthanum, platinum, palladium, rhodium, and rubidium) are more active, operate at lower pressure (1–10 atm) and temperature (less than 525 K), and yield less oxygenated by-products.

Two Fischer-Tropsch technologies are commercially operative: low temperature Fischer-Tropsch (LTFT) for the synthesis of high molecular hydrocarbons and waxes, and high temperature Fischer-Tropsch (HTFT) for the synthesis of alkenes and gasoline. The operating temperature for the LTFT (slurry reactor) depends on whether the catalyst is a supported cobalt on metal oxide, but is normally below 525 K to minimize wax hydrocracking and methane formation. For HTFT, the operating temperature is usually around 625 K, with the syngas passing through a fluidized bed of finely dispersed iron catalyst. The two industry leaders in Fischer-Tropsch chemistry are Sasol (LTFT) and Shell (HTFT).

Recent research in the area of Fischer-Tropsch has focused on:

- Attempting to modify the distribution of products away from Anderson-Schultz-Flory statistics.
- Controlling the rate of hydrocarbon growth on the surface of the metal catalyst.
- Studying the effects of various promoters for improving higher hydrocarbon yield while reducing catalyst deactivation.

1.2.7 Methane-to-Methanol

Converting methane to alternative forms of energy, such as methanol, is the preferred method for its valorization. Several relevant technologies are available for converting methane to methanol (Ravi et al. 2017), including conventional catalytic processes, plasma technology, photo-catalysts, supercritical water processes, and biological processes. Methanol is an energy-dense liquid that can be transported easily with existing infrastructure. In addition, it is a versatile molecule that can be used for fuel cells; blended with gasoline; converted to gasoline or dimethyl ether, which is a component of diesel fuel; and converted to ethylene and propylene, which are precursors to a wide range of chemicals.

Industrially, methane is converted to methanol by partial oxidation to hydrogen gas and carbon monoxide (syngas) at high temperatures. Syngas is then catalytically converted over a copper catalyst to methanol at several hundred degrees Celsius. Methanol synthesis catalysts usually combine copper, zinc oxide, alumina, and magnesia. New studies show compositions of carbon, nitrogen, and platinum may serve as a potential catalyst. This process is only around 5% or 10% efficient due to overoxidation to carbon dioxide and water.

Current research in this area has concentrated on the use of copper exchanged zeolites for direct conversion of methane to methanol. Much of this work is inspired by the enzyme methane monoxygenase. Zeolites used include wide pore zeolites such as mordenite and faujasite. Evidence has shown that the copper exists as a Cu–O–Cu dimer (van Bokhoven 2016). The microporous nature of the zeolite is believed to improve the methanol selectivity. Similar copper clusters have shown to have reactivity when put on ceria supports where the ceria controls the redox chemistry of the copper (Tamura et al. 2016).

In addition to these encouraging heterogeneous catalysts, some very interesting work has been done with homogeneous systems. Most notable is the conversion of methane to methyl bisulfate in the presence of a platinum catalyst. The reaction is carried out in 100% sulfuric acid using SO_3 as a “soft” oxidant (Periana et al. 1998). In similar work, methane undergoes direct partial oxidation using iodate salts with catalytic amounts of chloride in protic solvents. In HTFA (where TFA is trifluoroacetate), greater than 20% methane conversion with more than 85% selectivity for MeTFA were achieved (Fortman et al. 2014). Work is continuing for closing the catalytic cycle.

Finally, recent studies have shown that platinum tethered to ordered mesoporous carbons can serve as fuel cells for electrochemical oxidation of methane in a proton exchange membrane fuel cell at 80 °C (*vide infra*; Topic 3). This work could lead to a system providing both electrical power and methanol as a transportation fuel or chemical intermediate.

Recent research in the area of methane-to-methanol has focused on:

- Improving the yield per gram of Cu via the use of zeolite supports.
- Improving the yield of syngas.
- Using solution phase catalysts to lower the reaction severity.

1.2.8 Methanol-to-Gasoline (MTG) Process

As stated above, methanol is a good starting material for the manufacture of formaldehyde, acetic acid, and methyl t-butyl ether among many other platform chemicals. One of these is gasoline via the Mobil methanol to gasoline (MTG) process (Figure 9).

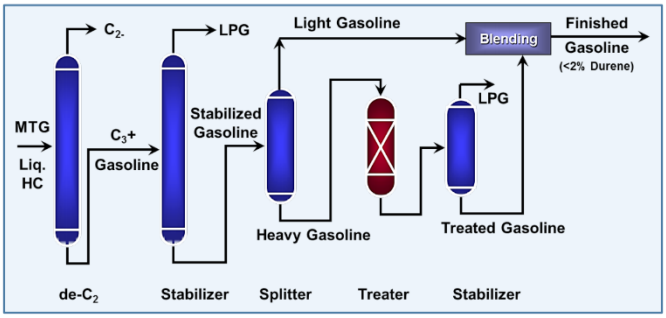


Figure 9. MTG plant design. Image from ExxonMobil "Proven Process. Proven Plants. Proven Performance." Brochure No. L0617-056E49, Courtesy of ExxonMobil (2016).

The process, first commercialized in New Zealand in 1985, makes use of the stranded natural gas reserves in the country and operated until 1997. The MTG process is considered to be an alternative technology to Fischer-Tropsch for converting natural gas to liquid fuels. The methanol is derived from methane-derived syngas.

The process has the advantage that the methanol can be synthesized elsewhere and then transported to a second site for use as a fuel or for upgrading. The resulting gasoline is a relatively high octane owing to its branching, whereas Fischer-Tropsch liquids have little branching and therefore make a better diesel product. In the MTG process, most of the hydrocarbon products are in the gasoline range.

The MTG process catalyst is the zeolite ZSM-5, which was patented by Mobil in the late 1960s. ZSM-5 is a medium-pore zeolite (pore diameter of 5.5 angstroms) with a high concentration of Brønsted acidity and a high SiO_2/Al_2O_3 ratio. The process takes advantage of the low level of coking by zeolite, ZSM-5. Use of wider pore materials would result in higher levels of coking and therefore higher deactivation rates. The conversion of methanol to hydrocarbons and water is virtually complete (gasoline yields are around 90%) and essentially stoichiometric.

In a first step, methanol is dehydrated giving a high yield of dimethyl ether:

$$2\ CH_3OH \rightarrow CH_3OCH_3 + H_2O$$

The dimethyl ether is then further dehydrated over a ZSM-5 zeolite catalyst to yield a mixture (C_2–C_6) of light olefins (MTO process, Section 1.2.9):

$$CH_3OH + CH_3OCH_3 \rightarrow \text{light olefins} + H_2O$$

The C_5+ olefins are further polymerized, dehydrocyclized, and hydrogenated to give a high octane gasoline (R + M/2 = 87) with C_6–C_{10} hydrocarbons (~50% paraffins, 10% napthenes, 15% olefins, and 25% aromatics). The process yields a single liquid product (2,500–14,500 barrels per day) suitable for transportation fuel and allows manufacturing scalability.

Recent research is less extensive than it was 20 years ago. Work in several laboratories has concentrated on improved synthesis of the ZSM-5 catalyst and has included several different metals either in the framework of the zeolite or at cation exchange sites. As an example, adding iron to the ZSM-5 synthesis shows higher conversion of methanol to gasoline with lower deactivation rates than with H-ZSM-5. Iron promotes higher yields of iso-paraffins while lowering the yield of aromatics. Similar results have been reported for ZSM-5 with incorporated molybdenum, copper, Zn/Cu, and gallium oxides. Work has also concentrated on the use of other zeolites and zeolite composites, such as ZSM-5/MCM-48.

Recent research in the area of the methanol-to-gasoline process has focused on:

- Improving the yield of C_5^+ products to high-octane components such as aromatics and branched paraffins.
- Improving the synthesis of the ZSM-5 catalyst to include several different metals either in the framework of the zeolite or at cation exchange sites.
- Investigating the use of new zeolites to improve product selectivity.

1.2.9 Methanol-to-Olefins (MTO) Process

In addition to its use as a starting material for gasoline, methanol is an excellent feedstock for the manufacture of olefins for commodity chemicals (Tian et al. 2015). The primary reaction in this transformation is the acidic conversion of methanol via a dimethyl ether (DME) intermediate into C2 and higher olefins. At lower temperatures methanol reacts to form dimethyl ether. At higher temperatures, the desired olefins are produced with a concomitant decrease in DME selectivity.

The preferred catalyst for the MTO process is an acidic version of an intermediate pore molecular sieve; either ZSM-5 (MFI structure) or SAPO-34 (CHA structure). Catalyst selectivity improves with increasing Si (decreasing Al) concentration in the framework. SAPO-34 is the current preferred catalyst due to its excellent hydrothermal stability retaining more than 80% relative crystallinity after 100% steam treatment at 800 °C for 45 h.

The formation of the first C–C bond from either methanol or dimethyl ether has been intensely debated for decades and remains a controversial issue. Early studies proposed many direct mechanisms to explain C–C bond formation from either methanol or dimethyl ether, such as the carbene, oxonium ylide, carbocation, and free radical mechanisms. Each of these pathways later proved energetically unfavorable based on theoretical calculations.

As indicated by ^{13}C NMR spectroscopy, an aromatic intermediate is important for the lengthening of the carbon backbone leading to higher hydrocarbons (Wang et al. 2006). Methanol is believed to interact with an internal hexamethyl benzene (HMB) intermediate trapped in the cross channels of the pores. The currently accepted mechanism is referred to as the hydrocarbon pool (HCP) mechanism. If not supplied with sufficient additional methanol (or DME), the HMB eventually leads to coke formation. At reaction temperatures below 250 °C, no methanol conversion is observed. Only methanol and dimethyl ether appear in the effluents. There is a fast deactivation of the catalyst at lower temperatures with the appearance of light olefins and other hydrocarbons in the temperature of 300–325 °C. The yield of hydrocarbon products increases with temperature.

Traditionally, propylene has been produced cost-effectively in large-scale FCC units as a by-product of gasoline production. Lighter feedstocks, however, have changed production streams and the need for on-purpose production of olefins has expanded. The UOP/Hydro MTO process has made on-purpose production of light olefins from varying feedstocks, like natural gas, coal, and other hydrocarbon sources, commercially successful, especially over traditional production routes. The technology, developed in a UOP-Norsk Hydro (now Ineos) joint venture, uses partial oxidation to convert feedstocks first to syngas, then to methanol, and finally to light olefins with minimal formation of by-products and low catalyst consumption. The process exhibits high yields and is flexible in its range of ethylene and propylene production. The process is especially attractive to locations with access to low-cost alternative feedstocks (Honeywell UOP 2018b).

Recent research in the area of methanol-to-olefins has focused on:

- Improving the yield of light olefinic products at lower temperatures.
- Improving the synthesis of the preferred SAPO-34 catalyst to reduce the effects of pore mouth coking.
- Determining the mechanism for the formation of the first C–C bond.

1.2.10 Olefins-to-Gasoline and Middle Distillates (MOGD) Process

The Mobil Olefins to Gasoline and Middle Distillate (MOGD) process is an offshoot of the methanol to gasoline technology discussed in Section 1.2.8 and utilizes the reactivity of the olefins created from the methanol to olefin (MTO) process (Figure 10) (ExxonMobil 2016). The MOGD process was originally designed to make use of small size olefins (C3 to C6) from the FCC unit in the production of gasoline and diesel fuels. Mobil demonstrated their process using a mixed C_3/C_4 stream from an FCC unit at their refinery. The olefins generated by the MTO process are taken up by MOGD into a second reactor and oligomerized to achieve a product in the range of gasoline and distillate at greater than 95% total selectivity. The result is largely methyl branched iso-olefins from C_5 to C_{20} (PNNL 2013).

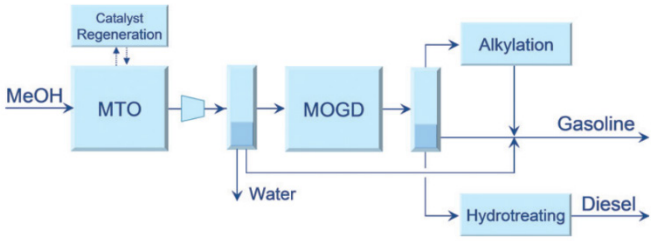


Figure 10. ExxonMobil Olefins to Gasoline and Distillate Process (MOGD). From Olsbye, U., S. Svelle, M. Bjorgen, P. Beato, T. Janssens, F. Joensen, S. Bordiga, and K. Lillerud, Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity, *Angewandte Chemie International Edition,* 2012, 51: 5810–5831. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

The flexible MOGD process has been tested with commercial catalyst and refinery scale equipment. Design changes can achieve distillate/gasoline ratios from 0/100 to 90/10, and process flexibility extends to feed streams, which can range from propylene and butylene to ethylene and naphtha. The C3/C4 and C5/C6 were found to provide the best distillate selectivity. Ethylene uniquely resulted in lower reactivity, required high processing temperature, and ultimately produced a higher gasoline range yield. Saturated compounds pass through MOGD unreacted, but light aromatic compounds alkylate with olefins and can move from gasoline to diesel boiling range (Romey et al. 1987). MOGD can produce liquid transport fuels using light olefins from a catalytic cracker, and as an MTO extension, it creates a means to upgrade methanol to higher olefins.

The high investment costs of the MTG and MTO-MOGD process have prohibited their wide implementation, and the resulting fuel production cost is not competitive with petroleum-derived fuel. Using biomass feedstocks exacerbates the price differential because transportation costs of biomass demand multiple, smaller plants. Finally, variable oil prices lead to volatile economics for synthetic fuels.

Recent research has concentrated on the use of biomass-based fuels. The techno-economic assessment is based on the use of dimethyl ether—considered to be the building block for both the methanol to gasoline and the olefin to gasoline processes. The assessment states that total energy efficiency for the production of gasoline and olefins ranges from 37.5% to 41.1%, respectively (PNNL 2011).

Other key works discuss the use of glycerol, a side product from the synthesis of bio-diesel, as a “green” starting material for olefins to gasoline. As with the original Mobil process, the bio-based method uses H-ZSM-5 as the catalyst. The process contains a number of oxygenated intermediates, which add to the need for additional H_2 (Blass et al. 2014).

Finally, the control of zeolite acidity has been studied recently as a means for controlling gasoline conversion and end point selectivity.

Recent research in the area of olefins-to-gasoline and middle distillates has focused on:

- Improving the yield of C_5^+ products to high-octane components such as aromatics and branched paraffins.
- Using biomass-based fuels such as glycerol with an H-ZSM-5 catalyst as the starting material.
- Controlling the Brønsted acidity of the zeolite to improve the selectivity to a gasoline fraction.

1.2.11 Conclusions and Outlook

The transformation of fossil fuels (natural gas, petroleum, and coke) will continue to dominate the chemical industry for the next few decades and continuous improvements in selectivity, yield, and stability will be needed. The abundance of natural gas will require the design of new catalysts to activate methane to take advantage of its abundance.

From the results presented in Topic 1.2, it is evident that the design of new catalysts is at the center of catalyst innovation. In particular new concepts to improve catalyst activity, catalyst selectivity, and catalyst stability (coke formation and sintering) will be required.

In addition, process design will play a significant role in bringing new technical advances to the chemical industry. Low temperature and low pressure catalysts will be required along with new reactor designs for fast heat transfer. The integration of flexible and modular processes that can adapt to a variety of feedstocks will be required. Also, the development of new catalysts based on Earth-abundant, non-precious metals will be essential.

1.3 BIOMASS AND FOOD-WASTE CONVERSION

The U.S. and global bioeconomy is constantly changing. Variable fossil fuel prices, shifting environmental policies, new technologies, and environmental concerns play into the unrest. As expressed in the DOE *2016 Billion-Ton Report*, U.S. production of biomass can reach over 700 million dry tons per year in 2017 at prices up to $60 per dry ton (DOE 2016). The report goes on to predict that U.S. biomass production could reach 1.1 billion dry tons per year by 2040, primarily from forest and agricultural residues, assuming energy crop production increases. These forecasts indicate that biomass could account for approximately 15% of total U.S. energy consumption (Schaidle et al. 2017).

Lignocellulosic material stems from living organisms and generally refers to plant-based matter not intended for food. Terrestrial lignocellulosic biomass includes woody types such as forest residues, and herbaceous types including crops like corn stover and switchgrass. All lignocellulosic biomass consists of cellulose (40–80 wt%), hemicellulose (15–30 wt%), and lignin (10–25 wt%), with weight percent depending on type. The lignocellulosic components are organic polymers made up of carbohydrate, such as glucose, and aromatics, such as phenol, which determine the structural properties of the biomass (Figure 11). As fuel or chemical product feedstocks, the polymers must undergo deconstruction, at least in part, and reconstruction through an upgrade process. Non-terrestrial bio-based feedstocks can include algae, biogas, and a variety of oils and fats (e.g., soybean, palm, canola, or rapeseed; animal fats; waste greases and oils) (Schaidle et al. 2017).

Conversion of biomass to liquid transportation fuels has attracted much attention in the last 20 years as a path forwarding several objectives. Conversion methods are a critical component in leveraging the Environmental Protection Agency's (EPA) Renewable Fuel Standard; reducing greenhouse gas emissions (and thereby U.S. dependence on foreign oil); and contributing to domestic economic growth. In 2014, the United States produced over 16 billion gallons of biofuel, comprised primarily of ethanol from corn-based feedstocks and biodiesel from vegetable oils, fats, and greases. However, production of biofuels from non-food lignocellulosic biomass is more challenging because the combination of high feedstock costs (compared to fossil fuel alternatives of crude oil and natural gas) and capital-intensive conversion technologies result in high processing costs that are non-competitive (Figure 12). Feedstock prices and conversion costs must decrease; and improved catalysts can enable the latter.

Another way to meet the challenge of high feedstock and process costs is co-production of fuels and chemicals derived from biomass, including both commodity and specialty chemicals. Capital investment costs can be offset by applying co-product credits, improving profitability of fuel production. Biomass feedstock can be more completely utilized by co-production of fuels and chemicals. Companies can benefit from a revenue stream from the co-products, especially important for commercial facilities breaking ground in new technologies.

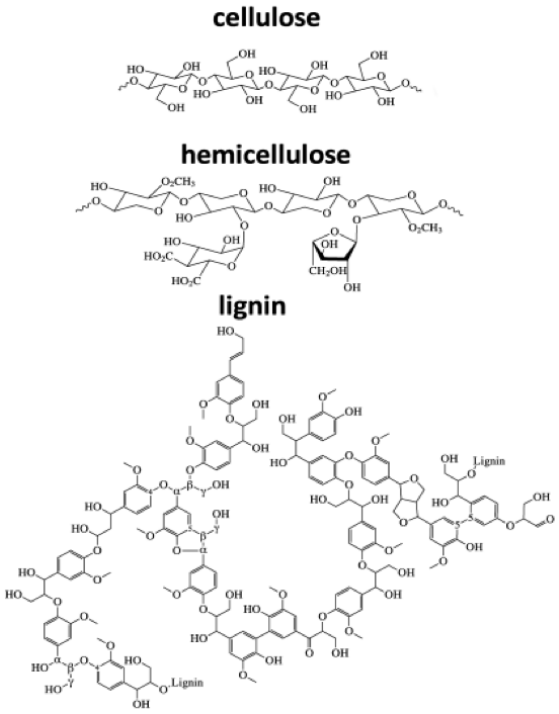


Figure 11. Polymeric structures of cellulose, hemicellulose, and lignin.

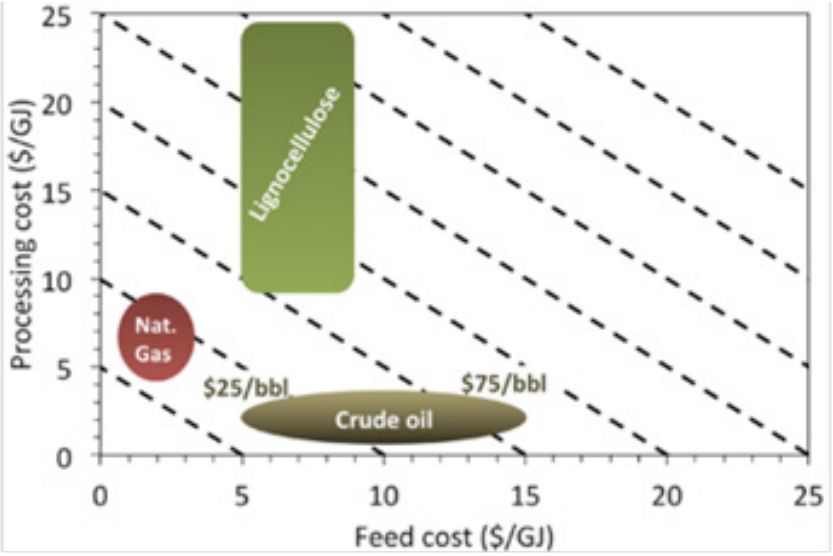


Figure 12. Feed cost vs. processing cost for fuel production from natural gas, crude oil, and lignocellulosic biomass. From Ruddy et al. (2014). Copyright The Royal Society of Chemistry.

Biomass and biomass-derived intermediates can, by their chemical functionality, potentially provide direct replacement chemicals using more efficient and lower cost routes than current methods, which are energy intensive and environmentally harmful. These intermediates may offer similar advantages for functional replacement chemicals, a group yet unexplored.

Co-production of chemicals and fuels from biomass requires a flexible product mix to manage risk and maximize profits as markets shift. Adding value by mixing product can be limited by potential production bottlenecks. Chemical and fuel production inherently have different constraints. Biomass conversion pathways determine accessibility of chemical products, and purity requirements for chemicals and polymer precursors may be significantly stricter than for fuels, even considering the demands of fuel regulatory policies. Chemical production tends to target a single compound, while fuels target mixtures. Finally, biomass, chemically diverse by nature, will

render a finished product that may be more costly to separate and purify than would a similar fossil fuel-sourced product. Furthermore, chemical volumes attainable from biomass may be difficult to justify production costs. Highly selective catalysts can mitigate these constraints and reduce separation complexity.

Bio-based feedstocks can be converted into fuels and chemicals through a variety of different pathways involving catalysis, although these feedstocks present unique challenges. The feedstocks typically have a high oxygen content (up to 50 wt%). They can be in the form of solid, liquid, or gas with diverse compositions depending upon the source. They possess multiple chemical functionalities often present within polymeric structures. They also contain water, both present in the feedstock and produced throughout the conversion process, and other impurities such as sulfur, nitrogen, alkali metals, and chlorine. It is clear from these challenges that no one approach is best suited for all feedstocks, that is, the feedstock needs to be matched with the conversion technology. The following subsections briefly introduce and describe these different conversion technologies, with an emphasis on approaches that are being pursued industrially, albeit at varying scales (pilot to commercial) as the bioeconomy is still in its infancy. Owing to the less established nature of the bio-economy, recent research within each of these technologies is also highlighted.

1.3.1 Gasification and Synthesis Gas Upgrading

Syngas, comprised primarily of H_2 and CO, can be produced through the gasification of solid feedstocks such as lignocellulosic biomass and municipal solid waste, or through reforming of biogas/landfill gas. Gasification involves heating the solid feedstock to between 700 °C and 900 °C in the presence of an oxidizing agent, such as steam or oxygen, to completely deconstruct the polymeric structure of cellulose, hemicellulose, and lignin (Huber et al. 2006). In addition to H_2 and CO, gasification also produces CH_4, tars (e.g., benzene, methylated benzene, and polycyclic aromatics), CO_2, and H_2S that need to be reformed (to produce additional H_2 and CO) or removed (e.g., through an amine scrubber system) prior to further catalytic upgrading. Biogas and landfill gas are comprised primarily of CH_4 (50%–75%) and CO_2 (25%–50%) with concentrations depending upon the anaerobic digestion process and the use of biocatalysts, but they can also include impurities such as H_2S and siloxanes. These raw gas streams are first purified and then catalytically reformed to produce H_2 and CO for further upgrading (see Section 1.2).

Although at varying stages of development (ranging from pilot to commercial), most biorefineries proceeding through a syngas intermediate stream are leveraging or plan to leverage the well-known commercial catalytic upgrading routes of methanol synthesis and Fischer-Tropsch synthesis (both discussed in Section 1.2). It is important to note that Fischer-Tropsch is one of the Federal Aviation Administration (FAA)/ASTM-approved pathways for producing alternative jet fuel (at blends up to 50%). In many cases, the methanol from methanol synthesis is then further catalytically upgraded through (1) dehydration to produce dimethyl ether as a diesel fuel, (2) methanol carbonylation for ethanol and acrylate production, and (3) MTO/MTG processes. Alternatively, syngas fermentation routes are being pursued for the production of ethanol and other oxygenates such as butanediol.

Recent research in the area of gasification and synthesis gas upgrading has focused on:

- Breaking the economy of scale paradigm for these large capital processes through alternative reactor configurations, such as microchannel and monolith reactors.
- Developing catalysts that operate at lower temperatures and pressures, thus enabling cost reduction for these capital-intensive technologies.
- Developing selective catalysts for direct synthesis of mixed alcohols and for coupling methanol, dimethyl ether, ethanol, and mixed alcohol intermediates into fuel-range molecules.
- Improving the feedstock-agnostic nature of gasification by developing advanced syngas clean-up technologies.

1.3.2 Catalytic Fast Pyrolysis

As opposed to gasification, the objective of thermolysis or liquefaction of solid biomass feedstocks is partial degradation of the bio-polymers to produce bio-oil, a complex mixture of many oxygenated organic compounds and water. These compounds are derived from the monomeric and dimeric units of cellulose, hemicellulose, and lignin. Fast pyrolysis, which involves the rapid heating of biomass in inert environments at low pressure to temperatures in the range of 400–550 °C, is one of the most promising liquefaction technologies owing to the ability to achieve high bio-oil yields (70–75 wt%) (Schaidle 2017; Bridgwater 2012). However, due to its high oxygen content and acidic/corrosive nature, fast pyrolysis bio-oil must first be upgraded before using as a transportation fuel or blendstock.

Catalytic fast pyrolysis (CFP) is an upgrading technique designed to improve the fuel quality and stability of the resulting bio-oil by reducing the oxygen content (i.e., oxygen to carbon [O/C] ratio). Prior to condensation, the pyrolysis vapors undergo a catalytic upgrading process, increasing the hydrogen content (i.e., hydrogen to carbon [H/C] ratio), and increasing the carbon number into a range suitable for gasoline, diesel, or jet fuel (Ruddy et al. 2014). For example, the oxygen content of CFP oil is typically 10–25 wt% as compared to 40–50 wt% for fast pyrolysis oil, although this oxygen reduction for CFP comes with the trade-off of lower liquid yields. CFP can be performed in either an *in situ* (within the pyrolysis unit) or *ex situ* (within a secondary reactor) configuration, each of which has different operational considerations as discussed in Table 1 (Ruddy et al. 2014). Industrially, this technology is under development at the pilot and demonstration scales, with the majority of applications utilizing fluidized bed or entrained flow (similar to fluid catalytic cracking units in a petroleum refinery) reactor systems with continuous catalyst regeneration. The catalysts are typically zeolites, metal-modified zeolites, or mixed metal oxides and need to be relatively low cost due to the high attrition rates for these types of reactor systems. The resulting CFP oil can be distilled to produce chemicals such as benzene, toluene, and xylene; hydrotreated to finished fuels; or co-processed at a petroleum refinery. Hydrotreating and co-processing will be discussed in more detail in Section 1.3.4.

Table 1. Operational considerations for *in situ* and *ex situ* catalytic fast pyrolysis process configurations.

***IN SITU* CFP**	***EX SITU* CFP**
Fluidized bed only	Fluidized, entrained flow, or fixed bed
Catalyst mixes with biomass, char, and ash creating a difficult operating environment	Biomass, char, and ash are reduced or removed, resulting in a more benign environment for the catalyst
Limited chemical transformations/catalysts are feasible	More diverse catalysts and chemistries are possible
Lower capital, but higher catalyst replacement rates	Higher capital, but lower catalyst replacement rates
Hot gas filtration is not required	Hot gas filtration may be included (required for fixed bed)
Operating conditions are tied to fast pyrolysis	Operating conditions can differ from fast pyrolysis

Recent research in the area of catalytic fast pyrolysis has focused on:

- Improving lifetime of zeolite-based catalysts and product yield by removing known catalyst poisons through feedstock pre-processing and catalytic hot gas filtration.
- Introducing mesoporosity and metal functionality to reduce coke formation and/or improve coke tolerance.
- Designing catalysts and integrated systems to maximize carbon efficiency by taking advantage of co-fed H_2, targeting removal of oxygen through formation of H_2O instead of CO and CO_2.
- Utilizing low-cost waste products from other chemical processes as CFP catalysts.

1.3.3 Hydrothermal Liquefaction

Similar to pyrolysis, hydrothermal liquefaction (HTL) targets partial degradation of the bio-polymers to produce bio-oil. However, HTL differs from pyrolysis in that it typically operates at lower temperatures (250–450 °C) and higher pressures (5–250 atm) and is compatible with wet feedstocks (e.g., algae) (Elliott et al. 2015; Dimitriadis and Bezergianni 2017). HTL utilizes the properties of supercritical water to achieve thermal hydrolysis and decarboxylation of the feedstock, often in the presence of additional solvents (e.g., methanol or ethanol), hydrogen donors, reducing gases, and/or catalysts. The bio-oil produced from HTL is typically higher energy content and lower oxygen content than fast pyrolysis bio-oil, although at the expense of slightly lower liquid bio-oil yield. The HTL process also requires higher capital cost owing to the elevated pressure and corrosive conditions. Similar to fast pyrolysis and CFP, HTL bio-oils need to be further upgraded prior to use as a fuel. Although still at an early stage of research and development, multiple HTL processes have been operated at the pilot and demonstration scale (5–200 $kg_{feedstock}$/h) on raw materials ranging from sewage sludge to lignocellulosic biomass.

Homogeneous and heterogeneous catalysts, such as Na_2CO_3, K_2CO_3, H_2SO_4, Fe, $FeSO_4$, and transition metal catalysts (e.g., Pd, Pt, Ru, and Ni), have been shown to affect the HTL bio-oil yield and product composition. Specifically, the role of the catalyst is to reduce the formation of solid residues (char), thus enabling higher liquid yields. Heterogeneous transition metal catalysts face specific challenges owing to the operating conditions, such as sintering, dissolution, and poisoning. However, catalyst selection depends primarily on the HTL feedstock and composition.

Recent research in the area of hydrothermal liquefaction has focused on:

- Optimizing process parameters (temperature, pressure, solvent) and reactor configuration (continuous flow vs. batch, two-step liquefaction) for multiple feedstocks to maximize bio-oil yield.
- Understanding the effect of homogeneous and heterogeneous catalysts on the HTL product distribution.
- Developing environmentally-benign catalysts and additives.

1.3.4 Hydroprocessing and Refinery Co-processing

Bio-oils produced from fast pyrolysis, CFP, HTL, algae, vegetable seeds, animal fats, and waste (grease) can benefit from further upgrading before being used as transportation fuels. This upgrading can be achieved through (1) hydrotreating, (2) co-processing within a petroleum refinery, or (3) transesterification. This section will focus on hydrotreating and refinery co-processing while transesterification will be discussed in section 1.3.9. Hydrotreating is a well-established process within petroleum refining and targets the removal of heteroatoms (sulfur, nitrogen, and oxygen) through the reaction with hydrogen, with concomitant saturation of olefins and aromatics. The operating conditions for hydrotreating in a petroleum refinery are typically 300–450 °C with H_2 pressures up to 130 atm, although the specific conditions depend upon the stream and its composition (e.g., naphtha, distillate, gas oil, gases, and residue), the quality of the crude oil, and the finished fuel specifications. The most commonly used catalysts are supported CoMo- and NiMo-based sulfide catalysts. Although this process has been practiced industrially for petroleum refining for many years, the predominant focus has been on removal of sulfur and nitrogen, as the oxygen content in petroleum streams is typically less than 0.3 wt%.

Bio-oil composition varies considerably depending upon the feedstock and process. For example, vegetable oils are predominantly long-chain fatty acids while biomass pyrolysis oil can contain over 400 different oxygenated compounds with varying carbon chain lengths. Depending upon the process, bio-oils can contain up to 50 wt% oxygen, thus bio-oil hydrodeoxygenation has been a focal point for research and development over the last 10–15 years (Wang et al. 2013). Industrially, bio-oil hydrotreatment is being practiced at the commercial scale, primarily for the production of renewable diesel and jet fuel (e.g., synthetic paraffinic kerosene derived from hydro-processed esters and fatty acids [denoted HEFA-SPK] is an FAA/ASTM-approved pathway for alternative jet fuel at blends up to 50%). The majority of these commercial biorefineries use vegetable and waste oils as the feedstock.

Depending upon the bio-oil properties, it is also possible to co-process bio-oil within existing petroleum refinery operations. As discussed above, refineries have multiple hydrotreating units that may be amenable to co-processing with bio-oil; however, recent work has demonstrated the feasibility of co-processing biomass fast pyrolysis oil with vacuum gas oil in an FCC unit (de Rezende Pinho et al. 2017). Co-processing with blends up to 10 wt% fast pyrolysis bio-oil were demonstrated using a commercial FCC equilibrium catalyst at the demonstration scale, and the renewable carbon efficiency to liquid products (e.g., gasoline and diesel cuts) was in the range of 30%. While not yet commercial, this technology is being pursued industrially. Outside of the zeolite-based CFP research discussed in section 1.3.2, little to no research has focused on developing catalysts specifically targeted at co-processing vacuum gas oil and bio-oil in an FCC unit.

Recent research in the area of bio-oil hydrotreating has focused on:

- Developing catalysts that tolerate water and other poisons, minimize coke formation, require no sulfur co-feed, and achieve high carbon yields to deoxygenated products at low hydrogen pressure.
- Designing and implementing multi-stage hydrotreating systems to limit polymerization and bed plugging.
- Probing reaction and deactivation mechanisms using both model compounds and raw bio-oils.
- Targeting oxygen removal through decarbonylation and decarboxylation to balance hydrogen consumption and carbon yield.

1.3.5. Hydrolysis and Fermentation

Alcohols, acids, and other oxygenates can be produced from lignocellulosic biomass hydrolysis and fermentation. This process typically requires three main conversion steps: biomass pretreatment, hydrolysis, and fermentation. However, it should be noted that in some cases these steps can be combined (see below) or even completely omitted (pretreatment). The goals of the pretreatment step are to (1) expose the cellulose and hemicellulose fractions (acidic pretreatment also hydrolyzes the hemicellulose), making them more amenable to hydrolysis, and (2) segregate the lignin, albeit often in a modified form. The lignin is often burned for process heat and power, although research is ongoing to develop routes to upgrade lignin to fuels and chemicals. The most common pretreatment methods include acid, base, hot water/steam, organic solvent, and ionic liquids.

The goal of the hydrolysis step is to liberate C_5 and C_6 sugars, and can be achieved through either acid or enzyme catalysis. Dilute-acid hydrolysis typically employs H_2SO_4 at temperatures in the range of 100–220 °C, while enzymatic hydrolysis employs a system of cellulases. Note that effective pretreatment is critical for enzymatic hydrolysis: sugar yield from enzymatic hydrolysis can vary from 20% of theoretical when no pretreatment is employed to greater than 90% with effective pretreatment.

Lastly, the liberated sugars can be biologically converted (aerobically or anaerobically) using a variety of different microorganisms or catalytically converted (see section 1.3.7) to produce fuels and chemicals. These main conversion steps can also be combined through (1) simultaneous saccharification and fermentation (SSF), which combines hydrolysis and fermentation into a single reactor, or (2) consolidated bioprocessing (CBP), which combines enzyme production, enzymatic hydrolysis, and fermentation into a single step.

In 2014, the United States produced 14 billion gallons of ethanol, primarily from corn (starch) (DOE 2016). However, multiple cellulosic ethanol plants are coming online at the demonstration to commercial scales. In addition to ethanol, there is considerable industrial effort to produce chemicals and chemical precursors, such as lactic acid, succinic acid (precursor for nylon), and adipic acid (requires additional steps beyond just fermentation) as well as higher alcohol fuels, such as isobutanol, through fermentation. The major challenges for the hydrolysis and fermentation of lignocellulosic biomass to fuels and chemicals include (1) Cost-effective pretreatment strategies (pretreatment is the second most expensive step in ethanol production) that produce a highly digestible solid while minimizing sugar degradation, limiting formation of toxic compounds (i.e., sugar degradation products such as furans, phenolics, and acids), and enabling lignin recovery; (2) Efficient low-cost cellulase and hemicellulase enzymes that can operate under high solids loadings (>15 wt%), reduce hydrolysis time, and achieve monomeric sugar yields of greater than 90%; (3) Engineered robust microorganisms for fermentation that can achieve volumetric productivities greater than 1 g/L/hr to the desired end product and sugar utilization greater than 90%; and (4) Low-cost separations (depends on desired end product).

1.3.6 Catalytic Upgrading of C_2+ Alcohols

The ability to produce C_2+ alcohols through fermentation of syngas and sugars has driven considerable effort to further upgrade these alcohols into drop-in hydrocarbon fuel blendstocks or polymers. The first step in this approach is typically dehydration of the alcohol or mixture of alcohols to olefins; however, single-step processes directly from alcohols to aromatics and paraffins are being pursued (e.g., Vertimass). This initial dehydration is typically achieved over Lewis or Brønsted acidic catalysts, such as zeolites, under moderate conditions. Since fermentation typically occurs in aqueous media, the ability of the catalyst to selectively dehydrate the alcohol in the presence of co-fed water will reduce the upstream separations burden. Through dehydration, ethanol can be converted into ethylene, which can be sold directly or polymerized to polyethylene.

To further upgrade to hydrocarbon fuel blendstocks, the olefin stream is then oligomerized and subsequently hydrogenated. Oligomerization (without cyclization) of ethylene is rather challenging and is typically performed industrially using organic solvents and homogeneous catalysts, such as trialkylaluminum and nickel complexes. Oligomerization of higher olefins (C_3+) and di-olefins is more easily accomplished and can often be achieved over acidic zeolites or ion-exchange resins, although aromatic by-products and coke are also produced depending upon the conditions. In some cases, synthesis of aromatics may be desirable as fuel components or as chemical co-products, such as benzene, toluene, and xylene. Hydrogenation of the resulting olefinic oligomers to paraffins is a relatively facile process. This dehydration-oligomerization-hydrogenation process is being pursued industrially at varying scales with ethanol, isobutanol, and butanediol as the alcohol feedstocks. The conversion of isobutanol to jet fuel (termed alcohol-to-jet [ATJ]) is an FAA/ASTM-approved pathway for alternative jet fuel at blends up to 30%. As an alternative to the above approach, alcohols can be reformed to produce H_2; however, this process appears to have limited industrial application at this time.

Recent research in the area of alcohol upgrading has focused on:

- Developing heterogeneous catalysts for ethylene oligomerization such as nickel on alumina and zeolites.
- Processing mixed alcohol streams that utilize modified zeolite catalysts to produce both fuels and chemical co-products (e.g., p-xylene) while mitigating coke formation.
- Controlling olefin oligomerization to target products in the desired carbon number range.
- Investigating alternative chemistries, such as the Guerbet and Tischenko reactions, and steps required for alcohol activation, such as dehydrogenation, to form an aldehyde.

1.3.7 Aqueous Phase Processing and Catalytic Upgrading of Sugars and Other Biomass-derived Intermediates

Biomass hydrolysis and fermentation produces aqueous streams rich in sugars, acids, and other biomass-derived intermediates. In addition, liquefaction technologies, such as CFP and HTL, discussed in Sections 1.3.2 and 1.3.3, produce aqueous waste streams that can contain up to 40 wt% organics. The composition of these organics depends on the liquefaction technology, but can include species such as acetic acid, propanoic acid, ethanol, phenol, and hydroxyacetone. A variety of approaches at varying stages of development, from lab-scale R&D to demonstration-scale in industry, exist for aqueous phase processing and catalytic upgrading of the organic species in these product and waste streams, and the approach varies based on the stream composition.

These approaches include, but are not limited to (1) aqueous phase reforming (e.g., Virent), (2) sugar and carbohydrate dehydration, (3) esterification and ketonization of carboxylic acids, and (4) catalytic reduction of carboxylic acids. Aqueous phase reforming of sugars and starches over heterogeneous bifunctional metal-acid catalysts combines hydrogen generation through reforming with deoxygenation, hydrogenolysis, hydrogenation, and cyclization. The resulting mixture of alcohols, ketones, acids, furans, and paraffins can then be catalytically upgraded with modified zeolites to produce drop-in hydrocarbon fuel blendstocks. Dehydration of sugars and carbohydrates results in the formation of furan derivatives (furfural, hydroxymethylfurfural, and methoxymethyl-furfural) that can then be catalytically upgraded through oxidation routes to chemical/polymer precursors or converted into distillate-range hydrocarbons through a combination of hydrogenation, condensation, and hydrodeoxygenation. Short-chain (C_2–C_6) carboxylic acids can be converted to alcohols through esterification followed by hydrogenolysis, or converted to hydrocarbon fuel blendstocks through ketonization, aldol condensation, and hydrodeoxygenation. Ketonization and aldol condensation increase the carbon chain

length of the starting acids into a range suitable for fuels, while also removing oxygen. Lastly, carboxylic acids, especially dicarboxylic acids such as succinic acid (which already has direct value as a precursor for nylon), can be reduced to produce alcohols and diols (e.g., 1,4-butanediol) for additional chemical applications.

As is apparent from this discussion, these catalytic approaches provide access to both fuels (oxygenates and hydrocarbons) and chemicals, and are as diverse as the initial feed streams. Thus, it is difficult to capture only a few highlights of recent research in this field. Overarching catalysis themes related to aqueous phase processing and catalytic upgrading of sugars and other biomass-derived intermediates are highlighted below.

Recent research in the area of catalysis related to aqueous phase processing and catalytic upgrading of sugars and other biomass-derived intermediates has focused on:

- Balancing reaction rates over multi-functional catalysts, such as heterogeneous catalysts with metallic and acidic functionality.
- Developing hydrothermally-stable metal oxides and tuning their reactivity through dopants and alloying.
- Tolerating impurities and poisons in the feed.
- Controlling selectivity, as a variety of products are accessible under these operating conditions.

1.3.8 Lignin Deconstruction and Upgrading

Fermentation approaches such as those described in section 1.3.5 are typically able to convert only the carbohydrate fraction of biomass (i.e., C_5 and C_6 sugars liberated from cellulose and hemicellulose) into fuels and chemicals. Thus, a large portion (15–30 wt%) of the plant material, lignin, is typically burned for process heat and power. Lignin is an aromatic polymer (Figure 11) that is heterogeneous and recalcitrant in nature, thus difficult to monetize. However, as more and more cellulosic biorefineries come on line, excess lignin waste will be generated, providing an opportunity to create a revenue generating stream (Ragauskas et al. 2014). Although not extensively practiced commercially, lignin potentially can be converted to a variety of high-value materials, including carbon fiber, engineered plastics, thermoplastic elastomers, and polymeric foams and membranes, and a number of fuels and chemicals (e.g., benzene, toluene, xylene, phenol, cresols, and adipic acid).

Lignin-rich streams are generated from biological-focused biorefineries through either a carbohydrate extraction process that leaves behind a solid lignin-rich residue or biomass fractionation through pretreatment to extract the lignin prior to carbohydrate conversion. Regardless of the extraction approach, lignin needs to be depolymerized and upgraded to produce fuels and chemicals. Due to the heterogeneity of C–O and C–C linkages in lignin (and their respective bond strengths) and the propensity of low-molecular-weight species to undergo recondensation, depolymerization is quite challenging. The subsequent upgrading of depolymerized lignin is also difficult due to the diversity of species and functional groups.

Various strategies for lignin depolymerization and upgrading are under development, including thermochemical treatments (e.g., pyrolysis), ionic liquids, homogeneous (e.g., acid and base catalysis) and heterogeneous (e.g., hydrogenolysis and hydrodeoxygenation over NiMo or CoMo materials; solid base materials) catalysis for both reductive and oxidative approaches, and biological routes.

Recent research on lignin depolymerization and upgrading has focused on:

- Biological funneling through the use of aromatic-catabolic microbes to convert heterogeneous lignin-derived streams into value-added compounds.
- Developing catalysts and optimizing reaction conditions for reductive and oxidative lignin depolymerization.
- Genetically modifying feedstocks for easier depolymerization.

1.3.9 Transesterification

Transesterification of lipids derived from edible and non-edible vegetable oil, animal fat, or algae produces biodiesel, which consists primarily of fatty acid esters. For biodiesel production, transesterification typically involves the reaction of long-chain (16–20 carbon atoms) triglycerides with short chain alcohols (e.g., methanol

or ethanol) in the presence of acid or base catalysts to produce mono-alkyl esters and glycerol (by-product). The most commonly used catalysts are homogeneous alkaline base catalysts including NaOH, KOH, and $NaOCH_3$. Free fatty acids remaining in the oil are either converted to soap or are further esterified using an acidic catalyst, typically a mineral acid. Through this process, the United States produced approximately two billion gallons of biodiesel in 2014, primarily from edible soybean oil.

One of the major challenges for cost-competitive biodiesel production is feedstock cost, which can make up 60%–80% of the total cost of biodiesel production. Thus, significant effort is being dedicated to utilization of lower cost feedstocks such as non-edible oils and used cooking oils; however, feedstock selection affects the yield and properties of the resulting bio-diesel. For example, non-edible oils contain high concentrations of free fatty acids, which react undesirably with homogeneous alkaline base catalysts to form soap, thereby creating considerable separations challenges. Current transesterification processes using alkaline catalysts can accept a maximum of 2.5 wt% of free fatty acids; above this level a pretreatment step is required. Improved catalyst formulations and catalytic approaches have the potential to reduce biodiesel cost by achieving high biodiesel yields from a broader pool of lower-quality feedstocks. In this context, the development of heterogeneous solid acid and base catalysts as well as enzymes has received considerable attention. Heterogeneous catalysts offer the advantages of simple recycle and reduced separations while enzyme catalysts do not catalyze saponification and are environmentally benign.

Recent research in the area of transesterification has focused on:

- Developing robust heterogeneous solid base and acid catalysts that exhibit rates comparable to homogeneous catalysts while operating at low temperatures.
- Engineering lower-cost lipase enzymes with reduced water inhibition.
- Reducing processing steps for conversion of algal lipids to biodiesel through *in situ* transesterification or reactive extraction.

1.4 REFERENCES

Abbas, H. F., and Wan Daud, W. M. A. 2010. "Hydrogen Production by Methane Decomposition; a Review." *International Journal of Hydrogen Energy* 35: 1160–1190. doi: 10.1016/j.ijhydene.2009.11.036.

Armin, A. M., Croiset, E., and Epling, W. 2011. "Review of Methane Catalytic Cracking for Hydrogen Production." *International Journal of Hydrogen Energy* 36: 2904–2935. doi: 10.1016/j.ijhydene.2010.11.035.

Avdeeva, L. B., Kochubey, D. I., and Shaikhutdinov, S. K. 1999. "Cobalt Catalysts of Methane Decomposition: Accumulation of the Filamentous Carbon." *Applied Catalysis A: General* 177: 43–51. doi: 10.1016/S0926-860X(98)00250-6.

Blass, S. D., Hermann, R. J., Persson, N. E., Bhan, A., and Schmidt, L. D. 2014. "Conversion of Glycerol to Light Olefins and Gasoline Precursors." *Applied Catalysis A: General* 475: 10–15. doi: 10.1016/j.apcata.2014.01.013.

Bridgwater, A. V. 2012. "Review of Fast Pyrolysis of Biomass and Product Upgrading." *Biomass and Bioenergy* 38: 68–94. doi: 10.1016/j.biombioe.2011.01.048.

Clariant. 2016. "Clariant's Breakthrough HGM Concept for Propane Dehydrogenation Unit–A Proven Success in China." Clariant website. http://www.clariant.com/en/Corporate/News/2015/03/Clariants-breakthrough-HGM-concept-for-Propane-dehydrogenation-Unit-a-proven-success-in-China.

de Rezende Pinho, A., de Almeida, M., Mendes, F. L., Casavechia, L. C., Talmadge, M. S., Kinchin, C. M., and Chum, H. L. 2017. "Fast Pyrolysis Oil from Pinewood Chips Co-Processing with Vacuum Gas Oil in an FCC Unit for Second Generation Fuel Production." *Fuel* 188: 462–473. doi: 10.1016/j.fuel.2016.10.032.

Dimitriadis, A., and Bezergianni, S. 2017. "Hydrothermal Liquefaction of Various Biomass and Waste Feedstocks for Biocrude Production: A State of the Art Review." *Renewable and Sustainable Energy Reviews* 68: 113–125. doi: 10.1016/j.rser.2016.09.120.

Dodge, E. 2014. "Is Small-Scale GTL the Next Big Thing?" *Energy Collective*. http://www.theenergycollective.com/ed-dodge/2151961/small-scale-gtl-next-big-thing.

Echegoyen, Y., Suelves, I., Lázaro, M. J., Moliner, R., and Palaciou, J. M. 2007. "Hydrogen Production by Thermocatalytic Decomposition of Methane over Ni-Al and Ni-Cu-Al Catalysts: Effect of Calcination Temperature." *Journal of Power Sources* 169: 150–157. doi: 10.1016/j.jpowsour.2007.01.058.

Elliott, D.C., Biller, P., Ross, A. B., Schmidt, A. J., and Jones, S. B. 2015. "Hydrothermal Liquefaction of Biomass: Developments from Batch to Continuous Process." *Bioresource Technology* 178: 147–156. doi: 10.1016/j.biortech.2014.09.132.

ExxonMobil. 2016. "Methanol to Gasoline Synthesis." https://www.exxonmobilchemical.com/en/products-and-services/technology-licensing-and-services/methanol-to-gasoline-synthesis.

Foley, T. 2013. "Cyclar™ Process Produces High-quality Aromatic Products." *Technology and More*, no. 17, https://www.uop.com/cyclar-process-produces-high-quality-aromatic-products/.

Fortman, G. C., Boaz, N. C., Munz, D. M., Konnick, M., Periana, R. A., Groves, J. T., and Gunnoe, T. B. 2014. "Selective Monooxidation of Light Alkanes Using Chloride and Iodate." *Journal of the American Chemical Society* 136: 8393–8401. doi: 10.1021/ja502657g.

Galadima, A., and Muraza, O. 2016. "Revisiting the Oxidative Coupling of Methane to Ethylene in the Golden Period of Shale Gas: A Review." *Journal of Industrial and Engineering Chemistry* 37: 1–13. doi: 10.1016/j.jiec.2016.03.027.

Guo, X., Fang, G., Li, G., Ma, H. H., Fan, L. Y., Ma, C., Wu, X., Deng, D., Wei, M., Tan, D., Si, R., Zhang, S., Li, J., Sun, L., Tang, Z., Pan, X., and Bao, X. 2014. "Direct, Nonoxidative Conversion of Methane to Ethylene, Aromatics, and Hydrogen." *Science* 344: 616–619. doi: 10.1126/science.1253150.

Hartwig, J. F. 2016. "Evolution of C-H Bond Functionalization from Methane to Methodology." *Journal of the American Chemical Society* 138: 2–24. doi: 10.1021/jacs.5b08707.

Honeywell UOP. 2018a. "Petrochemicals Flow Scheme." https://www.uop.com/petrochemicals-flow-scheme/.

Honeywell UOP. 2018b. "Ethylene." https://www.uop.com/processing-solutions/petrochemicals/olefins/ethylene/.

Horn, R., and Schlögl, R. 2015. "Methane Activation by Heterogeneous Catalysis." *Catalysis Letters* 145: 23–39. doi: 10.1007/s10562-014-1417-z.

Huber, G. W., Iborra, S., and Corma, A. 2006. "Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering." *Chemical Reviews* 106: 4044–4098. doi: 10.1021/cr068360d.

James, O. O., Chowdhury, B., Mesubi, M. A., and Maity, S. 2012. "Reflections on the Chemistry of the Fischer–Tropsch Synthesis." *RSC Advances* 2: 7347-7366. doi: 10.1039/C2RA20519J.

Keller, G. E., and Bhasin, M. M. 1982. "Synthesis of Ethylene via Oxidative Coupling of Methane: I. Determination of Active Catalysts." *Journal of Catalysis* 73: 9–19. doi: 10.1016/0021-9517(82)90075-6.

Kogel, J. E., Trivedi, N. C., Barker, J. M., and Krukowski, S. T., eds. 2006. *Industrial Minerals & Rocks: Commodities, Markets and Uses, Seventh Edition.* Littleton, CO: Society for Mining, Metallurgy and Exploration, Inc.

Kondratenko, E. V., Peppel, T., Seeburg, D., Kondratenko, V. A., Kalevaru, N., Martin, A., and Wohlrab, S. 2017. "Methane Conversion into Different Hydrocarbons or Oxygenates: Current Status and Future Perspectives in Catalyst Development and Reactor Operation." *Catalysis Science & Technology*, 7: 366–381. doi: 10.1039/C6CY01879C.

Maffia, G. J., Gaffney, A. M., and Mason, O.M. 2016. "Techno-Economic Analysis of Oxidative Dehydrogenation Options." *Topics in Catalysis* 59: 1573–1579. doi: 10.1007/s11244-016-0677-9.

Narsimhan, K., Iyoki, K., Dinh, K., and Román-Leshkov, Y. 2016. "Catalytic Oxidation of Methane into Methanol over Copper-exchanged Zeolites with Oxygen at Low Temperature." *ACS Central Science 2*: 424–429. doi: 10.1021/acscentsci.6b00139.

NASEM (National Academies of Sciences, Engineering, and Medicine). 2016. The Changing Landscape of Hydrocarbon Feedstocks for Chemical Production: Implications for Catalysis: Proceedings of a Workshop. Washington, D.C.: The National Academies Press. https://doi.org/10.17226/23555.

NFIB (National Federation of Independent Business). 2016. "Shell to Build Ethane Cracker Plant in Beaver County—What it Means for Small Business!" Website for *National Federation of Independent Business*, June. https://www.nfib.com/content/nfib-in-my-state/pennsylvania/usiness-74355/.

Olsbye, U., Svelle, S., Bjorgen, M., Beato, P., Janssens, T. V. W., Joensen, F., Bordiga, S., and Lillerud, K. P. 2012. "Conversion of Methanol to Hydrocarbons: How Zeolite Cavity and Pore Size Controls Product Selectivity." *Angewandte Chemie International Edition* 51: 5810–5831. DOI: 10.1002/anie.201103657.

Periana, R. A., Taube, D. J., Gamble, S., Taube, H., Satoh, T., and Fujii, H. 1998. "Platinum Catalysts for the High-Yield Oxidation of Methane to a Methanol Derivative." *Science* 280: 560–564. doi: 10.1126/science.280.5363.560.

PNNL (Pacific Northwest National Laboratory). 2011. *Techno-economic Analysis for the Thermochemical Conversion of Biomass to Liquid Fuels*. Report No. PNNL-19009. Richland, WA: Pacific Northwest National Laboratory. https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-19009.pdf.

PNNL (Pacific Northwest National Laboratory). 2013. *Single-Step Syngas-to-Distillates (S2D) Synthesis via Methanol and Dimethyl Ether Intermediates: Final Report*. Report No. 22984. Richland, WA: Pacific Northwest National Laboratory. http://www.pnnl.gov/main/publications/external/technical_reports/PNNL-22984.pdf.

Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F., Davison, B. H., Dixon, R. A., Gilna, P., Keller, M., Langan, P., Naskar, A. K., Saddler, J. N., Tschaplinski, T. J., Tuskan, G. A., and Wyman, C. E. 2014. "Lignin Valorization: Improving Lignin Processing in the Biorefinery." *Science* 344(6185): 1246843. doi: 10.1126/science.1246843.

Ravi, M., Ranocchiari, M., and van Bokhoven, J. A. 2017. "The Direct Catalytic Oxidation of Methane to Methanol—A Critical Assessment." *Angewandte Chemie International Edition* 56: 16464–16483.

Romey, I. P. F. M. Paul, and G. Imarisio, eds. 1987. *Synthetic Fuels from Coal: Status of the Technology.* London, UK: Graham and Trotman, Ltd.

Ruddy, D. A., Schaidle, J. A., Ferrell, J. R., Wang, J., Moens, L., and Hensley, J. E. 2014. "Recent Advances in Heterogeneous Catalysts for Bio-oil Upgrading via 'Ex-situ Catalytic Fast Pyrolysis': Catalyst Development through the Study of Model Compounds." *Green Chemistry* 16: 454–490. doi: 10.1039/C3GC41354C.

Sattler, J. J. H. B., Ruiz-Martinez, J., Santillan-Jimenez, E., and Weckhuysen, B. M. 2014. "Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides." *Chemical Reviews* 114: 10613–10653. https://pubs.acs.org/doi/pdf/10.1021/cr5002436.

Schaidle, J., Talmadge, M., Biddy, M., Nimlos, M., and Bratis, A. 2017. "Chemicals Derived from Biomass Thermolysis and Gasification." In *Encyclopedia of Sustainable Technologies*, edited by Abraham, M. A. Elsevier, pp. 587–600.

Shell Global. 2016. "Pearl GTL—Overview." https://www.shell.com/about-us/major-projects/pearl-gtl/pearl-gtl-an-overview.html.

Snoeck, J. W., Froment, G. F., and Fowles, M. 2002. "Steam/CO_2 Reforming of Methane. Carbon Filament Formation by the Boudouard Reaction and Gasification by CO_2, by H_2, and by Steam: Kinetic Study." *Industrial and Engineering Chemistry Research* 41: 4252–4265. doi: 10.1021/ie010666h.

Spivey, J. J., and Hutchings G. 2014. "Catalytic Aromatization of Methane." *Chemical Society Reviews* 43: 792–803. doi: 10.1039/C3CS60259A.

Tamura, M., Kitanaka, T., Nakagawa, Y., and Tomishige, K. 2016. "Cu Sub-nanoparticles on Cu/CeO_2 as an Effective Catalyst for Methanol Synthesis from Organic Carbonate by Hydrogenation." *ACS Catalysis* 6: 376–380. doi: 10.1021/acscatal.5b02258.

Tian, P., Wei, Y., Ye, M., and Liu, Z. 2015. "Methanol to Olefins (MTO): From Fundamentals to Commercialization." *ACS Catalysis* 5: 1922–1938. doi: 10.1021/acscatal.5b00007.

U.S. Department of Energy (DOE), National Energy Technology Laboratory. 2013. *Modern Shale Gas Development in the United Strates: An Update*. https://www.netl.doe.gov/File%20Library/Research/Oil-Gas/shale-gas-primer-update-2013.pdf.

U.S. Department of Energy (DOE), National Energy Technology Laboratory. 2018. "Commercial Examples of Gasification-based Chemicals Production." https://www.netl.doe.gov/research/coal/energy-systems/gasification.

U.S. Department of Energy (DOE). 2016. *2016 Billion-Ton Report: Advancing Domestic Resources for a Thriving Bioeconomy.* M. H. Langholtz, B. J. Stokes, and L. M. Easton (Leads). ORNL/TM-2016/160. Oak Ridge, TN: Oak Ridge National Laboratory. doi: 10.2172/1271651.

U.S. Department of Energy (DOE), Office of Fossil Energy. 2018. "Shale Research and Development." https://energy.gov/fe/science-innovation/oil-gas-research/shale-gas-rd.

U.S. Energy Information Administation (EIA). 2011. "The Geology of Natural Gas Resources." *Today in Energy.* February. https://www.eia.gov/todayinenergy/detail.php?id=110.

U.S. Energy Information Administation (EIA). 2014. "AEO 2014 Early Release Overview." http://www.fe.doe.gov/programs/gasregulation/authorizations/2013_applications/sc_exhibts_13_116_118/Ex._109_-_AEO_2014_Early_Release_Overvie.pdf.

Wang, W., Jiang, Y., and Hunger, M. 2006. "Mechanistic Investigations of the Methanol-to-Olefin (MTO) Process on Acidic Zeolite Catalysts by In Situ Solid-state NMR Spectroscopy." *Catalysis Today* 113: 102–114. doi: 10.1021/cs400069z.

Wang, H., Male, J., and Wang, Y. 2013. "Recent Advances in Hydrotreating of Pyrolysis Bio-oil and Its Oxygen-containing Model Compounds." *ACS Catalysis* 3: 1047–1070. doi: 10.1021/cs400069z.

Yang, W. C. ed. 2003. *Handbook of Fluidization and Fluid-Particle Systems*. New York: Marcel Dekker, Inc.

Yang, M., Tian, X., and You, F. 2018. "Manufacturing Ethylene from Wet Shale Gas and Biomass: Comparative Technoeconomic Analysis and Environmental Life Cycle Assessment." *Industrial and Engineering Chemistry Research* 57: 5980–5988. doi: 10.1021/acs.iecr.7b03731.

Zavyalova, U., Holena, M., Schlögl, R., and Baerns, M. 2011. "Statistical Analysis of Past Catalytic Data on Oxidative Methane Coupling for New Insights into the Composition of High-performance Catalysts." *ChemCatChem* 3: 1935–1947. doi: 10.1002/cctc.201100186.

Topic 2: Novel Approaches to Energy Transformations

Topic 2 focuses on catalysis research that will enable greater and more diverse uses of emerging and under-utilized energy resources such as solar energy, wind energy, and electrical energy. The panel will also explore catalysis for transformations that provide chemical storage of energy such as carbon dioxide reduction, water splitting, and (hybrid) redox flow reactors.

2.1 CHARACTERISTICS OF RENEWABLE SOURCES OF ELECTRICITY

2.1.1 Geographic Distribution of Resources

It is well known that renewable resources vary geographically because of differences in topology, weather, and climate. Solar resources are most prevalent in the Southwestern United States, while on-shore wind is prevalent in the Midwest plains (Figure 13). Off-shore wind generation is localized in the coastal states and around the great lakes. Interestingly, if all renewable resources were combined, this regional variation smooths out. Nevertheless, the total estimated technically available annual generation, using U.S.-based, rural, utility-scale photovoltaic (PV) technology, is a staggering 280,600 terawatt-hours (TWh) for an installed capacity of 153 TW. For concentrated solar power, another 116,100 TWh is possible. Similarly, wind energy, both off-shore and on-shore could potentially supply 49,700 TWh per year (Lopez et al. 2012).

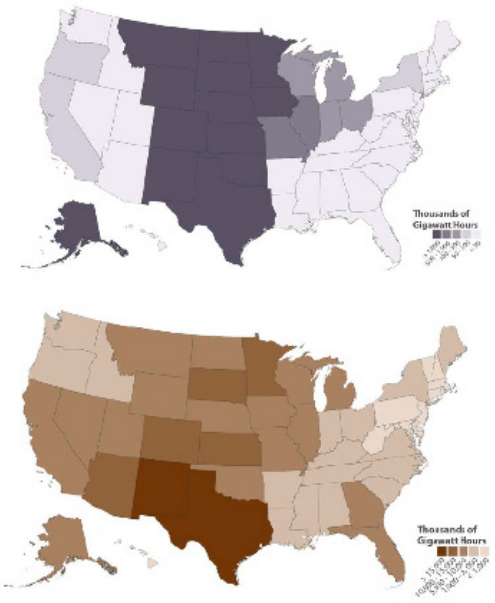


Figure 13. Top: Estimated technical potential on-shore wind power in the United States. Bottom: Estimated technical potential rural utility-scale photovoltaics. Lopez et al. (2012). Figures courtesy of National Renewable Energy Laboratory.

In addition to wide geographic distribution, renewable sources of electricity exhibit both daily and seasonal variability. This variation poses challenges for grid operation. Peak times for renewable electricity generation do not necessarily overlap with peak electricity use. However, several major studies have found that the potential of the electrical grid to utilize very high amounts of renewable generation is much larger than often assumed. For example, a 2010 study of the Western grid (GE Energy 2010) found that it could accommodate 30% wind generation and 5% solar assuming that moderate changes would happen such as increased balancing, increased use of sub-hourly scheduling for generation, and the use of granular solar forecasts. Similarly, a more modern 2016 study of the Eastern grid (Bloom et al. 2016) found that 30% renewable generation with instantaneous penetrations on the order of 50% are possible without impacting grid reliability provided some adjustments are made in how loads are scheduled and how electricity flows through the grid interconnects (Figure 14). This analysis remains valid even with the assumption of inaccuracies in wind and solar forecasting, seasonal and diurnal patterns, and weather and system operating constraints.

Figure 15 illustrates the challenge in making the nation's grid sufficiently flexible to handle the variable nature of renewable generation. This analysis shows that increased penetrations of solar energy on the grid lead to increased curtailment of solar energy, considerably increasing cost. The amount of curtailment is strongly dependent on the flexibility of the grid and the operation strategy of the grid authorities. Fundamentally, the curtailment of solar is related to the cost of ramping down traditional power generation in response to the

diurnal cycle of solar generation. This relationship causes the so-called "duck-curve" that illustrates how typical baseload power generators, such as coal and nuclear facilities, would have to be taken off the grid during the middle of the day to accommodate increased solar generation. Because these baseload power plants cannot respond rapidly (i.e., long start up and shut down times), grid operators would rather curtail solar power (see Figure 15) (Denholm et al. 2016).

On the other hand, a tangible example of the potential of renewables to supply a large amount of the nation's energy occurred on February 12, 2017, when the electricity grid of the plains states hit a record 52% wind power from Montana to Texas (Martin 2017). A myriad of examples on a smaller scale exist, such as cities like Burlington, Vermont, which runs on 100% renewable electricity (Woodard 2016). These cities can reach such numbers because they connect to a large-scale grid that acts like a large storage buffer, an arrangement that is not yet running on a majority of variable renewable energy systems.

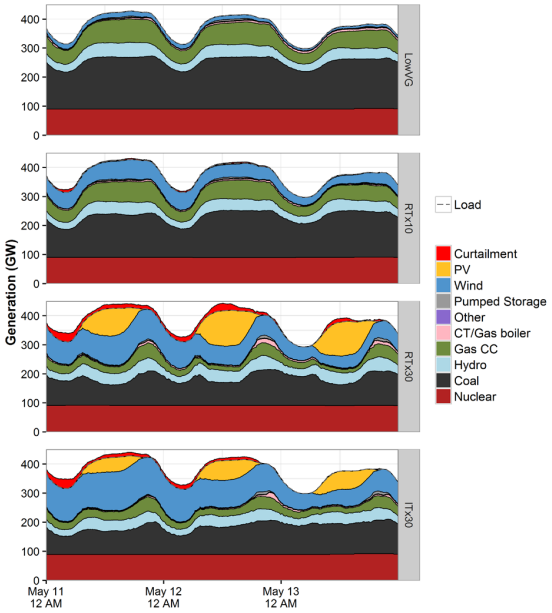


Figure 14. Projected energy dispatch in the eastern interconnect simulated for low (top) to high (bottom) penetrations of variable sources such as photovoltaic and wind. Traditional sources such as gas must ramp up and down two times per day to cope with the daily variation in solar generation. From Bloom et al. (2016). Figure courtesy of National Renewable Energy Laboratory.

Costa Rica provides an interesting example. In 2016, the entire country ran on renewables for two months uninterrupted (Crew 2016). Such scenarios rely heavily on pumped hydroelectric energy storage or in other electrical storage, and are economically feasible on island nations because of the large cost of transporting fossil fuels. A 100% renewable, larger-scale grid on the U.S. mainland is not feasible using present-day technologies as it would need a (currently) economically unviable expansion of electrical storage. Examples of adding storage to the grid to increase renewable penetration on a smaller scale are numerous, such as the Tesla battery plant recently installed in southern California (Cardwell 2017). Such systems help time-shift power from the solar generation peak during the middle of the day to the grid demand peak during the evening and morning hours.

The total potential of renewable resources of electricity mentioned above compares well with the total energy use of the United States. In 2015, total U.S. energy use in all energy sectors was 97.5 quadrillion Btus (quads) (LLNL 2015) or 28,574 TWh, a fraction of the potential total generation from renewable resources of close to 500,000 TWh. However, only 38 quads or 39% of the total energy use in the United States is associated with electricity generation, which is where solar, wind, and other renewables contribute. Even more pertinent, a stunning 59.1 quads of energy is rejected each year, mainly from inefficiencies in generation and in the transportation system. While generating 30% of electricity by renewable resources appears feasible, this fraction still represents only 12% of the total U.S. energy use. Larger scale penetrations of renewables in transportation and industry are possible if the transportation sector is increasingly electrified (i.e., electric cars and trucks) and grid-scale electrical energy storage becomes economical.

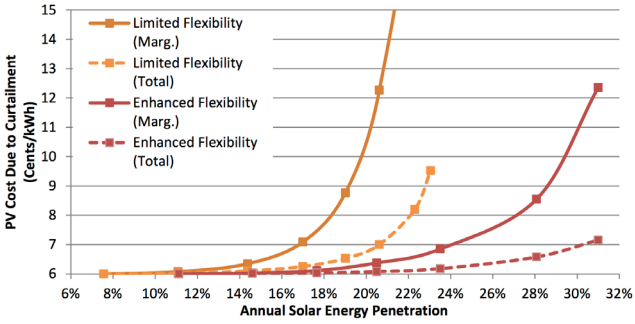


Figure 15. Projected cost of PV electricity as a function of average annual solar penetration. Curtailment, depending on the flexibility of the grid, increases the cost of solar electrons considerably. From Denholm et al. (2016). Figure courtesy of National Renewable Energy Laboratory.

Alternatively, renewable electrons could be steered into fuels generation such as hydrogen from water splitting or carbon-based fuels from CO_2 reduction. A myriad of analyses have appeared describing the pros and cons

of electrical vs. chemical energy storage, concluding that fuels provide the highest energy density (~10^3 Wh/kg) and electrical energy provides the highest power density (~10^3 W/kg) (Cook et al. 2010). A recent study by Lawrence Livermore National Laboratory (LLNL) and the National Renewable Energy Laboratory (NREL) found that when excess renewable electrons are used to generate H_2, renewables could account for 66% of all electricity generation (LLNL 2015). In such scenarios, the excess power generated during peak hours that would normally be curtailed could be diverted to water electrolysis (Pivovar 2016). This strategy would lead to major new connections of the electricity system to the industrial and transportation centers, as well as a reduction of rejected energy, allowing a decrease in total energy use between now and 2050.

The advent of abundant, renewable electricity is making large-scale use of electrolysis for chemical transformations into fuel economically viable. The major chemistries in use or under development that would enable large-scale renewable energy storage via fuels production are described in Sections 2.2 and 2.3.

Recent research in the area of renewable integration into the energy system has focused on:

- Increasing the power utilization from renewable sources through electrochemical storage.
- Developing electrons-to-fuels type scenarios that increase the amount of renewable electricity generation.
- Generating hydrogen and hydrocarbon fuels from renewable sources for industries reliant on fossil fuels such as metals refining and fertilizer synthesis.

2.2 ELECTROCATALYTIC TRANSFORMATION OF CO_2 INTO CHEMICAL FEEDSTOCKS

The use of electrolysis to convert CO_2 into useful chemicals was discussed in Appendix 1 of the report, "Basic Research Needs: Catalysis for Energy," from the U.S. Department of Energy (DOE), Office of Basic Energy Sciences (2007). The summary pointed out the important opportunity of finding non-petrochemical sources for hydrogen and using the H_2 to react with CO_2, effectively recycling it to create useful chemicals, especially fuels. The report recognized that using fossil fuels to provide the electricity needed to recycle carbon dioxide would itself generate significant CO_2, so renewable sources of energy would be preferred. At the time, however, renewable electricity was much more costly than fossil fuel-derived electricity, posing a significant challenge to the viability of the technology. In the intervening decade, the cost of renewable electricity has plummeted, its availability has increased dramatically (as noted in Section 2.1), and significant focus on advancing the relevant science and technology has emerged. Judging by the growing level of corporate activity and government investments, recycling of CO_2 appears to be on a path to becoming commercially attractive (Quadrelli et al. 2011).

Electrocatalytic recycling of CO_2 can be performed in a cell using CO_2 dissolved in liquid electrolytes or CO_2 permeated into a membrane impregnated with a catalyst (membrane electrode assembly [MEA]). Another technology at a much earlier stage of development uses solid oxide electrolyzers at high temperature (Zeng et al. 2012). These technologies can be driven by grid electricity, but substituting photoelectrolysis for grid electrolysis has been demonstrated only in liquid electrolyte systems. When the reaction is photoelectrochemical, an integrated semiconductor light absorber is used to generate the electrons and holes needed to perform the redox reactions, as exemplified in a recent publication (Arai et al. 2015). In all cases, protons are generated by catalytic water oxidation and transported to a cathode, where electroreduction of CO_2 takes place. The potential required is determined by the overpotential for the reduction reaction, typically one volt (V) or more using a metal catalyst. Reduction products are typically C_1–C_3 small molecules and require at least two electrons (formate) and up to 18 electrons (1propanol) (Kuhl 2012). These reactions compete with H_2 formation, which directly reduces efficiency and could require product separation depending on the application. Because the solubility of CO_2 in water is low (on the order of 10^{-2} molar [M]), (photo)electroreduction currents are in the 10 mA/cm^2 range when liquid aqueous systems are used (Singh et al. 2015; Jhong et al. 2013). This limitation is overcome by gas-fed devices, which have been demonstrated to operate in the 100 mA/cm^2 range (Cook et al. 1990). Note that at high pH, the CO_2 is concentrated as carbonate/bicarbonate. Hydrogenation under these conditions suggests carbonate/bicarbonate can easily be reduced to formate. Unlike grid electrocatalytic reduction, which is under development for commercial applications as noted below, photoelectroreduction of CO_2 is in a low technology readiness level (TRL) research phase. Recent progress has been significant, however,

and photoelectrochemical efficiencies in aqueous electrolyte of 5%–10% solar energy to chemical energy for two-electron products have been reported (Arai et al. 2015; Zhou et al. 2016).

Electrochemical processes to reduce CO_2 are enjoying significant corporate investment in systems and materials development. Molecular catalysts for this purpose are still in an early stage of development, although progress has been made (Kumar et al. 2012; Tatin et al. 2016). Heterogeneous systems are more likely to be scalable at this time—this section summarizes their status and a recent review published by Qiao et al. (2014).

Recent research in the area of electrocatalytic transformation of CO_2 into chemical feedstocks has focused on:

- Investigation of whether hot electrons generated near the electrode-electrolyte interface can directly drive CO_2 reduction, a potentially lower overpotential route to this process.
- Investigation of the photoelectrocatalytic activity of p-type semiconductor materials toward CO_2 reduction.
- Investigation of interfacial structuring to open plasmonic and photonic routes to efficient interfacial photoexcitation.

2.2.1 Feedstocks for Downstream Processes

Electroreduction of CO_2 to generate CO, formate, and hydrogen. The simplest electrochemical transformation of CO_2 is typically performed in aqueous electrolyte, and requires two electrons to generate CO and/or formate using an overpotential in the range of 1 V, depending on the catalyst used. Seminal work by Hori (Hori, Kukuchi, and Suzuki 1985; Hori et al. 1994) guides selection of elemental cathode materials for heterogeneous CO_2 reduction. CO is produced on Au, Ag, Zn, Pd, and Ga cathodes. Formate is generated at Pb, Hg, In, Sn, Cd, and Tl electrodes. Most current work still involves these metals or mixtures of them (Qiao et al. 2014).

A mixture of CO and H_2 can be immediately useful as syngas, a feedstock for the Fischer-Tropsch process to generate higher hydrocarbons. Companies such as Dioxide Materials are developing energy efficient electrolyzers for this application.

Electroreduction of CO_2 to generate selected higher hydrocarbons. Electrochemical transformation of CO_2 to produce compounds more complex than CO or formate (e.g., alkenes, alkanes, and oxygenates) requires a sequence of multiple electron-proton transfer steps at the catalyst surface. For example, formation of methane requires 8 electrons and ethylene requires 12. Copper is the only elemental catalyst known to efficiently make this transfer, and it typically produces a number of products in a mixture whose composition changes with applied potential (Kuhl et al. 2012). This lack of selectivity can present challenges with product separations post-reduction. Research is actively identifying efficient and selective catalysts for fuels and feedstock chemicals and commercial development is underway for scalable reactors (e.g., Opus 12) and processes (Liquid Light, recently acquired by Avantium).

Electropolymerization of CO_2 to higher hydrocarbon mixtures. Only a few reports have been made of the formation of larger hydrocarbons (greater than C_5) by CO_2 electroreduction (Centi et al. 2007; Shibata et al. 2008). The reported yields are low relative to the smaller products, however their production is relatively enhanced in vapor-fed device configurations. Electropolymerization to form higher hydrocarbons for use as fuels or feedstocks appears to be impractical at this stage, but may eventually be feasible to use for carbon sequestration.

Recent research in the area of feedstocks for downstream processes has focused on:

- Discovering non-Cu electrocatalysts that can form C–C or C–O bonds selectively with minimal formation of H_2.
- Understanding the mechanism of CO_2 electroreduction by copper and its oxides and alloys, to identify factors at the molecular level that control selectivity and activity.
- Modifying the electrode environment (electrolyte composition, coatings, catalyst morphology and support, phase state of CO_2) to assess impacts on selectivity and activity.

2.3 ELECTROCATALYTIC GENERATION OF H_2 FROM WATER: H_2 AT SCALE

Splitting of water to form O_2 and H_2, a component of CO_2 reduction systems, is an important reaction in its own right. Two primary catalytic processes are involved: the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. McCrory et al. (2015) has benchmarked catalysts for these reactions in 1 M acid and base (see Section 2.3.2, Photoelectrochemical systems), establishing the overpotentials required and stability in operation at 10 mA/cm^2 for 2 hours and 24 hours (for selected catalysts). While a number of stable, low overpotential options exist for the HER in acid and base at this current density, it is evident that the OER reaction cannot operate below about 300 mV overpotential in base, and that no stable OER catalysts besides IrO_x and IrRu alloys in acid are available. Less is known about catalysts for these reactions at other levels of pH, where electrolyzers can operate, as is the case with interaction of the catalyst with solid electrolyte (ionomer) that can cause large changes in activity, particularly for anion exchange systems. Additionally, the findings for catalyst activity and stability at low current density may not apply to high current density (A/cm^2) as is used in electrolyzers. Under high currents, catalyst performance is more severely challenged than at low currents.

2.3.1 Continuous Operation: Grid Electricity

Water electrolysis was first recognized by van Troostwijk and Deiman in 1789 and later confirmed by others, most notably Nicholson and Carlisle in 1800 (Kreuter and Hofmann 1998; de Levie 1999; Chisholm and Cronin 2016). By the 1920s, hydrogen was being produced via electrolysis on an industrial scale for use in ammonia for fertilizer and in petroleum refining. Large plants, on the order of 100 MW, based on alkaline liquid electrolyte technology were eventually replaced in favor of coal gasification and steam methane reforming (SMR) that could produce hydrogen on significantly larger scales (Zeng and Zhang 2010). A niche market in very large-scale (≥60 Nm^3/hr) commercial electrolyzers still relies on alkaline liquid electrolyte technology and is available from companies such as De Nora S.A.P., Nel Hydrogen, Electrolyzer Corp. Ltd., and Teledyne Energy Systems. For most power plant-scale electrolyzers operating at 10–30 Nm^3/hr, proton exchange membrane (PEM) technology now competes with alkaline liquid electrolyzers.

Proton Exchange Membrane electrolyzers. In 1966, General Electric (GE) used DuPont's Nafion™ to demonstrate the use of a PEM in a fuel cell that was later adapted for use in an electrolyzer. Today, this technology is available commercially from Siemens, Hydrogenics Corporation, ITM Power, Proton OnSite, and others. In PEM electrolyzers, the fluoropolymer-based ionomer replaces the alkaline liquid electrolyte and conducts protons between the electrodes.

Carmo et al. (2013) recently reviewed a comparison of the advantages and disadvantages of PEM water electrolysis systems vs. traditional alkaline liquid electrolyte technologies. PEM systems offer high current efficiencies, a compact system design, and high product gas purity, although, until recently, their commercialization has been limited by the drawbacks of high component cost and an acidic corrosive electrolyte. Key PEM electrolyzer benefits include quick response to load fluctuations and an ability to sustain high efficiency and product purity at low loads (down to approximately 10% full load range), in stark contrast to alkaline liquid electrolyte systems. PEM electrolyzers also generate hydrogen at differential pressure (most often 30 bar), whereas the alkaline liquid systems are either ambient (at very large scale) or balanced pressure (at smaller scale pressures up to 10–30 bar), which requires dealing with high-pressure oxygen gas and thus a more complex balance of plant. These factors make PEM electrolyzers more attractive for variable power and/or grid buffering applications.

Based on a 2014 techno-economic analysis of the life cycle of the PEM electrolyzer, total capital costs (including cell stack, balance of plant, and indirect/replacement costs) make up 25%–30% of dollar per kilogram of hydrogen production ($4–5.80/kg H_2), and electricity feedstock costs make up the bulk of remaining total costs (DOE 2014). As the cost of electricity falls (or as curtailment of variable power makes electricity less valuable), reductions in capital cost of PEM electrolyzers will become increasingly important if they are to compete economically with SMR.

A major cost driver of PEM electrolyzers is the MEA, with the membrane material itself and labor for MEA fabrication roughly equal in cost to the noble metal catalysts at large scale. Unlike alkaline liquid electrolyte electrolyzers that can operate using common industrial metal catalysts such as nickel, cobalt, and iron, employing platinum (cathode) and iridium (anode) catalysts minimizes the hydrogen and oxygen evolution

reaction overpotentials in acidic media. Four decades ago, Miles and Thomson (1976) summarized the overpotentials for HER and OER in an 0.1 M H_2SO_4 electrolyte at 80 °C, noting that the oxides of each metal dominate their catalytic activity and durability. Given their high cost and low natural abundance of the metals, research efforts are geared toward reducing or replacing the noble metal catalysts. An alternative catalyst to these noble metals would have to resist the harsh, corrosive low pH environment (pH ~2) while remaining tolerant to high overvoltage (~2 V), especially at high current densities (>1 A/cm^2) (Carmo et al. 2013).

State of the art PEM electrolyzer cathodes rely on platinum nanoparticles supported on carbon black (Pt/C), with typical catalyst loadings of 0.5–1 mg/cm^2. In recent laboratory results, Proton OnSite and Giner have found that the new 3M nanostructured thin film (NSTF) Ir and $Pt_{68}Ir_{32}Mo_3$ catalysts with loadings as low as 0.25 mg Pt/cm^2 outperform conventional Pt/C with loadings of greater than 2 mg Pt/cm^2 (Lewinski et al. 2015).

High surface area carbons such as Vulcan and carbon nanotubes (CNTs) are frequently employed as alternative supports to carbon black. Core-shell concepts popularized for the fuel cell oxygen reduction reaction (ORR) (Brankovic et al. 2001) have recently shown success in electrolyzer HER (Ayers et al. 2016), though in one case the activity of a single platinum monolayer supported on low-cost tungsten carbides (WC and W_2C) was found to be comparable to that of Pt/C (Esposito et al. 2012). Also, single atom Pt catalysts are being explored for catalytic purposes and showing large potential (Jacoby 2016, Figure 16). Promising platinum-free alternatives for HER, such as transition metal dichalcogenides (Hinnemann et al. 2005), cobalt and nickel molecular catalysts (Pantani et al. 2007; Tsay and Yang 2016), and transition metal phosphides such as CoP (Popczum et al. 2014), to name a few, frequently are studied on metal foil electrodes or in half cells only, where direct comparison to Pt/C in a PEM MEA is not possible. Recent work using MoS_x, MoP|S or $[Mo_3S_{13}]^{2-}$ loaded onto carbon supports (Ng et al. 2015) has begun to bridge this gap.

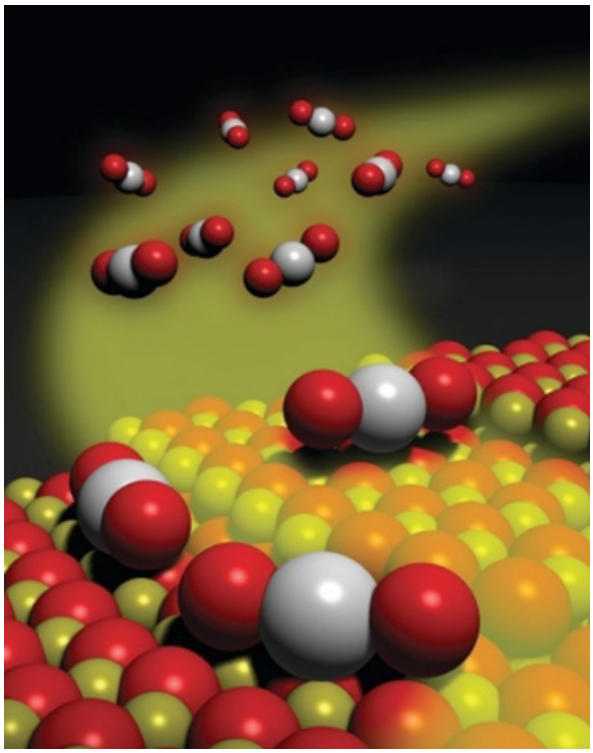


Figure 16. When exposed to high temperature in air, platinum desorbs from Pt nanocrystals as PtO_2 (grey and red), and can be trapped on CeO_2 (gold and red). Figure from Jacoby 2016; courtesy of Abhaya Datye (University of New Mexico); artist Cortland Lewis (Pacific Northwest National Laboratory).

The bulk of the cell overpotential (and thus greatest research challenge) comes from the anode (greater than 0.3 V at 1 A/cm^2 current density, cf. ~0.1 V for HER). State of the art anodes are made from unsupported IrO_x, which is typically characterized by large, agglomerated particles, low surface area (20–50 m^2/g), and poor catalyst utilization owing to the difficulties in manufacturing large-scale, uniform electrodes. Improved catalyst utilization through core-shell and alloying strategies similar to those described above for HER have resulted in some successes, though preparing finely divided IrO_x or its alloys remains an area of significant research (Ayers et al. 2016). The high surface area carbon supports used for HER catalysts cannot be used since they corrode at high potential. Transition metal oxide and carbide supports such as a suboxide or defective oxide TiO_x and TiC have been investigated (Ma et al. 2008), but are often not sufficiently conductive, especially at high potential where they fully oxidize to form non-conductive TiO_2. Wu and Scott (2011) have found some success supporting the more highly active OER RuO_2 catalyst with tin or antimony oxides. For both HER and OER in acidic environments, the real phenomena dictating how a support material modifies catalysis are poorly understood (Halck et al. 2014).

Recent research in the area of continuous operation of grid electricity has focused on:

- Developing durable, high performance, low-loaded anode electrocatalyst layers.
- Elucidating the degradation mechanisms and quantification of degradation rates including the effects of operating conditions.
- Understanding two phase flow (liquid and gaseous water) including mass transport limitations at the anode/porous transport layer (PTL) interface.

Alkaline Exchange Membrane electrolyzers. The relatively recent development of alkaline exchange membrane (AEM) electrolyzers has sought to capitalize on the positive attributes of both alkaline liquid electrolyte and PEM electrolysis systems. Like PEM electrolyzers, AEM cells conceivably should offer fast response times and efficient, high purity product formation suitable for variable power applications (owing to the ability to operate at differential pressure). In contrast to PEM electrolyzers that rely on a proton-conducting ionomer, an AEM electrolyzer ionomer membrane conducts hydroxide ions. AEM ionomers are typically comprised of quaternary ammonium, phosphonium, guanidinium, imidazole, and other cation-based polymers, and improving the ionomer hydroxide ion conductivity and durability is an active area of research. Ensuring good catalyst activity in conjunction with the membrane/ionomer material is key for any potential commercial viability.

The main advantage of AEM over PEM electrolyzers is the ability to use non-precious group metal HER and OER catalysts and nickel or stainless steel anode materials rather than titanium. Though NiMo alloys are currently the most active and durable alkaline HER catalysts, they still are not sufficient for a commercial AEM cell. For example, an ionomer-impregnated stainless steel mesh coated with a 40 mg/cm^2 loading of NiMo catalyst exhibited an HER overpotential of ~0.11 V in 1.0 M KOH solution at 400 mA/cm^2 and 40 °C (Xiao et al. 2012). Though IrO_x is the most active OER catalyst in either acid or base, much work has gone toward developing alternatives suitable for alkaline media. Transition metal oxides of the spinel or perovskite structure, such as Co_3O_4 that exhibit overpotentials of ~350 mV at a current density of 10 mA/cm^2 in 1.0 M KOH, have shown the most success (Esswein et al. 2009). A Ni foam ionomer-impregnated Ni-Fe cathode, which exhibited ~0.35 V overpotential at 400 mA/cm^2 in 1.0 M KOH solution at 40 °C, displayed even better OER performance (Xiao et al. 2012). Other catalysts, such as the recently developed ultrathin Ni-Fe layered double hydroxide (NiFe-LDH) nanoplates on mildly oxidized multiwalled CNTs (Gong et al. 2013), are difficult to compare directly to AEM electrolyzers, since the catalyst loading, catalyst morphology, interaction between catalyst and AEM ionomer, and mass transport challenges in ionomer-impregnated anodes are not present in model systems (Shen et al. 2016).

Recent research in the area of AEM electrolyzers has focused on:

- Discovering new ionomer membrane materials that achieve high hydroxide ion conductivity while remaining stable in high potential, high pH, and oxygenated environments.
- Understanding fundamental properties (e.g., conductivity, water uptake, swelling, and mechanical) of ionomer membrane in 3 states—as-prepared, during hot pressing/MEA fabrication, and under operation—over its range of exchanged state.

2.3.2 Variable Operation: Wind and Solar Electricity

Electrolyzers. As discussed in the previous section, PEM and AEM membrane-based electrolyzers have a more dynamic range for fluctuations in electrical current than alkaline liquid electrolyzers. Wind turbines and electrolyzers have already reached similar capacities for good load matching. A recent DOE workshop analyzed the current state of the art, and R&D needs for these electrolyzers and published the results in a 2016 report (DOE, Office of Energy Efficiency and Renewable Energy 2016). The workshop, sponsored by the Fuel Cell Technologies Office of the Office of Energy Efficiency and Renewable Energy (EERE), included many aspects of the systems and materials in addition to the need for non-platinum group metal catalysts.

Photoelectrochemical systems. As an alternative to electrolyzers, photoelectrochemical (PEC) systems that split water to generate H_2 consist of a semiconductor light absorber element with catalysts deposited on the cathode and anode sides forming an integrated unit (Ager et al. 2015; Xiang et al. 2016; Modestino et al. 2016; Haussener et al. 2012). The catalyst on the anode performs the OER producing gaseous oxygen, and HER on the cathode side generating hydrogen. The most efficient systems operate in aqueous electrolyte at or near pH 0 or pH 14. Ion-conducting membrane separators between the anode and cathode chambers to keep O_2 and H_2 from mixing are essential in the product gas stream because the explosive limit in O_2 is about 4% H_2 (Berger et al. 2014; Walczak et al. 2015). The catalysts used must be stable under operating conditions and have low overpotential for their chemistry (Figure 17). As noted in Section 2.3.1, while suitable catalysts exist for the HER, there is considerable room for improvement of water oxidation reaction catalysts, particularly those that operate in acid. A prospective lifecycle assessment of energy returned on energy invested has shown that efficiency and durability are key to the viability of this technology (Sathre et al. 2014). Target efficiencies set by DOE are 20% solar-to-hydrogen (STH) chemical energy in 2020, with an ultimate target of 25% and cost of $2.10 per kg. Demonstrated highest efficiencies are lower, in the range of 10%–15% (Ager et al. 2015; Verlage et al. 2015; Walczak et al. 2017), with a new record just established at 16.2% STH (Young et al. 2017). Lifetimes of 10 years or more are needed to reach sustainability targets (Sathre et al. 2014), however durability of up to a week under diurnal light cycling is the highest demonstrated (Walczak et al. 2017). The advantage of a fully integrated photoelectrochemical architecture is a potential for higher overall efficiency relative to electrolyzers driven by electrons supplied by the grid. Seitz et al. (2014) recently published a detailed analysis of the factors that affect performance as well as an architecture capable of 25% efficiency). At present, this technology is at low TRL and has not been commercialized; however, several corporate R&D laboratories (e.g., Panasonic) have programs for its development.

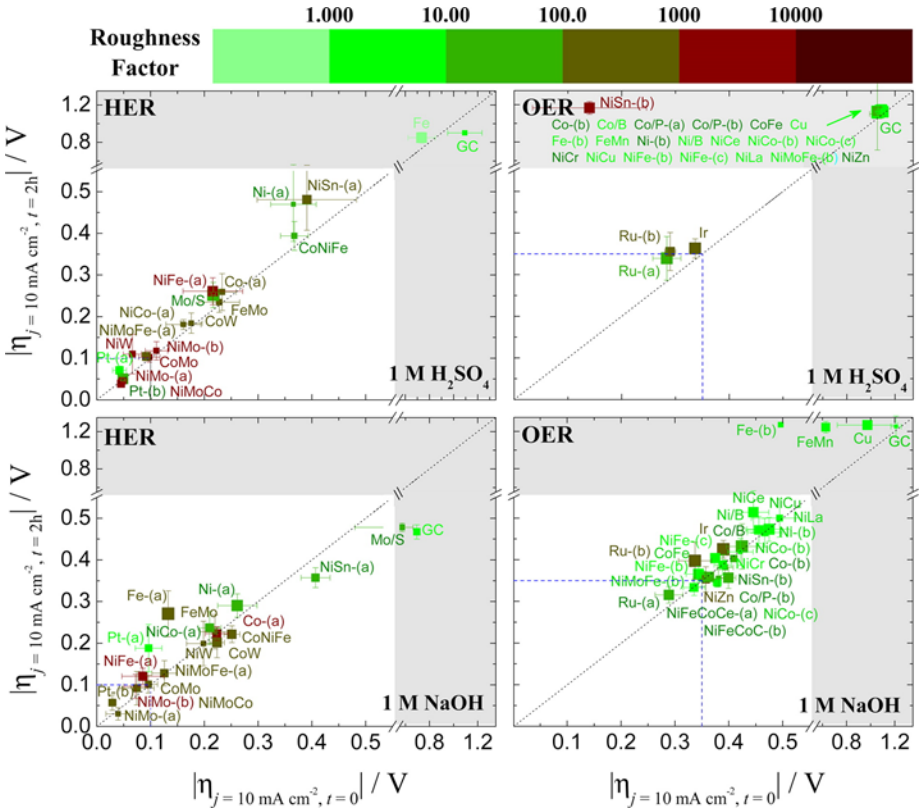


Figure 17. Overpotentials before and after two-hour continuous testing of HER and OER catalysts in aqueous base (pH 14) or acid (pH 0). Reprinted with permission from *Journal of the American Chemical Society*, Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices, McCrory et al. (2015). Copyright © 2015, American Chemical Society.

Recent research in the area of photoelectrochemical water splitting has focused on:

- Discovering stable, optically transparent catalysts that can be integrated with semiconductor photoanode materials without causing either component to lose function.
- Demonstrating catalytic photoelectrode-electrolyte anticorrosion strategies that enable long-term stability of the assembly in extreme pH while preserving or enhancing water splitting efficiency.
- Discovering OER catalysts that are stable and efficient in acidic solutions.

2.3.3 Downstream Uses for H_2 from Water Splitting

Hydrogen generated from either electrolyzer or PEC systems can target major industries such as petroleum refining, ammonia production, metals heat treating, brazing, glass processing, semiconductors, and potentially steel-making. This hydrogen could also service nascent industries such as fuel cells for stationary or mobile power, bio-oil upgrading, and metals refining. Hydrogen produced via SMR requires membrane or adsorption technologies to generate the high purities required for these technologies, increasing the cost of delivered hydrogen. International Organization for Standardization (ISO) 14687-2 and Society of Automotive Engineers (SAE) standard J2719 currently specify purity for fuel cell applications with 99.97% overall H_2 purity and allowable levels of key impurities (0.2 ppm CO and additional upper limits on sulfur compounds, formaldehyde, etc.) (Lipman 2011). Note that H_2 produced by low temperature photoelectrolytic processes can be ultrapure (with the only significant impurity being water), avoiding the costs of SMR separations. ISO 22734-1 and ISO 22734-2 standards also exist for electrolysis.

2.3.4 Grid Electricity Storage Applications

With the advent of abundant renewable electricity from intermittent sources, the use of electrolyzers to convert electrical energy into chemical energy has emerged as a potential complement to compressed air, batteries, and pumped hydroelectric for storage of power that cannot be placed on the grid. The energy density and transportability of chemicals makes this an attractive possibility. Technology development is actively underway

to generate H_2 from water electrolysis for this purpose. The hydrogen could be directly used for fuel cells or it could be used to synthesize a variety of more valuable chemicals. An international effort in the latter application is known as Power-to-Gas (Gotz et al. 2016), which most commonly uses CO_2 as a feedstock to make CH_4. When Power-to-Gas was first proposed, electricity was too costly for the process to be commercially viable, but the landscape has changed dramatically in the past 10 years. The full Power-to-Gas process chain is very flexible compared to conventional large-scale chemical synthesis technologies. It consists of CO_2 capture and purification, water electrolysis to produce H_2, and use of more conventional catalytic reactors to generate CH_4. The synthetic natural gas can then be injected into the gas distribution grid or used to synthesize other chemicals, such as dimethyl ether, methanol, or Fischer-Tropsch products. Major corporations and governments worldwide are actively studying or conducting pilot and demonstration projects for this technology.

Leveraging biological processes is another recent development in converting renewable energy electrons to fuels and chemicals. There have been several reports of hybrid artificial photosynthesis/biological conversion systems utilizing CO_2-fixing microorganisms (Nevin et al. 2011; Nichols et al. 2015; Schwander et al. 2016; Xiong et al. 2016). Near-term targets are C_1–C_5 small molecule chemical feedstocks (e.g., methanol, acetone, acetate, butyrate) via so-called biomanufacturing (Clomburg et al. 2017). For (photo)electrolysis producing hydrogen gas as the redox mediator, Liu et al. (2016) recently showed that *Ralstonia eutropha* synthesizes biomass and fuels or chemical products from low CO_2 concentrations. Though this process currently is rate-limited by biological conversion, transporting reducing equivalents to the organisms would eventually become rate limiting since, like CO_2, hydrogen gas has limited solubility in aqueous media. Matching the electron flux from a 1 A/cm^2 electrode surface and into the much slower biological processes is a significant challenge. A huge field exists in so-called microbial fuel cells where either a non-hydrogen redox mediator or direct electrical contact between an electrode and organism facilitate electron transfer (Logan et al. 2006; Wang et al. 2015). Catalytic concepts to efficiently generate a high concentration of stable redox mediator offers a potential way to store reducing equivalents for later biological conversion akin to a redox flow battery.

Recent research in the area of grid electricity storage has focused on:

- Discovering redox flow battery systems that offer low-cost and stable electrolytes and membrane separators that prevent crossover.
- Understanding bioenergetics to increase carbon, electron, and energy flux at an electrode/microbe interface.

2.4 REFERENCES

Ager III, J. W., Shaner, M., Walczak, K., Sharp, I. D., and Ardo, S. 2015. "Experimental Demonstrations of Spontaneous, Solar-driven Photoelectrochemical Water Splitting." *Energy and Environmental Science* 8: 2811-2824. doi: 10.1039/C5EE00457H.

Arai, T., Sato, S., and Morikawa, T. 2015. "A Monolithic Device for CO_2 Photoreduction to Generate Liquid Organic Substances in a Single-Compartment Reactor." *Energy and Environmental Science* 8: 1998–2002. doi: 10.1039/C5EE01314C.

Ayers, K. E., Renner, J. N., Danilovic, N., Wang, J. X., Zhang, Y., Maric, R., and Yu, R. H. 2016. "Pathways to Ultra-low Platinum Group Metal Catalyst Loading in Proton Exchange Membrane Electrolyzers." *Catalysis Today* 262: 121–132. doi: 10.1016/j.cattod.2015.10.019.

Berger, A. R., Segalman, A., and Newman, J. 2014. "Material Requirements for Membrane Separators in a Water-Splitting Photoelectrochemical Cell." *Energy and Environmental Science* 7: 1468–1476. doi: 10.1039/C3EE43807D.

Bloom, A., Townsend, A., Palchak, D., Novacheck, J., King, J., Barrows, C., Ibanez, E., O'Connell, M., Jordan, G., Roberts, B., Draxl, C., and Gruchalla, K. 2016. *Eastern Renewable Generation Integration Study.* NREL/TP-6A20-64472, Golden, Colorado: National Renewable Energy Laboratory. https://www.nrel.gov/docs/fy16osti/64472.pdf.

Brankovic, S. R., Wang, J. X., and Adžić, R. R. 2001. "Metal Monolayer Deposition by Replacement of Metal Adlayers on Electrode Surfaces." *Surface Science* 474 (1–3): L173–L179. doi: 10.1016/S0039-6028(00)01103-1.

Cardwell, D. 2017. "Tesla Gives the California Power Grid a Battery Boost." *New York Times*, January 30. https://www.nytimes.com/2017/01/30/business/energy-environment/battery-storage-tesla-california.html.

Carmo, M., Fritz, D. L., Mergel, J., and Stolten, D. 2013. "A Comprehensive Review on PEM Water Electrolysis." *International Journal of Hydrogen Energy* 38 (12): 4901¬4934. doi: 10.1016/j.ijhydene.2013.01.151.

Centi, G., Perathoner, S., Wine, G., and Gangeri, M. 2007. "Electrocatalytic Conversion of CO_2 to Long Carbon-chain Hydrocarbons." *Green Chemistry* 9: 671–678. doi: 10.1039/B615275A.

Chisholm, G., and Cronin, L. 2016. *Hydrogen from Water Electrolysis in Storing Energy.* Cambridge, MA: Elsevier. https://www.sciencedirect.com/science/article/pii/B9780128034408000166.

Clomburg, J. M., Crumbley, A. M., and Gonzalez, R. 2017. "Industrial Biomanufacturing: The Future of Chemical Production." *Science* 355 (6320). doi: 10.1126/science.aag0804.

Cook, R. L., Macduff, R. C., and Sammelis, A. F. 1990. "High-rate Gas-phase CO_2 Reduction to Ethylene and Methane Using Gas-diffusion Electrodes." *Journal of the Electrochemical Society*, 137: 607–608. http://jes.ecsdl.org/content/137/2/607.

Cook, T. R., Dogutan, D. K., Reece, S. Y., Surendranath, Y., Teets, T. S., and Nocera, D. G. 2010. "Solar Energy Supply and Storage for the Legacy and Nonlegacy Worlds." *Chemical Reviews* 110: 6474–6502. http://pubs.acs.org/doi/abs/10.1021/cr100246c.

Crew, B. 2016. "Costa Rica Has Been Running on 100% Renewable Energy for 2 Months Straight." *Science Alert*, September 7. https://www.sciencealert.com/costa-rica-has-been-running-on-100-renewable-energy-for-2-months-straight.

de Levie, R. 1999. "The Electrolysis of Water." *Journal of Electroanalytical Chemistry* 476: 92–93. doi: 10.1016/S0022-0728(99)00365-4.

Denholm, P., Clark, K., and O'Connell, M. 2016. On the Path to SunShot: Emerging Issues and Challenges in Integrating High Levels of Solar into the Electrical Generation and Transmission System. NREL/TP-6A20-65800. Golden, CO: National Renewable Energy Laboratory. https://www.nrel.gov/docs/fy16osti/65800.pdf.

Esposito, D. V., Hunt, S. T., Kimmel, Y. C., and Chen, J. G. 2012. "A New Class of Electrocatalysts for Hydrogen Production from Water Electrolysis: Metal Monolayers Supported on Low-Cost Transition Metal Carbides." *Journal of the American Chemical Society* 134: 3025–3033. doi: 10.1021/ja208656v.

Esswein, A. J., McMurdo, M. J., Ross, P. N., Bell, A. T., and Tilley, T. D. 2009. "Size-Dependent Activity of Co_3O_4 Nanoparticle Anodes for Alkaline Water Electrolysis." *The Journal of Physical Chemistry C* 113 (33): 15068–15072. doi: 10.1021/jp904022e.

GE Energy. 2010. *Western Wind and Solar Integration Study.* NREL/SR-550-47434. Prepared for the National Renewable Energy Laboratory. Golden, CO. https://www.nrel.gov/docs/fy10osti/47434.pdf.

Gong, M., Li, Y., Wang, H., Liang, Y., Wu, J. Z., Zhou, J., Wang, J., Regier, T., Wei, F., and Dai, H. 2013. "An Advanced Ni–Fe Layered Double Hydroxide Electrocatalyst for Water Oxidation." *Journal of the American Chemical Society* 135: 8452–8455. doi: 10.1021/ja4027715.

Gotz, M., Lefebvre, J., Mors, F., Koch, A. M., Graf, F., Bajohr, S., Reimert, R., and Kolb, T. 2016. "Renewable Power-to-Gas: A Technological and Economic Review." *Renewable Energy* 85: 1371–1390. doi: 10.1016/j.renene.2015.07.066.

Halck, N. B., Petrykin, V., Krtil, P., Rossmeisl, J. 2014. "Beyond the Volcano Limitations in Electrocatalysis - Oxygen Evolution Reaction." *Physical Chemistry Chemical Physics* 16: 13682–13688. doi: 10.1039/C4CP00571F.

Haussener, S., Xiang, C. X., Spurgeon, J. M., Ardo, S., Lewis, N. S., and Weber, A. Z. 2012. "Modeling, Simulation, and Design Criteria for Photoelectrochemical Water-Splitting Systems." *Energy and Environmental Science* 5: 9922–9935. Doi 10.1039/C2EE23187E.

Hinnemann, B., Moses, P. G., Bonde, J., Jørgensen, K. P., Nielsen, J. H., Horch, S., Chorkendorff, I., and Nørskov, J. K. 2005 "Biomimetic Hydrogen Evolution: MoS_2 Nanoparticles as Catalyst for Hydrogen Evolution." *Journal of the American Chemical Society* 127: 5308–5309. doi: 10.1021/ja0504690.

Hori, Y., Kukuchi, K., and Suzuki, S. 1985. "Production of CO and CH_4 in Electrochemical Reduction of CO_2 at Metal Electrodes in Aqueous Hydrogencarbonate Solution." *Chemistry Letters* 14: 1695–1698. doi: 10.1246/cl.1985.1695.

Hori, Y., Wakebe, H., Tsukamoto, T., and Koga, O. 1994. "Electrocatalytic Process of CO Selectivity in Electrochemical Reduction of CO_2 at Metal Electrodes in Aqueous Media." *Electrochimica Acta* 39: 1833–1839. doi: 10.1016/0013-4686(94)85172-7.

Jacoby, M. 2016. "High Temperatures Turn Nanoparticles into Single-atom Catalysts." *Chemical and Engineering News* 94(28): 6. https://cen.acs.org/articles/94/i28/High-temperatures-turn-nanoparticles-single.html

Jhong, H. R., Ma, S. C., and Kenis, P. A. 2013. "Electrochemical Conversion of CO_2 to Useful Chemicals: Current Status, Remaining Challenges, and Future Opportunities." *Current Opinions in Chemical Engineering* 2: 191–199. doi: 10.1016/j.coche.2013.03.005.

Kreuter, W., and Hofmann, H. 1998. "Electrolysis: The Important Energy Transformer in a World of Sustainable Energy." *International Journal of Hydrogen Energy* 23: 661–666. doi: 10.1016/S0360-3199(97)00109-2.

Kuhl, K. P., Cave, E. R., Abram, D. N., and Jaramillo, T. F. 2012. "New insights into the electrochemical reduction of carbon dioxide on metallic copper surfaces." *Energy and Environmental Science* 5: 7050–7059. doi: 10.1039/C2EE21234J.

Kumar, B., Llorente, M., Froehlich, J., Dang, T., Sathrum, A., and Kubiak, C. P. 2012. "Photochemical and Photoelectrochemical Reduction of CO_2." *Annual Review of Physical Chemistry*, 63: 541–569. doi: 10.1146/annurev-physchem-032511-143759.

Lewinski, K. A., van der Vliet, D., and Luopa, S. M. 2015. NSTF "Advances for PEM Electrolysis – The Effect of Alloying on Activity of NSTF Electrolyzer Catalysts and Performance of NSTF Based PEM Electrolyzers." *ECS Transactions* 69: 893–917. doi: 10.1149/06917.0893ecst.

Lipman, T. 2011. An Overview of Hydrogen Production and Storage Systems with Renewable Hydrogen Case Studies. Clean Energy States Alliance report.

Liu, C., Colón, B. C., Ziesack, M., Silver, P. A., and Nocera, D. G. 2016. "Water Splitting–Biosynthetic System with CO_2 Reduction Efficiencies Exceeding Photosynthesis." *Science* 352 (6290): 1210–1213. doi: 10.1126/science.aaf5039.

LLNL Flow Charts. 2015. "Estimated U.S. Energy Consumption in 2015." https://flowcharts.llnl.gov/content/assets/images/energy/us/Energy_US_2015.png.

Logan, B. E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., and Rabaey, K. 2006. "Microbial Fuel Cells: Methodology and Technology." *Environmental Science and Technology* 40: 5181–5192. doi: 10.1021/es0605016.

Lopez, A., Roberts, B., Heimiller, D., Blair, N., and Porro, G. 2012. *U.S. Renewable Energy Technical Potentials: A GIS-Based Analysis*. NREL/TP-6A20-51946. Golden, CO: National Renewable Energy Laboratory.

Ma, L., Sui, S., and Zhai, Y. 2008. "Preparation and Characterization of Ir/TiC Catalyst for Oxygen Evolution." *Journal of Power Sources* 177: 470–477. doi: 10.1016/j.jpowsour.2007.11.106.

Martin, C. 2017. "For the First Time, Wind on the Plains Supplied More Than Half Region's Power." *Bloomberg News*, February 13.

McCrory, C. C. L., Jung, S., Ferrer, I. M., Chatman, S. M., Peters, J. C., and Jaramillo, T. F. 2015. "Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices." *Journal of the American Chemical Society* 137: 4347–4357. doi: 10.1021/ja510442p.

Miles, M. H., and Thomason, M. A. 1976. "Periodic Variations of Overvoltages for Water Electrolysis in Acid Solutions from Cyclic Voltammetric Studies." *Journal of the Electrochemical Society* 123: 1459-–1461. doi: 10.1149/1.2132619.

Modestino, M. A., Hashemi, S. M. H., and Haussener, S. 2016. "Mass Transport Aspects of Electrochemical Solar-hydrogen Generation." *Energy and Environmental Science* 9: 1533–1551. doi: 10.1039/C5EE03698D.

Nevin, K. P., Hensley, S. A., Franks, A. E., Summers, Z. M., Ou, J., Woodard, T. L., Snoeyenbos-West, O. L., and Lovley, D. R. 2011. "Electrosynthesis of Organic Compounds from Carbon Dioxide Is Catalyzed by a Diversity of Acetogenic Microorganisms." *Applied and Environmental Microbiology* 77: 2882–2886. doi: 10.1128/AEM.02642-10.

Ng, J. W. D., Hellstern, T. R., Kibsgaard, J., Hinckley, A. C., Benck, J. D., and Jaramillo, T. F. 2015. "Polymer Electrolyte Membrane Electrolyzers Utilizing Non-precious Mo-based Hydrogen Evolution Catalysts." *ChemSusChem* 8: 3512–3519. doi 10.1002/cssc.201500334.

Nichols, E. M., Gallagher, J. J., Liu, C., Su, Y., Resasco, J., Yu, Y., Sun, Y., Yang, P., Chang, M. C. Y., and Chang, C. J. 2015. "Hybrid Bioinorganic Approach to Solar-to-Chemical Conversion." *Proceedings of the National Academy of Sciences* 112: 11461–11466. doi: 10.1073/pnas.1508075112.

Pantani, O., Anxolabéhère-Mallart, E., Aukauloo, A., and Millet, P. 2007. "Electroactivity of Cobalt and Nickel Glyoximes with Regard to the Electro-Reduction of Protons into Molecular Hydrogen in Acidic Media." *Electrochemistry Communications* 9: 54–58. Doi: 10.1016/j.elecom.2006.08.036.

Pivovar, B. H. 2016. "H2@SCALE: Deeply Decarbonizing our Energy System." https://www.energy.gov/sites/prod/files/2016/07/f33/fcto_webinarslides_h2_at_scale_072816.pdf.

Popczun, E. J., Read, C. G., Roske, C. W., Lewis, N. S., and Schaak, R. E. 2014. "Highly Active Electrocatalysis of the Hydrogen Evolution Reaction by Cobalt Phosphide Nanoparticles." *Angewandte Chemie International Edition* 53: 5427–5430. doi: 10.1002/anie.201402646.

Qiao, J. L., Liu, Y. Y., Hong, F., and Zhang, J. J. 2014. "A Review of Catalysts for the Electroreduction of Carbon Dioxide to Produce Low-carbon Fuels." *Chemical Society Review* 43: 631–675. doi: 10.1039/C3CS60323G.

Quadrelli, E. A., Centi, G., Duplan, J. L., and Perathoner, S. 2011. "Carbon Dioxide Recycling: Emerging Large-Scale Technologies with Industrial Potential." *ChemSusChem* 4: 1194–1215. doi: 10.1002/cssc.201100473.

Sathre, R., Scown, C. D., Morrow, W. R., Stevens, J. C., Sharp, I. D., Ager III, J. W., Walczak, K., Houle, F. A., and Greenblatt, J. B. 2014. "Life-cycle Net Energy Assessment of Large-Scale Hydrogen Production via Photo-Electrochemical Water Splitting." *Energy and Environmental Science* 7: 3264-3278. doi: 10.1039/C4EE01019A.

Schwander, T., von Borzyskowski, L., Burgener, S., Cortina, N. S., and Erb, T. J. 2016. "A Synthetic Pathway for the Fixation of Carbon Dioxide in Vitro." *Science* 354(6314): 900–904. doi: 10.1126/science.aah5237.

Seitz, L. C., Chen, Z. B., Forman, A. J., Pinaud, B. A., Benck, J. D., and Jaramillo, T. F. 2014. "Modeling Practical Performance Limits of Photoelectrochemical Water Splitting Based on the Current State of Materials Research." *ChemSusChem* 7: 1372–1385. doi: 10.1002/cssc.201301030.

Shen, P. K., Wang, C.-Y., Jian, S. P., Sun, X., and Zhang, J. (Editors). 2016. *Electrochemical Energy: Advanced Materials and Technologies*. Boca Raton, Florida: CRC Press.

Shibata, H., Moulijn, J. A., and Mul, G. 2008. "Enabling Electrocatalytic Fischer-Tropsch Synthesis from Carbon Dioxide over Copper-based Electrodes." *Catalysis Letters* 123: 186–192. doi: 10.1007/s10562-008-9488-3.

Singh, M. R., Clark, E. L., and Bell, A. T. 2015. "Effects of Electrolyte, Catalyst, and Membrane Composition and Operating Conditions on the Performance of Solar-Driven Electrochemical Reduction of Carbon Dioxide." *Physical Chemistry Chemical Physics* 17: 18924–18936. doi: 10.1039/C5CP03283K.

Tatin, A., Comminges, C., Kokoh, B., Costentin, C., Robert, M., and Savéant, J-M. 2016. "Efficient Electrolyzer for CO_2 Splitting in Neutral Water Using Earth-abundant Materials." *Proceedings of the National Academy of Sciences* 113: 5526–5529. doi: 10.1073/pnas/1604628113.

Tsay, C., and Yang, J. Y. 2016. "Electrocatalytic Hydrogen Evolution under Acidic Aqueous Conditions and Mechanistic Studies of a Highly Stable Molecular Catalyst." *Journal of the American Chemical Society* 138: 14174–14177. doi: 10.1021/jacs.6b05851.

U.S. Department of Energy, Hydrogen and Fuel Cells Program. 2014. "Hydrogen Production Cost from PEM Electrolysis." DOE Hydrogen and Fuel Cells Program Record #14004, July. https://www.hydrogen.energy.gov/pdfs/14004_h2_production_cost_pem_electrolysis.pdf.

U.S. Department of Energy (DOE), Office of Basic Energy Sciences. 2007. "Basic Research Needs: Catalysis for Energy." http://www.sc.doe.gov/bes/reports/list.html.

U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy. 2016. *Advanced Water Splitting Materials Workshop*. Fuel Cell Technologies Office. https://energy.gov/sites/prod/files/2016/12/f34/fcto_awsm_workshop_report_2016.pdf.

Verlage, E., S. Hu, R. Liu, R. J. R. Jones, K. Sun, C. Xiang, N. Lewis, N., and J. H. A. Atwater. 2015. "A Monolithically Integrated, Intrinsically Safe, 10% Efficient, Solar-Driven Water-Splitting System Based on Active, Stable Earth-Abundant Electrocatalysts in Conjunction with Tandem III-V Light Absorbers Protected by Amorphous TiO_2 Films." *Energy and Environmental Science* 8: 3166–3172. 10.1039/C5EE01786F.

Walczak, K., Chen, Y. K., Karp, C., Beeman, J. W., Shaner, M., Spurgeon, J., Sharp, I. D., Amashukeli, X., West, W., Jin, J., Lewis, N. S., and Xiang, C. X. 2015. "Modeling, Simulation, and Fabrication of a Fully Integrated, Acid-stable, Scalable Solar-Driven Water-Splitting System." *ChemSusChem* 8: 544–551. doi: 10.1002/cssc.201402896.

Walczak, K. A., Segev, G., Larson, D. M., Beeman, J. W., Houle, F. A., and Sharp, I. D. 2017. "Hybrid Composite Coatings for Durable and Efficient Solar Hydrogen Generation under Diverse Operating Conditions." *Advanced Energy Materials* 7: 1602791. doi: 10.1002/aenm.201602791.

Wang, H., Park, J.-D., and Ren, Z. J. 2015. "Practical Energy Harvesting for Microbial Fuel Cells: A Review." *Environmental Science and Technology* 49: 3267–3277. doi: 10.1021/es5047765.

Woodard, C. 2016. "America's First All-renewable-Energy City." *Politico*, November 17.

Wu, X., and Scott, K. 2011. "RuO_2 Supported on Sb-doped SnO_2 Nanoparticles for Polymer Electrolyte Membrane Water Electrolysers." I*nternational Journal of Hydrogen Energy* 36: 5806–5810. doi: 10.1016/j.ijhydene.2010.10.098.

Xiang, C. X., Weber, A. Z., Ardo, S., Berger, A., Chen, Y. K., Coridan, R., Fountaine, K. T., Haussener, S., Hu, S., Liu, R., Lewis, N. S., Modestino, M. A., Shaner, M. M., Singh, M. R., Stevens, J. C., Sun, K., and Walczak, K. 2016. "Modeling, Simulation, and Implementation of Solar-driven Water-splitting Devices." *Angewandte Chemie International Edition* 55: 12974–12988. doi: 10.1002/anie.201510463.

Xiao, L., Zhang, S., Pan, J., Yang, C., He, M., Zhuang, L., and Lu, J. 2012. "First Implementation of Alkaline Polymer Electrolyte Water Electrolysis Working Only with Pure Water." *Energy and Environmental Science* 5: 7869–7871. doi: 10.1039/C2EE22146B.

Xiong, W., Lin, P. P., Magnusson, L., Warner, L., Liao, J. C., Maness, P.-C., and Chou, K. J. 2016. "CO_2-fixing One-carbon Metabolism in a Cellulose-degrading Bacterium Clostridium Thermocellum." *Proceedings of the National Academy of Sciences* 113: 13180–13185. doi: 10.1073/pnas.1605482113.

Young, J. L., Steiner, M. A., Döscher, H., France, R. M., Turner, J. A., and Deutsch, T. G. 2017. "Direct Solar-to-Hydrogen Conversion via Inverted Metamorphic Multi-junction Semiconductor Architectures." *Nature Energy* 2, 17028. doi: 10.1038/nenergy.2017.28.

Zeng, H. B., Du, X. W., Singh, S. C., Kulinich, S. A., Yang, S. K., He, J. P., and Cai, W. P. 2012. "Nanomaterials via Laser Ablation/Irradiation in Liquid: A Review." *Advanced Functional Materials* 22: 1333–1353. doi: 10.1002/adfm.201102295.

Zeng, K., and Zhang, D. 2010. "Recent Progress in Alkaline Water Electrolysis for Hydrogen Production and Applications." *Progress in Energy and Combustion Science* 36: 307–326. doi: 10.1016/j.pecs.2009.11.002.

Zhou, X. H., Liu, R., Sun, K., Chen, Y. K., Verlage, E., Francis, S. A., Lewis, N. S., and Xiang, C. X. 2016. "Solar-Driven Reduction of 1 atm of CO_2 to Formate at 10% Energy-conversion Efficiency by Use of a TiO_2-protected III-V Tandem Photoanode in Conjunction with a Bipolar Membrane and a Pd/C Cathode." *ACS Energy Letters* 1: 764–770. doi: 10.1021/acsenergylett.6b00317.

Topic 3: Advanced Chemical Conversion Approaches

Topic 3 focuses on catalysis research associated with emerging and under-utilized manufacturing and generation approaches such as distributed and/or low-temperature chemical manufacturing and fuel generation, integrated catalytic processes, and producing/utilizing hydrogen at scale. These spaces have tremendous opportunities for innovation. Petroleum refining is the quintessential example of the long-standing tenet that bigger production plants are more economical. There is renewed interest, however, in considering options for distributed and smaller-scale production of chemicals driven by advances in manufacturing approaches, the need for production flexibility, and interest in utilizing distributed resources (e.g., that are uneconomical to transport to centralized processing).

3.1 MODULAR PROCESSES: AN INTRODUCTION TO MODELING AND ECONOMIES OF SCALE

A new paradigm is emerging for the industrial production and processing of chemicals—one that involves modular processes and reactor designs to convert feedstocks. Before discussing the industrial state of the art, it is important to define what is meant by modular processes and their benefits, economic and otherwise. Modular chemical processes are designed to take advantage of cost reductions through mass production of units rather than one-of-a-kind construction of today's large chemical production plants. This is the difference between so-called number up versus scaling up to reduce costs. For the chemical industry, numbering up is the equivalent of the mass production of cars started by Henry Ford. Ford worked to keep his designs simple and easy to manufacture (Ford 2015). By doing so, car ownership became possible for many people.

Conversion of feedstocks that are non-economical to transport to a centralized facility (i.e., some biomass, natural gas from small wells, etc.) are well-positioned for distributed processing and are an example of an application that could benefit from the economies of scaling a number of small plants vs. a single centralized facility, like a refinery. Interest is increasing in distributed manufacturing of fuels and chemicals from the feedstocks mentioned later in this section and in Topic 1. Converting these feedstocks at the sources of production would reduce the need to dispose of currently wasted feedstocks, reduce transportation costs, provide an opportunity to meet fuel needs in remote areas locally, and yield economic benefits from numbering up, and reduce investment risk by lowering capital costs needed per individual unit. The number of companies with sufficient assets to design, permit, and build large refineries, for example, with capital costs exceeding $5 billion is very limited. We already see distributed manufacturing of dangerous chemicals at point-of-use (e.g., sodium cyanide, hydrogen peroxide, and fluorine) to manage safety concerns of their transportation by truck or other means. Small-scale chemical production could benefit point-of-use needs that are irregular including disaster recovery operations.

In modular manufacturing, a necessary component of modular chemical processing, units are produced offsite in controlled environments and built with standardized connections to join the modules, enabling simple assembly onsite. Contrasted with traditional, on-site construction of the facility, the process gains efficiency by using highly trained labor experienced in the construction of modular units, eliminating the need to find such skilled labor at the plant construction site. Other advantages include faster startup because companies can work to obtain permits while the plant components are being built elsewhere; units can be designed to be tested in the controlled environment where they are built, and then readied for transportation to the prepared, permanent site where they will be assembled. Although construction of a modular manufacturing facility to fabricate chemical reactors, separation units, and other components will incur a substantial capital cost (compare to around $1 billion for an auto plant), improvements in manufacturing processes and unit operation and increases in knowledge can be incorporated into future versions of the modular units. The car analogy can be used to compare improvements from one model (year) to the next.

Modular manufacturing methods, modular design principles, and economies of mass production enable investors to reduce risk and gain benefits from offsite manufacturing of chemical production plants. Other advantages of modular processing include the ability to take advantage of technologies previously shelved because they do not scale up well. In particular, this may speed the adoption of new electrocatalytic, membrane, and other intensified catalytic processes. Furthermore, the iterative model improvements possible with smaller systems may enable new catalysts to be adopted by changing reactor or operating conditions from one model to the next version. In this way, new catalysts can be commercialized more economically than retrofit of a large-scale plant. Applying this new paradigm to small scale chemical production has the added benefit of the ability to produce fuels and other chemicals from distributed feedstocks that are difficult or expensive to transport.

The modular manufacturing approach need not apply only to smaller scale processing systems, but can be used to add components to existing larger facilities; numbering up is not required to provide economic gains. In some cases, using modular manufacturing methods alone provides sufficient cost benefits that result in one-offs costing less than stick-built systems.

Modular process design is not limited to portable, small scale units the size of a shipping container, for example. Innovation is possible by applying a plug-and-play approach to manufacturing where by many units can be bolted together conceptually (like putting together Legos®). Catalysis units, separations units, and so forth can be designed to be assembled to suit different needs. They can be pulled apart and other units added and rapidly reassembled (compared to stick built-plants) as needs change. The modular approach demands standardization to be a critical aspect of planning how units link together. Like with Ford, simplicity and robustness are key.

Many examples of modular reactor and unit approaches are under development and deployment. One instance is repurposing the large investment in automobile and other engines in the form of engine reformers (Lim et al. 2016; Bromberg et al. 2014) for GTL at distributed shale gas sites. In other examples, such as SMR reactors, additional process intensification is employed. The goals of this approach combine reduction of operating costs, provide for distributed production, reduce temperatures and pressures of processes, improve safety, and decrease energy costs, including for catalytic processes and separations. Finally, to keep operating and labor costs down for a large number of distributed sites, remote sensing and operation of the units need to be employed; this subject area is beyond the scope of this document.

Economies of size have been so important in the past because, from a capital vantage point, capital costs for plants scale by the so-called rule of six-tenths (first mentioned in Chemical Engineering in 1947, Williams). Generally speaking, volumetric processes tend to follow the rule that bigger is better. In petroleum refining, for example, taking advantage of the economies of size is very beneficial. Processes are based on diameter scale much closer to one, at which point the advantages of scale no longer exist for costs (Smith 2016). Additionally, processes such as photo and electrocatalytic methods have not been sufficiently explored because of scale-up cost concerns. New approaches to chemical processing that have been previously discarded can be considered (or reconsidered) in light of advances in modular manufacturing.

3D printing for process intensification. Many manufacturing sectors have seen significant growth in application of 3D printing, also known as additive manufacturing, and though the ability to 3D print chemical reactors and catalysts offers great potential, the technology is still in its infancy in the chemical industry, where the focus has mostly been on developing new compounds for the 3D printing process (Guertzgen 2016). Only recently have reports appeared describing 3D printing applications for manufacture of chemical reactors and chemicals.

Efforts for 3D printing of chemical reactors have mainly concentrated on producing small-scale continuous flow microreactors that manufacture various organic compounds traditionally produced in batch reactors. Gutmann and co-workers used 3D printing to produce a stainless steel microflow reactor for the continuous difluoromethylation using fluoroform (Gutmann et al. 2017). Chemtrix markets 3D printed flow reactors for a wide range of high pressure and high temperature applications for both process development and scale-up (Chemtrix 2018). Researchers at IFP Energies nouvelles (IFPEN) used 3D printing to produce a stirred tank reactor for producing clean fuels. The IFPEN design uses a unique internal geometry that could not be produced by traditional manufacturing methods to optimize the reaction between the gas and liquid phases (IFPEN 2016). A team from Air Liquide was awarded the European Federation of Chemical Engineering (EFCE) 2017 Process Intensification Award for Industrial Innovation for developing a 3D printed milli-structured heat exchanger reactor

for steam reforming of natural gas that significantly increases the overall efficiency of producing hydrogen by reusing the heat that normally produces excess steam (Duckett 2017).

Manzano and co-workers have expanded applications in catalysts by using 3D printing to produce architectures containing carboxylic acid, amine, and copper carboxylate functionalities that were catalytically-active for the Mannich, aldol, and Huisgen cycloaddition reactions, respectively (Manzano et al. 2017). Diáz-Marta and co-workers used 3D printing to produce palladium and copper silica-supported monolithic catalysts for performing copper-mediated alkyne-azide cycloaddition and palladium-catalyzed cross-coupling reactions (Diáz-Marta 2018).

While past experience has led to manufacturing models of bigger is better, the advent of modern modular manufacturing methods combined with improved sensors and controls, opportunities in additive manufacturing, accelerated high performance computing, and the potential for additional advances in catalysts and separations are leading to a confluence that makes this new approach to manufacturing exceptionally attractive. The next sections contain salient examples where this approach of modular processing is being integrated into commercial settings.

3.1.1 Fischer-Tropsch: Large-scale vs. Small-scale GTL and Velocys vs. "Ultra Scale" (PEARL)

GTL is a process for converting natural gas or other gaseous hydrocarbons into long chained hydrocarbons, typically in the range of gasoline to diesel. Most GTL processes are based on first converting the natural gas to syngas, which is then converted to the long chain hydrocarbons using the Fischer-Tropsch process in slurry or multi-tubular fixed-bed reactors, both well-established technologies (Urban 2016).

Large chemical plants, such as GTL, benefit from economy of scale, where the capital cost per unit of production decreases with increasing size of the plant. Large-scale plants reduce overhead, increase efficiency, and reduce personnel cost by pushing the plant design to the physical limits in size, leading to an overall cost reduction per unit of product (Gupta 2017). Shell's Pearl GTL plant located near Doha, Qatar, is the world's largest chemical plant built at a cost of $18–19 billion. The plant consists of more than 2,300 pieces of equipment with 3,500 control loops, 50,000 tons of piping, 30,000 tons of steel, and 200,000 m^3 of concrete covering nearly one square mile (Hoek 2006). Pearl has the world's largest industrial waste water treatment plant, the world's largest air separation units for producing oxygen, and the largest steam generation capacity of any hydrocarbon processing plant (including petroleum refineries) in the world. Based on Shell's proprietary Shell Middle Distillate Synthesis (SMDS) process, the plant is capable of processing up to 1.6 billion cubic feet of natural gas per day from 22 offshore wells to produce 140,000 barrels per day (bpd) of products ranging from gasoil, kerosene, and base oil to naphtha and normal paraffins; and 120,000 bpd of dry natural gas and ethane. The plant consists of 18 gasifiers and 24 fixed bed, multitubular FT reactors. The FT reactors contain collectively 29,000 tubes filled with Shell's second generation cobalt FT synthesis catalyst with a combined surface area of almost 18 times the size of Qatar (Shell Qatar 2017; Shell Global 2017).

Unlike coal and oil, which are easy and cost-effective to transport, natural gas is difficult and expensive to transport. Only about 5% of the world's conventional stranded gas fields are sufficiently large enough (with reserves of more than one trillion cubic feet [tcf]), to make a large-scale GTL, with a typical production level of 30,000 bpd or greater, economically viable. In contrast, up to 50% of the stranded gas fields (with reserves ranging from 0.1 to 1 tcf), could be monetized using small-scale GTL that produces from 100 to 15,000 bpd (Gas Processing 2017; Taboada 2015).

Two key deficiencies of the large GTL plants that must be avoided in smaller-scale GTL are the large surface area required for heat exchange and the low cobalt loading of the catalyst (Urban 2016). Because the Fischer-Tropsch reaction is highly exothermic and the selectivity to the desired higher hydrocarbon products is favored by lower temperatures, the FT reactor is densely filled with stainless-steel tubing to provide the heat exchange necessary to maintain the optimal reaction temperature. Catalysts with low cobalt loadings are used to assure thermal stability of the catalyst bed that fills the tubes, and the cobalt loading is restricted to about 10% of the overall catalyst weight because of intrapellet diffusion limitations. Both of these factors contribute to the high weight of fixed-bed and slurry reactors and must be addressed in the design of small-scale GTL plants.

To address the issues associated with the use of slurry or fixed-bed reactors, microchannel reactors, which intensify the heat transfer, reduce the reactor size per unit of product produced, and improve the reactor stability at smaller production rates (Urban 2016), have received considerable interest by companies who build small-scale GTL plants. Velocys employed microchannel reactor designs in ENVIA Energy's Oklahoma City plant (Figure 18) (Voegele 2017). Key technologies that enable Velocys to build these small-scale GTL plants are its FT microchannel reactor design and its highly active catalyst (LeViness et al. 2014). The Velocys microchannel FT reactor contains thousands of thin process channels filled with its proprietary FT catalyst interleaved with coolant channels containing water. The diameters of FT reactor process channels are in the range 0.1–10 mm compared to 25–40 mm in conventional FT reactors (Velocys 2017a). These microchannels are able to dissipate the heat produced by the highly-exothermic FT reaction significantly faster than conventional reactors. Process economics require that the catalyst exhibit a CO conversion of >90% with >80% selectivity to C_5+ liquids in a single pass reactor system without recycle (LeViness et al. 2014). Conventional FT catalysts cannot operate at >90% conversion in a single pass due to unfavorable reaction kinetics and the high partial pressure of water generated. Key to Velocys catalyst technology is not the composition but the synthetic method for producing the catalyst (Velocys 2017b). Velocys' organic matrix combustion (OMX) catalyst synthesis method produces catalysts with higher metal loadings than conventional FT catalysts with nm-size crystallites with terraced surfaces that enhance both catalyst activity and stability.

Another key to the cost-competitiveness of small-scale GTL plants is that their design and construction is based on "economies of mass manufacturing," that is, the production of large numbers of identical short-lived units, which reduces cost by improving accuracy and response by pushing the limits of automation and coordination (Gupta 2017). Small-scale GTL plants are constructed using modular components with about 70% of the construction completed before reaching the plant site, which significantly reduces the on-site construction cost (Taboada 2015).

Figure 18. ENVIA's gas-to-liquids (GTL) plant in Oklahoma City, OK. From Voegele (2017). Photo courtesy of Velocys.

Recent research in the area of large-scale vs. small-scale Fischer-Tropsch has focused on:

- Improving the single-pass conversion of Fischer-Tropsch catalysts with high selectivity towards heavy hydrocarbons.
- Improving catalyst performance at low syngas partial pressure.
- Developing catalysts that can be regenerated easily and reduced using syngas instead of pure hydrogen.

3.1.2 Bioprocessing: Batch

Bioprocessing uses living cellular systems (yeast, filamentous fungi, bacteria, and algae) or cell products (enzymes) to produce chemical products of value. Living cellular systems manage mass and energy balance in which energy released in one reaction is used in another reaction (e.g., fermentation) (Cortassa 2002). Conversely, enzymes, may also be used outside of cells as catalysts for specific transformations. Bioprocesses may be combined with catalytic processes to increase the number of chemicals and fuels of industrial interest (Werpy and Petersen 2004).

Industrial products of bioprocessing in cellular systems include alcohols (ethanol, isobutanol); organic acid derivatives (lactate, succinate, citric acid); fatty acids, polyketides (complex organic compounds); and isoprenoids (isoprene, farnesene) (Erickson et al. 2012).

Fermentation reactors are commonly run in batch and semi-batch reactor systems (Liu 2013). In semi-batch, either the reactant addition or product removal is done continuously. For sugar fermentation, microbes and medium are added to the stirred tank while product CO_2 is continuously removed. If the fermentation product has a high vapor pressure, such as isoprene, it may be continuously removed in a gas purge stream. Fully continuous reactors are also seeing use, at least at demonstration scales. One example is gas fermentation, where CO/H_2 are continuously fed into the reactor and alcohol products are continuously removed. Membranes are commonly used in continuous reactors.

At industrial scales, a number of reactor types may be used, including stirred tank; air-lift fermenters in which stirring is done by fluid flow; fluidized bed bioreactors used in three phase solid-liquid-gas systems; packed bed with biofilms (used in waste water treatment); and bubble column, in which a gas (air) is introduced at the base.

Non-cellular enzymatic reactions are performed at industrial scales. Two common examples include the use of lipases to break down starch to glucose and the use of isomerase for the isomerization of glucose to fructose. Other enzymatic reactions are utilized in detergents, textiles, pulp and paper, and animal feed industries (Aehle 2007). Immobilizing enzymes, which eases separations and improves thermal stability of the catalyst, is used in the production of fructose (Wu et al. 2013).

Coupling fermentation bioprocesses with chemical catalysis is used to produce chemical products and fuels from common building blocks. Two examples that have been demonstrated at large industrial scale use alcohols, such as ethanol or isobutanol as the building block. Alcohols are catalytically converted to high energy, dense fuels used in aviation (Brooks et al. 2016). The process includes dehydration, oligomerization, fractionation, and hydrogenation. Alcohols are also transformed to polymer intermediates, such as terephthalic acid, which are not available through fermentation via dimerization/oligomerization, cyclization, and aromatization (Collias et al. 2014).

3.2 LOW-TEMPERATURE AND LOW-PRESSURE CHEMICAL MANUFACTURING AND FUELS: AMMONIA SYNTHESIS

Ammonia synthesis (Boudart 1994; Schlögl 1991; Tamaru 1991) from the constituent elements is a mature, well optimized industrial process whose development has served to introduce important precepts in thermodynamics, catalysis, and process safety.

Ammonia feedstocks include natural gas, oil, naptha, or coal and provide both hydrogen and process heat (DOE, Advanced Manufacturing Office 2014). Natural gas has become a preferred feedstock because the process has the highest hydrogen to carbon ratio, leading to lower energy consumption and lower greenhouse gas emissions (U.S. EPA 2017). Natural gas accounts for nearly 100% of U.S. and 77% of world ammonia production (International Energy Agency 2007, 83). Of the 18 largest volume chemicals produced worldwide, ammonia is number one in both total energy use and total GHG emissions based on production volume, largely due to the production of hydrogen by SMR (International Energy Agency 2013). Hydrogen production by SMR results in the generation of 2.1 ton CO_2/ton NH_3, however, part of the CO_2 generated in ammonia production is captured and used as feedstock for urea production.

Natural-gas based ammonia production requires about 28.1–35.5 GJ/ton NH_3 (based on the low heating value [LHV]; U.S. EPA 2017). The process uses 20.4–22.3 GJ/ton NH_3 provided to the primary reformer as feedstock for generating hydrogen with an additional 7.2–9.0 GJ/ton NH_3 provided to the primary reformer to provide the heat required to drive the endothermic steam forming reaction. The remaining 0.5–4.2 GJ/ton NH_3 is used to fuel the auxiliary boiler or is flared. Ammonia plants employing state-of-the-art SMR technology do not import energy to drive mechanical equipment, such as the compressors used to compress the synthesis gas to 100–250 bar depending on the plant's operating pressure. Heat recovered from the primary and secondary reforming units, the shift reactors, ammonia synthesis reactor and waste heat boilers is used to produce high pressure steam for the turbines to drive the compressors and returned to the primary reforming unit.

The highest cost for ammonia production is natural gas, which can account for 72%–85% of the overall production cost, depending on the size of the plant and the price of natural gas. In 2012, estimates show the cost of natural gas to be $78 per ton of ammonia produced (U.S. EPA 2017) despite natural gas prices (wellhead price of $2.66/thousand cubic feet) at their lowest since 1999 and declining by more than 30% from the price in 2011 (DOE EIA 2018). For comparison, the selling price of anhydrous ammonia was about $800/ton in 2012 (Ibendahl 2017). Historically, the price of anhydrous ammonia has been tied to the price of natural gas (U.S. Geological Survey 2016). Between 1984 and 2006, the correlation coefficient between the prices of natural gas and anhydrous ammonia was 0.92 according to a study by the University of Illinois Urbana-Champaign (Schnitkey 2016). Ammonia prices increased sharply between 2000 and 2006 as natural gas prices more than doubled during this period. With the advent of fracking around 2006, natural gas prices dropped by more than 50% through 2014 whereas the price of ammonia continued to increase due to the high demand for nitrogen-based fertilizers for producing corn-based ethanol. With the recent drop in corn prices in the past few years, the price of ammonia has decreased.

While improving the conventional process still has scope (catalysts active at lower temperatures), the frontiers of research on this topic appear to involve either biological, electrochemical, or photochemical routes because, in principle, they could offer nearly zero greenhouse gas burdens provided that the feedstocks and energy inputs come from renewable sources. A recent report estimates that the practical potential energy savings for improving ammonia synthesis could be approximately 80 TBtu/year.

The industrial process was developed and optimized by Haber and Bosch in the early 1900s. The process combines H_2 and N_2 in the presence of a solid catalyst, typically containing highly exposed (nanometer-sized) particles of a group eight metal (viz. iron) in contact with promoters (e.g., MgO, K_2O) on a high surface area support (e.g., alumina) (Stolze 1995). The energy input for the industrial process spans a large range because it represents a survey across old and modern (more efficient) facilities and feedstocks (coal, natural gas) (International Energy Agency 2007, 83). Catalysis also plays a central role in the operation of other units critical for operation of the Haber-Bosch process (Eggeman 2000), notably in the production of hydrogen (steam reforming) and its purification (water gas shift, sulfur removal).

The biological synthesis of ammonia is catalyzed by the enzyme nitrogenase. The process requires eight equivalents of electrons, six to reduce the six protons that add to N_2, plus two more for the H_2 equivalent generated by the nitrogenase-catalyzed reaction (Equation 1):

$$N_2 + 8H^+ + 8e^- + 16\,ATP \rightarrow 2NH_3 + H_2 + 16ADP + 16\,P_i \quad (1)$$

Two equivalents of ATP are required to provide for each electron, and approximately 36 equivalents of ATP can be regenerated from ADP and the cleaved phosphate unit (P_i) by the oxidation of one equivalent of glucose (ΔH_{comb}=686 kJ/mol). The indicated CO_2 burden from the biological process arises from the oxidation of the glucose that powers the reaction. Given that the glucose was derived from renewable sources, the actual CO_2 burden of the biological process would arise from growing and transporting the sugar rather than its metabolism, as shown in Table 2.

Table 2. Comparison of industrial and biological production of ammonia.

PROCESS	GLOBAL ANNUAL PRODUCTION[a] (MT)	OPERATING CONDITIONS[b] (TEMPERATURE, K, AND PRESSURE, BAR)	ENERGY INPUT (GJ/TON)	CO_2 BURDEN (TON CO_2 PER T ON AMMONIA PRODUCED)	REFERENCE
Industrial (ex. natural gas)	145	~700 K, 10–30 bar	28–53	~2.1	IEA 2005
Biological (ex. glucose)	175	300 K, 1 bar	11	~0	Deacon 2017
Electrochemical	—	300 K, 1 bar	16	~0	Botte 2016
Photochemical	—	300 K, 1 bar	30	~0	Schrauzer & Guth 1977

a) 1 MT = 1 megaton = 1×10^9 kg
b) The enthalpy change for taking ammonia from 300 K, 1 bar, to 700 K, 30 bar, is ~ 1 GJ/T
Source: R. S. Weber, Pacific Northwest National Laboratory (2017).

A recent DOE roundtable (DOE, Office of Science 2016) discussed ways to make the manufacture of ammonia more sustainable, such as providing the hydrogen renewably (e.g., electrolysis of water powered by renewable electricity or by solar-powered photolysis) combined with the use of more active synthesis catalysts that permit operating the process under less severe conditions. Direct electrochemical synthesis of ammonia, as given in Equation 2:

$$N_2 + 6\,H_2O + 6\,e^- \rightarrow 2\,NH_3 + 6\,OH^- \qquad E_0 = -0.77\ \text{V at 300 K} \tag{2}$$

The result has also been achieved using metal nitrides as the cathode catalysts (Abghoui et al. 2016), and patented, claiming the utility of alloys, carbides, and nitrides as the cathode catalyst (Botte 2016; Denvir et al. 2013).

Recent research (Milton et al. 2017) marries the biological and electrochemical approaches through the use of an enzymatic fuel cell. The productivity of that system is in the range typical of microbial fuel cells (~100 $\mu A/cm^2 \simeq 1$ $nmol/cm^3/s$), which is three orders of magnitude below that ascribed by Paul Weisz (1982) to commercially viable chemical reactors.

The photochemical route uses light to photolyze water to make H_2, which then is reacted with N_2, either directly or indirectly, through thermally activated catalysis. The energy input listed in Table 2 corresponds to just that required to split water (286 kJ/mol).

All the processes that operate at low temperature and pressure produce ammonia, either at uneconomical rates, and/or as a dilute aqueous solution. The latter might not be a technical issue if the ammonia were produced close to its point of use, obviating either the cost of concentrating the solution or shipping water.

Recent research in the area of low-temperature and low pressure chemical manufacturing and fuels—synthesis of ammonia—has focused on:

- Lowering the temperatures and pressures of ammonia synthesis for distributed delivery of NH_3.
- Improving the efficiency of electrochemical ammonia synthesis and understanding how to efficiently integrate catalysts with electrochemical devices.
- Identifying new catalytic compositions and mechanisms that break linear scaling relationships.
- Investigating non-traditional systems for ammonia synthesis (e.g., plasma).
- Improving biological systems for ammonia synthesis.

3.3 'EXTREME' TEMPERATURES: SOLAR THERMAL-ASSISTED

High Temperature Thermal Processes for Producing "Clean" Hydrogen or Liquid Fuels. Concentrated solar power (CSP) (Solar EIS 2017; Koepf et al. 2017) and high-temperature gas-cooled (HTGR) nuclear reactors (NGNP Industry Alliance 2010) are two emerging technologies for providing heat at temperatures ranging from 700 to 2000 °C and 850 to 1000 °C, respectively, to drive highly-endothermic reactions. CPS technology provides heat directly by focusing radiant sunlight using a reflective surface onto a chemical reactor (Figure 19); or indirectly by focusing the sunlight onto a receiver such as a pipe containing a heat transfer medium (i.e., a molten salt) (Figure 20). The medium then exchanges heat with the reactor.

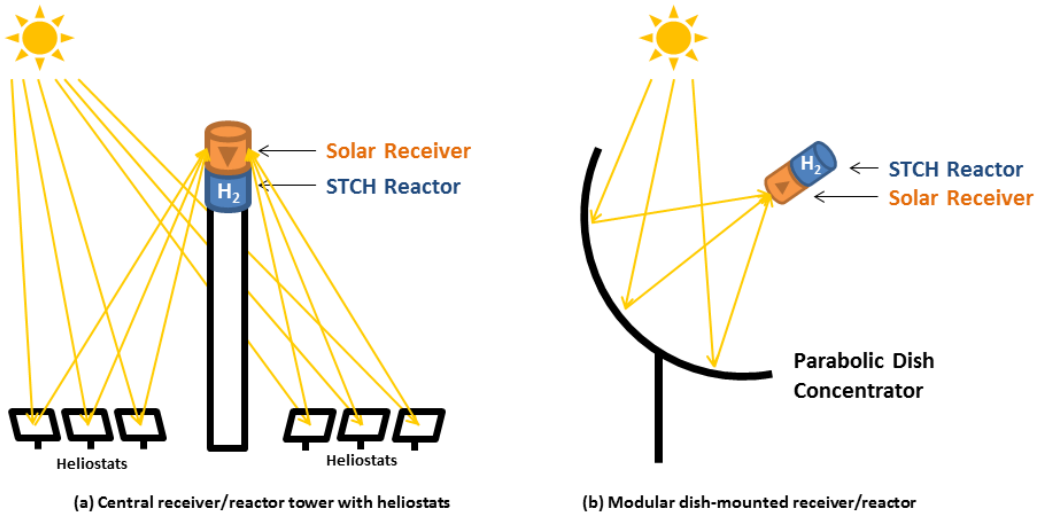


Figure 19. Two mirror-based approaches for focusing sunlight on a solar thermochemical (STCH) reactor to produce temperatures up to 2,000 °C: (a) Field of heliostat mirrors concentrates sunlight onto a central reactor tower, and (b) dish mirrors focus sunlight onto an attached reactor module. Image from U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (2018).

An HTGR nuclear reactor provides heat through a heat transfer medium. Among the reactions that have been investigated are:

- Water splitting to produce hydrogen (Steinfeld 2005; Steinfeld and Weimer 2010; Sattler et al. 2016; Sandia 2009; Brown et al. 2002; Weimer 2006; Summers 2008; Pickard 2008; Allen et al. 2014);
- Steam reforming or dry (CO_2) reforming of natural gas (Zheng et al. 2005; Roeb et al. 2011; Simako et al. 2015; Agrafiotis et al. 2016);
- Reduction of CO_2 to CO (Coker et al. 2008);
- Gasification or cracking of coal, petroleum, or natural gas (Steinfeld 2010; Agrafiotis et al. 2016), and
- Biomass gasification (Steinfeld and Weimer 2010; Agrafiotis et al. 2016).

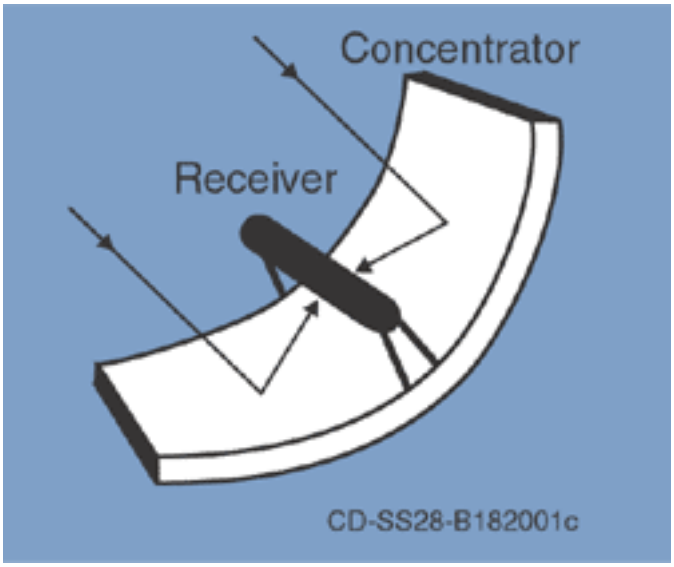


Figure 20. Schematic diagram of a parabolic trough system that focuses the incident sunlight onto an oil-filled pipe running along the center or focal point of the mirror. From Solar EIS (2017). Courtesy of Solar PEIS.

Other than water splitting, the major product from most of these processes is syngas (CO + H_2), which can be converted to liquid fuels using a conventional conversion technology such as Fischer-Tropsch. If solar energy is the heat source, these fuels are referred to as "solar fuels," which embody 26%–31% of their energy as solar energy in the chemical products (on a LHV basis) (Agrafiotis et al. 2016).

"Clean" hydrogen. Thermal decomposition, or thermolysis, of water to produce hydrogen (Equation 3) is conceptually a simple reaction for producing H_2 without generating CO_2 as a by-product.

$$H_2O_{(g)} \rightarrow H_{2(g)} + \tfrac{1}{2}O_{2(g)} \qquad \Delta G^\circ_{298} = 228.71\ \text{kJ/mol} \tag{3}$$

Because of the high positive Gibbs free energy, complete dissociation of water requires a temperature around 4500 K; however, reasonable conversion can be achieved at temperatures as low as 2500 K (Sattler et al. 2016). Providing heat at these temperatures is technically challenging and economically not feasible because severe thermal stability requirements are imposed on the materials of construction, significant re-radiation from the reactor causes a loss in absorption efficiency, and H_2 and O_2 must be separated at high temperatures to prevent the formation of an explosive mixture (Steinfeld 2005).

To address these technical challenges, thermochemical cycles are being developed that break the thermolysis reaction into two or more consecutive reaction steps, one that releases H_2 and a second reaction that releases O_2, with at least one of the steps being highly endothermic. The net result is the input of heat and water and the production of hydrogen and oxygen. All other process chemicals employed in the process are fully recycled. To date, more than 300 different cycles have been identified (Energy.Gov 2017). Two of the more investigated family of cycles are based on metal oxides or sulfur (Steinfeld 2005; Sattler et al. 2016; Weimer 2006; Summers 2008; Pickard 2008; Allen et al. 2014).

Metal oxides are attractive because they involve fewer and less difficult steps than other processes at lower temperatures with the potential to achieve higher overall process efficiencies (Energy.Gov 2017). The general reaction scheme for metal oxide-based cycles is shown in Equations 4 and 5:

$$MO_{(x+y)} \rightarrow MO_x + (y/2)O_2 \tag{4}$$

$$MO_x + yH_2O \rightarrow MO_{(x+y)} + yH_2 \tag{5}$$

The oxygen-evolution reaction (Equation 3) involves the partial reduction of the metal oxide to form either a metal or lower-valence metal oxide. This reaction is endothermic and uses solar heat to liberate lattice oxygen. The hydrogen-evolution reaction (Equation 4) involves the hydrolysis of the metal or lower-valence metal oxide

to reform the metal oxide. This reaction is exothermic and occurs at a much lower temperature than the oxygen-evolution reaction. For all cycles, the oxygen-evolution reaction is thermodynamically-limiting (Sattler et al. 2016). Since H_2 and O_2 are formed in separate reactions, the need for high-temperature gas separation is eliminated (Steinfeld 2005).

The Fe_3O_4/FeO and ZnO/Zn cycles are two of the most studied metal oxide cycles (Steinfeld and Wimer 2010; Sattler et al. 2016; Weimer 2006). The Fe_3O_4/FeO cycle requires temperatures above 1873 K to reduce Fe_3O_4 to FeO (Sattler et al. 2016). Quenching the reaction to prevent recombination of FeO with O_2 is a major challenge, and leads to a loss of FeO from vaporization and reduced process efficiency. The overall efficiency for the Fe_3O_4/FeO process is 20.4%–25.1% depending on the concentration of solar radiation coupled to the reactor. The ZnO/Zn cycle requires temperatures above 2273 K to reduce ZnO to Zn (Sattler et al. 2016; Weimer 2006). As with the Fe_3O_4/FeO cycle, quenching Zn to avoid recombination is a major challenge. With an overall efficiency of 29%, the ZnO/Zn cycle is one of the most thermodynamically efficient (Sattler et al. 2016). Other metal oxide systems that have been studied include ferrites, hercynites, and ceria (Sattler et al. 2016).

The sulfur-iodine cycle, given in Equations 6 through 8, is an example of one of the more developed sulfur-based cycles (Sattler 2016; Pickard 2008).

$$I_2 + SO_2 + 2\,H_2O \rightarrow 2\,HI + H_2SO_4\,(120\,^{\circ}C) \quad (6)$$

$$2\,H_2SO_4 \rightarrow 2\,SO_2 + 2\,H_2O + O_2\,(850\,^{\circ}C) \quad (7)$$

$$2\,HI \rightarrow I_2 + H_2\,(450\,^{\circ}C) \quad (8)$$

As with most sulfur cycles, the highly endothermic reaction is the thermal decomposition of sulfuric acid into SO_2 and O_2 (Equation 7), and requires temperatures above 1123 K, as well as efficient catalysts (Sattler et al. 2016). Because the reaction occurs at high temperatures in an extremely corrosive atmosphere, developing catalysts that can survive in this environment is a major challenge. For the sulfur-iodine cycle, catalysts for the decomposition of sulfuric acid that have been investigated include oxide-supported Pt catalysts and complex metal oxides, such as $CuFe_2O_4$ and $CuCr_2O_4$. Pt/TiO_2 was the most stable catalyst in short-term testing (Pickard 2008).

Another sulfur-based cycle, the hybrid sulfur (Equations 9 and 10), is an example of a hybrid thermochemical cycle that usually produces hydrogen. The cycle includes both chemical reaction steps and an electrolysis step of a non-water chemical compound (Sattler et al. 2016; Allen et al. 2014).

$$H_2SO_{4(aq)} \rightarrow H_2O_{(g)} + SO_{2(g)} + \tfrac{1}{2}\,O_{2(g)}\,(\text{thermochemical, } 850\,^{\circ}C) \quad (9)$$

$$SO_{2(aq)} + 2\,H_2O_{(l)} \rightarrow H_2SO_{4(aq)} + H_{2(g)}\,(\text{electrochemical, } 80\text{–}120\,^{\circ}C) \quad (10)$$

Although both thermal and electrical energy are required, the electrolysis step requires much less energy than does electrolysis of water. Both the electromechanical step and the decomposition of sulfuric acid require catalysts. Reducing the cost and improving the stability of the catalyst used in the electrochemical step is a major challenge. Noble metal catalysts, such as platinum or palladium, have been investigated with most studies showing that platinum has higher activity than other noble metals. Dissolution is problematic for palladium and is accelerated by increasing temperature and acid concentration (Allen et al. 2014).

Steam reforming or dry reforming of methane (natural gas). The use of CSP for methane reforming has received considerable interest worldwide (Zheng et al. 2005; Roeb et al. 2011; Simako et al. 2015; Agrafiotis et al. 2016). Temperatures well in excess of 800 °C are required to achieve nearly complete conversion of natural gas at the elevated pressures that industrial applications require. Catalysts similar to those used in conventional steam reforming have been investigated, including transition metals (such as nickel, cobalt, or iron), as well as platinum group metals (including ruthenium, rhodium, iridium, platinum, and palladium), supported on ceramic or refractory oxides catalysts. While most transition metal catalysts are highly active at these temperatures, stability against sintering is poor and severe thermal stresses are induced by the recurring cooling and heating cycles owing to the cyclic nature of solar irradiation. CSP systems employ lower steam-to-carbon ratios because of their

higher capital cost compared to conventional technologies, rendering nickel, cobalt, and iron-based catalysts unsuitable because of their propensity to coke at low steam-to-carbon ratios.

Recent research in the area of 'extreme' temperatures—solar thermal-assisted—has focused on:

- Investigating thermally-robust catalysts and materials for water-splitting to produce hydrogen.
- Developing catalysts for reforming methane that can absorb solar thermal radiation directly, are stable at high temperatures, and can withstand the thermal and mechanical stresses introduced during heating and cooling cycles.
- Researching catalysts for solar-thermal gasification of natural gas, biomass, and coal to produce syngas.

3.4 INTEGRATED CATALYTIC PROCESSES

3.4.1 High-intensity FCC

FCC additives for increasing ethylene and propylene content. The demand for ethylene and propylene for the chemicals and polymer industries is rising faster than the demand for gasoline worldwide. In addition to on-purpose production via cracking and dehydrogenation, a number of existing FCC units have been retrofitted and their catalyst profile modified to increase the amount of olefins (Corma et al. 2017), with the primary focus being increasing propylene content and competing with propylene-on-purpose dehydrogenation technology. The precise weight percent of C_2 and C_3 olefins in the product stream is heavily dependent on the input feed; however, large increases (as much as <10 to ≥20 wt%) of propylene have been reported in commercial testing. Modifying existing FCC units can be advantageous relative to on-purpose construction (Knight and Mehlberg 2011; Lambert et al. 2016). In addition to changes to the catalyst feed, modifications include increasing separation capacity to deal with the excess propylene and possibly additional heat exchangers to efficiently manage the heat flow. The scale of refinery operations make the change in olefin production through a retrofit attractive for many reasons—not least of which is that it avoids building a new plant, saving in capital costs and providing quicker time to market.

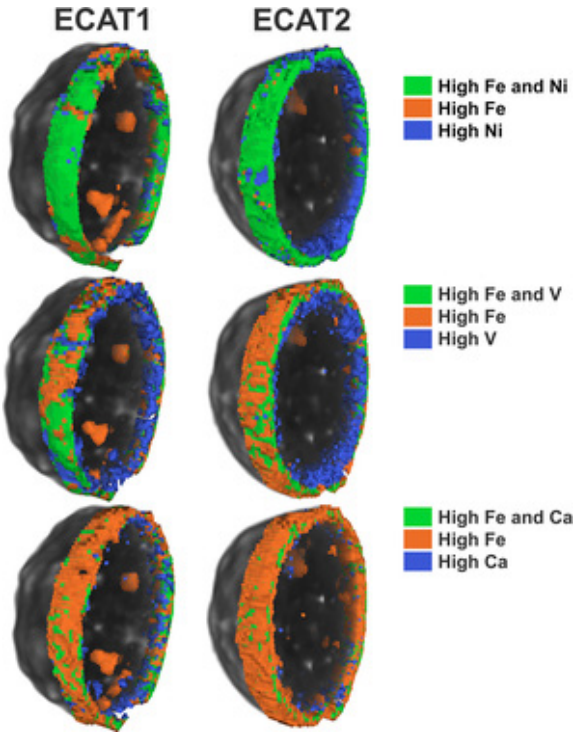


Figure 21. Two dimensional slices for each elemental channel of the two different FCC catalyst particles. From Kalirai S., U. Boesenberg, G. Falkenberg, F. Meirer, and B. Weckhuysen, *ChemCatChem*, 2015, 7: 3674–3682. Copyright Wiley-VCH Verlag GmbH & Co. KGaA (NonCommercial 4.0 International [CC BY-NC 4.0]).

The increase in olefin yields is primarily owing to the addition of ZSM-5 to the modern Y zeolite-based FCC catalyst (consisting of mesoporous zeolite crystals in a carefully controlled matrix; see Topics 1.2.4 and 1.2.8). Some catalyst suppliers may add ZSM-5 to the FCC reactor as a separate catalyst feed, while other formulations include both Y zeolite and ZSM-5 in the catalyst particles. Precise operating conditions vary depending on feed and plant design, but are generally in the range of 500–600 °C, with regeneration conducted in the range of 650–750 °C. Catalyst is injected into the riser, often with two cracking zones—the first with a higher weight hourly space velocity (WHSV) (approximately 50+ h^{-1}) and the second with a lower WHSV (approximately 30 h^{-1}). After regeneration, some fresh catalyst and, occasionally, coked catalyst are added back into the stream for the recycle.

The primary catalyst challenges are similar to those for traditional FCC catalysts, including catalyst activity, selectivity to the desired products, and regeneration stability of the zeolites and binder matrix. Catalytic performance during the lifetime of the catalyst and over many regeneration cycles is critical. Importantly, changes in inherent catalyst selectivity are observed during the

lifetime of a given FCC catalyst. Dealumination and deposition of metals from the feed have been proposed as potential deactivation pathways. Advances in fluorescence (Ristanović et al. 2015) and X-ray characterization (Bare et al. 2014; Kalirai et al. 2015; Kalirai et al. 2016; Meirer et al. 2015a; Meirer et al. 2015b; Liu et al. 2016) have shed light on metal deposition as a major contributor. Deposition of iron, nickel, and vanadium are observed (Figure 21), with particles of differing age showing a deposition of the metals eventually blocking access to the active catalyst, leading to deactivation. A model based upon resistance was used to model the onset of mass-transport limitations at multiple length scales. This approach was able to simulate the aging of the particles and the closing of the mesopore network as a function of metal deposition (Liu et al. 2016).

Recent research and development in fluid catalytic cracking (FCC) includes:

- Incorporation of multiple zeolite types to increase light olefin production.
- Investigating multiple temperature zones, continuous regeneration, and other process-intensification strategies.
- Performing life-cycle studies of working and spent FCC catalysts to identify metal deposition, pore blocking, and other deactivation mechanisms.

3.4.2 Membrane Reactors

Membrane reactors integrate a hydrogen-producing catalytic process (typically a thermodynamically-limited reaction such as SMR) with a membrane separations process into a single unit operation. The continuous and selective removal of one of the product components (i.e., hydrogen, in the case of SMR), or the controlled addition of one of the reactants (i.e., oxygen, in the case of oxidative coupling of methane), causes the equilibrium to shift more towards the products, resulting in a higher conversion at a given temperature than is realized in a conventional reactor, as illustrated in Figure 22. Table 3 lists some of the different classes of reactions that could be amenable to membrane reactor technology.

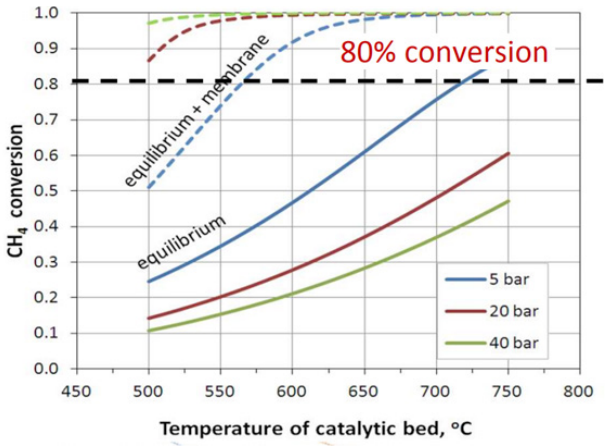


Figure 22. Predicted CH_4 conversion achieved for SMR as a function of temperature and pressure with and without a H_2 membrane. From Saric (2015). Reproduced with permission.

A membrane reactor offers several potential advantages over a conventional design, where the reactor is combined with downstream separation processes. Because the design involves a smaller reactor and separation unit, capital costs decrease, which also corresponds to a decrease in catalyst requirements; the equilibrium shift effect improves yield and selectivity; integrated separation reduces downstream separations cost; and the design is expected to bring higher energy and overall process efficiencies (Gallucci et al. 2013). Process intensification technologies (such as membrane reactors) are critical for small-scale modular processes because unit operations associated with balance of plant (BOP) (i.e., preparation and conditioning of the feedstock; separations and product recovery from the reactor) can account for as much as 85% or more of the equipment cost. For a conventional large-scale plant, unit operations associated with BOP typically account for 50% or more of the equipment cost (Gupta 2017).

Several different membrane reactors were studied, including packed bed, fluidized bed, micro-, and catalyst types (Gallucci et al. 2013). In a packed bed membrane reactor (PBMR), the catalyst is in a fixed bed configuration, packed inside the membrane tube or on the shell side of the tube, and is in contact with the membrane. A PBMR is the most studied type of configuration, making it easy to compare its performance to a conventional packed bed reactor. The bed-to-wall mass transfer limitation, however, influences the membrane area required, posing a disadvantage. A fluidized bed membrane reactor (FBMR) has a bundle of membranes immersed in a catalyst bed operated in the bubbling or turbulent regime. The bed-to-wall mass transfer limitation in a PBMR is reduced with a FBMR, yet allowing almost isothermal operation. A micro-membrane reactor (MMR) uses technologies such as microchannel reactors to reduce the scale length of the system. MMR benefits include improved heat and

mass transfer owing to the decreased scale length of the microchannels; no mass transfer limitations; and a high degree of process intensification from integration of the different process steps into a small device. In a catalyst membrane reactor (CMR), the membrane material acts as the membrane and catalyst for the reaction of interest. A CMR design eliminates the mass transfer step from the catalyst bed to the membrane, but requires optimizing both catalytic and mass transfer performance.

Table 3. Reaction classes that are amenable to membrane reactor technology.

REACTION CLASS	EXAMPLE	ROLE OF MEMBRANE
Hydrogenation	$C_2H_2 + H_2 \rightarrow C_2H_4$ in presence of C_2H_4	Controlled addition of H_2
Hydrogenolysis	Cyclopentadiene + $H_2 \rightarrow$ cyclopentene and cyclopentane	Controlled addition of H_2
Dehydrogenation	Cyclohexane $\rightarrow$ Benzene + H_2	Removal of H_2 to shift equilibrium
Partial oxidation	Butane + $O_2 \rightarrow$ maleic anhydride	Recovery of intermediate product of control reactant to promote formation of intermediate product
Esterifications	R-OOH + $CH_3OH \rightarrow$ R-O-OCH_3 + H_2O	Selective removal of H_2O to shift equilibrium without loss of reactant
Syngas (Partial oxidation)	$CH_4 + 1/2O_2 \rightarrow CO + 2H_2$	Controlled addition of O_2 to prevent formation of hot spots
Syngas (Steam methane reforming)	$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$	Selective removal of H_2 to shift equilibrium
Water-gas shift	$H_2O + CO \rightarrow H_2 + CO_2$	Selective removal of H_2 to shift equilibrium
Oxidative coupling	$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O$	Controlled addition of O_2 to prevent oxidation to CO_2

Source: Rezac, M. E. 2000. "Catalytic Membrane Reactors." In *Encyclopedia of Separations Sciences*, 1st ed. Edited by I. Wilson, C. Poole, and M. Cooke. Academic Press, pp.1676–1682.

For commercialization, industry has shown the most interest in membrane reactors for SMR to produce high purity hydrogen (Gallucci et al. 2013; Iulianelli et al. 2016). Different types of membranes investigated include polymeric, microporous ceramic, porous carbon, dense metallic, and proton- or oxide-conducting dense ceramics. Of these types, for SMR, dense metallic, and the palladium and palladium-alloy membranes in particular, have received the most interest. Palladium-based membranes are highly selective for hydrogen (selectivity factor of >1000), have a high hydrogen flux (60–300 10^{-3} mol·m^{-2}·s^{-1} at a ΔP = 1 bar), and are able to operate at relatively high temperatures (300–700 °C) (Gallucci et al. 2013). The major drawbacks are membrane embrittlement, which is caused by a phase change from the α-phase to the β-phase at temperatures below 300 °C and pressures below 2 MPa; surface poisoning of the membrane caused by sulfur, chlorine, carbon, and unsaturated hydrocarbons; and cost.

The refractory metals (e.g., vanadium, niobium, and tantalum) exhibit high permeability to hydrogen at lower temperatures, are cheaper and more stable at higher temperatures, compared to palladium. However, at room temperature hydrogen embrittlement hinders the refractory metal membranes and poor surface properties impede hydrogen transport. Polymeric membranes, such as polyamides, cellulose acetate, and polysufones, typically operate at temperatures below 100 °C with low hydrogen selectivity and flux. Major drawbacks include swelling, compaction, and poor mechanical strength. Microporous ceramic membranes such as zeolites offer the advantages of size and shape selectivity, given that zeolites have well-defined pore and channel sizes and good thermal and chemical stability. Other common membrane materials include silica, alumina, zirconia, and titania.

Hydrogen selectivity factors range from 5–139 with hydrogen flux ranging from 60–300 10^{-3} mol·m^{-2}·s^{-1} at a ΔP = 1 bar. Stability in the presence of steam is an issue. Carbon membranes exhibit good thermal and chemical stability but are brittle and easily oxidized. H_2 selectivity factors range from 4–20 and hydrogen fluxes range

from 10–200 10^{-3} mol·m^{-2}·s^{-1} at a ΔP = 1 bar. Proton and oxide conducting membranes, such as perovskites and cermets, exhibit very high selectivity factors for hydrogen (>1000) and oxygen transport, respectively, but require high temperatures (600–900 °C) for optimal performance. Membrane stability issues caused by thermal stresses and reactions with compounds such as CO_2 and H_2S are major drawbacks as are the challenges of fabricating large defect-free membranes. Because of these issues, smaller modular reactor systems are attractive routes to commercialization. For example, standardizing reactors could lead to a 'cartridge' replacement system where the membrane is easily replaced and that could be a way to overcome long-term stability issues.

In terms of catalyst design and development, membrane reactors can often overcome the mass and heat transfer issues that lead to low catalyst effectiveness factors (~0.01) and large temperature gradients that plague the nickel-based catalysts used in conventional fixed-bed SMR processes (Medrano 2016). Optimizing the overall performance of the membrane reactor often requires the development of new catalyst technology, even when existing commercial catalyst technology is well established, because the process conditions (i.e., temperature, pressure, feed composition) are often quite different from the process conditions employed in conventional processes (Palma et al. 2016). For example, membrane reactors designed for processing involving hydrocarbon reforming or dehydrogenation by selectively removing H_2 require catalysts with better coke resistance than catalysts employed in conventional reactors because of the lower H_2 partial pressure present in the membrane reactor. One possible solution is using catalyst supports based on rare earth oxides with high oxygen mobility, which reduces carbon formation. Catalyst structure also plays an important role. The use of highly thermal conducting foams as catalyst supports not only reduces the pressure drop across the catalyst bed but greatly improves thermal management within the catalyst bed, which plays a significant role in maximizing both catalyst and membrane lifetime.

Recent research in the area of membrane reactors has focused on:

- Developing active catalysts for process conditions in membrane reactors that differ significantly from the process conditions in conventional reactors.
- Investigating new water-gas shift catalyst formulations that are better suited for use in membrane reactors than the commercial Cu/ZnO (low-temperature shift) and FeCrO (high-temperature shift) catalysts.
- Designing new catalysts for alkane dehydrogenation to produce olefins that exhibit higher activity at lower temperatures and are more resistant to coke formation.

3.5 NON-FOOD WASTE TO FUELS

World waste generation is estimated at approximately 1.3 billion tons, and that quantity will increase as the world population increases (Hoornweg and Bhada-Tata 2012). DOE's Bioenergy Technologies Office (BETO) estimates 572 million tons of dried, terrestrial feedstocks will be generated in 2017, with more energy and carbon available in wet feedstocks and gases (Philbrick et al. 2017). Approximately 50% of the world-wide solid waste streams are organic materials, 17% paper, and 10% plastic, although these numbers vary depending upon a region's economy, climate, and method of energy production. Many waste streams contain mixtures or are derived from unused energy-containing residuals from manufacturing processes, energy production, and agricultural industries; thus, the streams may be converted to fuels using developing or emerging technologies for those components. Gas, liquid, and solid wastes are all potential sources for fuels. Many of the issues facing waste-to-fuels technologies or approaches mirror those facing other emerging feedstocks, yet additional technical, economic, and societal challenges confront adding value to currently discarded substances.

The decision to utilize a waste as feedstock for fuels and the choice of technology for its conversion depends considerably on the physical form, complexity, variability, quantity, and energy content of the waste stream. In addition, the value of products and competing applications also dictate process choices. Moreover, wastes are not cost-free. For example, the value of lignin waste from cellulosic ethanol production or the paper industry is benchmarked against its application as boiler fuel for the plant itself.

3.5.1 Types of Waste

Non-food wastes include gaseous streams, such as methane from wastewater treatment and livestock; carbon dioxide from cement production, combustion processes and manufacturing; carbon monoxide from steel production; and associated natural gas from "stranded" oil wells.

Liquid streams include waste fats, oils, and greases; nitrate-rich aqueous streams from industrial and agricultural manufacturing; and high moisture content waste-water streams.

Solid wastes include municipal solid waste (MSW); lignin residues from the paper and pulp industry, as well as the emerging cellulosic ethanol industry; and wastewater sludges and bio-solids. Plastics are a significant component of solid waste, with total worldwide annual plastic production topping 300 million tons—including polyolefins, with polyethylene annual global production on the order of 80 million tons.

Recent research in the area of non-food waste conversion includes:

- Converting sludges from waste water treatment plants into liquid fuels.
- Investigating new tactics to convert animal manures into usable biogas.
- Advancing the conversion of CO_2 to liquid fuels and chemicals as well as synthesis gas.
- Developing small-scale methods to convert plastics waste into chemicals.

3.5.2 Conversion Approaches

Industrial transformations of non-food waste to fuels have involved thermal processes or biochemical treatments. While both types of processes may involve catalysis at some stage, thermochemical catalysis offers potential for improvements to the process. Biochemical treatments involve thermal pretreatment (up to 200 °C) with acid, water, or ammonia to partially deconstruct the cell wall, followed by enzymatic or microbial catalysis to convert the waste to liquids or gases for fuel applications. Thermochemical treatments (pyrolysis or gasification) tend to involve high temperatures and short residence times to generate liquids or gases and are thus energy intensive.

Incineration. In many manufacturing processes, wastes are utilized for heat and power through combustion in a boiler. Combustion is estimated to provide 1.9 thousand Btu (MBtu) of electrical energy per ton of conventional mixed MSW in a power plant, whereas the energy content of dried biomass is 16–19 MBtu/ton. Often, MSW is mixed with gas or coal in power plants, but this practice can result in increased emissions of nitrogen and sulfur compounds and, without additional scrubbing, soot particulates. More recently, an approach of mixing biomass with coal for conversion to produce fuels is being explored.

Gasification. Conversion of solid mixtures to syngas (primarily hydrogen and carbon monoxide) may be effected by gasification (Petrus and Noordermeer 2006), which is then used in catalytic FT production of a broad distribution of hydrocarbons, methanol, or higher alcohols. Syngas may be utilized as a drop-in intermediate by the petrochemical industry and is useful for creating a common intermediate from feedstock mixtures; however, this approach breaks all carbon-carbon bonds. Challenges and requirements in the gasification approach include maximizing CO yields and minimizing CO_2 and carbon production; controlling the CO and H_2 composition of syngas; obtaining syngas free of impurities because nitrogen and sulfur compounds poison FT catalysts; followed by upgrading the hydrocarbon mixture to liquid fuel-range molecular weight distributions. Examples of this approach include InEnTec's multistep gasification and plasma enhanced melting process for conversion of mixed waste streams.

Torrefaction. Torrefaction is a mild thermochemical treatment used to convert biomass to a coal-like material known as biochar. The process is carried out at moderate temperatures ranging from 200–300 °C in the absence of air. Under process conditions hemicellulose, and to a lesser extent cellulose and lignin, are partially broken down releasing water and various volatile compounds and yielding a material that is brittle, easy to grind, and suitable for densification into briquettes or pellets. The final, densified material is more homogeneous and has a higher mass and energy density than the original biomass from which it is made. In addition, the final product is hydrophobic instead of hydrophilic, no longer supports the biological activity that leads to rot or decay, and can be stored for long periods of time without appreciable change in moisture content or heating value, unlike the original biomass.

Hydrothermal liquefaction. Hydrothermal liquefaction (HTL) is used to treat wet feedstocks with a range of moisture content, such as sewage sludge and animal manures, in water under sub-supercritical conditions to generate a bio-oil, organic-rich aqueous phase, solid, and gas. An advantage of the HTL process is that it can be tuned to the feedstock (Philbrick et al. 2017). Water is supercritical above 22.1 MPa and 374 °C and this approach requires a sufficiently wet stream. Subcritical or supercritical solvents other than water may also be applied, although the processing of wet waste streams could be complicated by non-aqueous conditions.

Pyrolysis. Pyrolysis is performed at higher temperatures (above 500 °C) on relatively dry solid streams to produce a gas stream, pyrolysis oil, and biochar. However, slow pyrolysis of manure at 650 °C did not provide an oil product, and the gas phase contains sulfides, mercaptans, and disulfides (Ro et al. 2010). The biochar may be used as fertilizer. Pyrolysis is also used for the deconstruction of plastics and polymers.

Catalytic processes. Catalytic processes for converting plastic into fuels are emerging. For example, EcoFuels Technologies is using catalysts and electromagnetic induction heating to depolymerize plastics to fuel-grade materials (4–14 carbons) (Mohandy and Ramesh 2013; Ramesh and Sibul 2007). The catalytic reactor system can convert thermoplastics, thermosets, or mixtures of plastics including polyolefins, polyvinylchlorides, or polyurethanes.

Anaerobic digestion. Anaerobic digestion uses microbial treatments to convert organic wastes such as sewage, MSW, manure, and industrial wastes to biogas, which is useful as a natural gas substitute (Visvanathan 2010). These processes may operate on wet or dry organic wastes and under moderate conditions (35–40 °C or >45 °C, depending on the bacteria), but require much longer residence times than thermochemical or thermocatalytic approaches (e.g., 10–30 days), and produce ~100 or 300–400 Nm^3 per ton of volatile solids. The biochemical pathways are sensitive to temperature and other control parameters; however, a number of plants are in operation, the microbes are commercially available, and the solid byproducts (digestates) may be used as soil conditioner. There are over 2000 sites in the United States producing biogas on farms, in wastewater treatment plants, and in landfills (U.S. Department of Agriculture 2015).

Recent research in the conversion of non-food waste includes:

- Developing catalysts to lower energy costs associated with pyrolysis of a variety of waste streams including manures and plastics.
- Developing catalysts that can lower the energy costs and provide higher yields of bio-oil produced from hydrothermal liquefaction.
- Investigating catalysts that reduce char formation during both pyrolysis and hydrothermal liquefaction of waste streams.
- Advancing novel biochemical pathways for processing municipal solid waste.

3.6 LOW TEMPERATURE EMISSION CONTROL

Vehicle technologies are changing to meet tighter standards for fuel efficiency and greenhouse gas emissions, and one primary method of increasing fuel efficiency is to increase the combustion efficiency of the internal combustion engine. New advanced combustion techniques achieve greater fuel efficiency in laboratory studies, but their commercialization potential will depend on meeting emission standards for the control of the criteria pollutants that affect air quality—CO, NO_x, and non-methane organic gases (NMOGs). The exhaust temperature range of advanced combustion engines is significantly lower than conventional engines; consequently, catalysts in the emission control system will need to operate at much lower temperatures to convert criteria pollutants sufficiently to meet emission regulations. Accordingly, the U.S. Department of Energy Vehicle Technologies Office has a goal of 90% conversion of all criteria pollutants at 150 °C (or ~100 °C lower than current state of the art commercial automotive catalysts).

Recent research in the area of low temperature emission control has focused on:

- Improving the effectiveness of Cu zeolite deNO_x catalysts through the use of other zeolites including chabazite.
- Lowering the light-off temperature of deNO_x catalysts.
- Increasing the effectiveness of deNO_x catalysts under diesel operating conditions (i.e., low temperature and high oxygen content).

3.7 REFERENCES

Abghoui, Y., Garden, A. L., Howalt, J. G., Vegge, T., and Skülason, E. 2016. "Electroreduction of N_2 to Ammonia at Ambient Conditions on Mononitrides of Zr, Nb, Cr, and V: A DFT Guide for Experiments." *ACS Catalysis* 6: 635–646. doi: 10.1021/acscatal.5b01918.

Aehle, W., ed. 2007. *Enzymes in Industry: Production and Applications*, 3rd ed. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA.

Agrafiotis, C., von Storch, H., Roeb, M., and Sattler, C. 2016. "Solar Thermal Reforming." In *Hydrogen Science and Engineering Materials Processes, Systems, and Technologies, First Edition*, edited by Stolten, D., and B. Emonts. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co KGaA.

Allen, J. A., Rowe, G., Hinkley, J. T., and Donne, S. W. 2014. "Electrochemical Aspects of the Hybrid Sulfur Cycle for Large Scale Hydrogen Production." *International Journal of Hydrogen Energy* 39: 11376–111389. doi: 10.1016/j.ijhydene.2014.05.112.

Anwu, L., Lim, C. J., and Grace, J. R. 2008. "Staged-separation Membrane Reactor for Steam Methane Reforming." *Chemical Engineering Journal* 138: 452–459. doi: 10.1016/j.cej.2007.06.024.

Bare, S. R., Charochak, M. E., Kelly, S. D., Lai, B., Wang, J., and Chen-Wiegart, Y.-C. K. 2014. "Characterization of a Fluidized Catalytic Cracking Catalyst on Ensemble and Individual Particle Level by X-ray Micro- and Nanotomography, Micro-X-ray Fluorescence, and Micro-X-ray Diffraction." *ChemCatChem* 6: 1427–1437. doi: 10.1002/cctc.201300974.

Botte, G. G. 2016. Electrochemical Synthesis of Ammonia in Alkaline Media. U.S. Patent 20160083853 A1, filed March 26, 2014, and published March 24, 2016.

Boudart, M. 1994. "Ammonia Synthesis: The Bellwether Reaction in Heterogeneous Catalysis." *Topics in Catalysis* 1:405-414. doi: 10.1007/BF01492292.

Bromberg, L. III, Green, W. H., Sappok, A., Cohn, D. R., and Jalan, A. 2014. "Engine Reformer Systems for Lower Cost, Smaller Scale Manufacturing of Liquid Fuels." U.S. Patent 20140144397 A1, filed March 14, 2013, and published May 29, 2014.

Brooks, K. P., Snowden-Swan, L. J., Jones, S. B., Butcher, M. G., Lee, G.-S. J., Anderson, D. M., and Frye, J. 2016. "Low-carbon Aviation Fuel through the Alcohol to Jet Pathway." In *Biofuels for Aviation*, edited by Chuck, C. Elsevier, Chapter 6. doi: 10.1016/B978-0-12-804568-8.00006-8.

Brown, L. C., Besenbruch, G. E., Schultz, K. R., Marshall, A. C., Showalter, S. K., Pickard, P. S., and Funk, J. F. 2002. "Nuclear Production of Hydrogen using Thermochemical Water-splitting Cycles." Presented at the International Congress on Advanced Nuclear Power Plants (ICAPP), Hollywood, FL, June 9–13. https://fusion.gat.com/pubs-ext/MISCONF02/A23944.pdf.

Chemtrix. 2018. "3D Printed Flow Reactors." Accessed February 16, 2018. http://www.chemtrix.com/products/3d-printed-flow-reactors.

Collias, D. I., Harris, A. M., Nagpal, V., Cottrell, I. W., and Schultheis, M. W. 2014. "Biobased Terephthalic Acid Technologies: A Literature Review." *Industrial Biotechnology* 10: 91–105. doi:10.1089/ind.2014.0002.

Corma, A., Corresa, E., Mathieu, Y., Sauvanaud, L., Al-Bogami, S., Al-Ghrami, M. S., and Bourane, A. 2017. "Crude Oil to Chemicals: Light Olefins from Crude Oil." *Catalysis Science & Technology* 7: 12–46. doi: 10.1039/C6CY01886F.

Cortassa, S., Aon, M. A., Iglesias, A. A., and Lloyd, D. 2002. "Material and Energy Balance." In *An Introduction to Metabolic and Cellular Engineering*. Singapore: World Scientific Publishing Co., Chapter 2.

Deacon, J. 2017. "The Microbial World: The Nitrogen Cycle and Nitrogen Fixation." http://archive.bio.ed.ac.uk/jdeacon/microbes/nitrogen.htm.

Denvir, A. J., Murphy, O. J., Cisar, A. J., Robertson, P., and Uselton, K. 2003. "Electrochemical Synthesis of Ammonia." U.S. Patent 20030164292 A1, filed March 4, 2002, and published September 4, 2003.

Díaz-Marta, A. S., Tubío, C. R., Carbajales, C., Fernandez, 'C., Escalante, L., Sotelo, E., Guitian, F., Barrio, V. L., Gil, A., and Coelho, A. 2018. " Three-Dimensional Printing in Catalysis: Combining 3D Heterogeneous Copper and Palladium Catalysts for Multicatalytic Multicomponent Reactions," *ACS Catalysis* 8:392−404. doi: 10.1021/acscatal.7b02592.

Duckett, A. 2017. "EFCE Honours Individuals and Team that Developed 3D-printed Reactor." *The Chemical Engineer.* October. Accessed February 16, 2018. https://www.thechemicalengineer.com/news/efce-honours-individuals-and-team-that-developed-3d-printed-reactor/.

Eggeman, T. 2000. "Ammonia." In *Kirk-Othmer Encyclopedia of Chemical Technology*, pp. 1–33. doi: 10.1002/0471238961.0113131503262116.a01.pub3.

Energy.gov. 2017. "Hydrogen Production: Thermochemical Water Splitting." U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy. https://energy.gov/eere/fuelcells/hydrogen-production-thermochemical-water-splitting.

Erickson, B., Nelson, J. E., and Winters, P. 2012. "Perspective on Opportunities in Industrial Biotechnology in Renewable Chemicals." *Biotechnology Journal* 7: 176–185. doi: 10.1002/biot.201100069.

Ford. 2015. "100 Years of the Moving Assembly Line." http://corporate.ford.com/innovation/100-years-moving-assembly-line.html.

Gallucci, F., Fernandez, E., Corengia, P., and van Sint Annaland, M. 2013. "Recent Advances on Membranes and Membrane Reactors for Hydrogen Production." *Chemical Engineering Science* 92: 40–66. doi: 10.1016/j.ces.2013.01.008.

Gallucci, F., Medrano, J. A., Roses, L., Brunetti, A., Barbieri, G., and Viviente, J. L. 2016. "Process Intensification via Membrane Reactors, the DEMCAMER Project." *Processes* 4: 16–42. doi: 10.3390/pr4020016.

Gas Processing. 2017. "Setting the Stage for the Future of Smaller-scale GTL." http://gasprocessingnews.com/features/201508/setting-the-stage-for-the-future-of-smaller-scale-gtl.aspx.

Guertzgen, S. 2016. "How 3D Printing Will Energize the Chemical Industry." *Processing Solutions for the Process Industries*. December. Accessed February 16, 2018. https://www.processingmagazine.com/how-3d-printing-will-energize-the-chemical-industry/.

Gupta, R. 2017. "A Case Study in Technological and Business Challenges of a Modular Process Technology." Presented at the NSF/DOE Modular Process Intensification Roadmap Workshop, Washington, D.C., January 18–19.

Gutmann, B., Köckinger, M., Glotz, G., Ciaglia, T., Slama, E., Zadravec, M., Pfanner, S., Maier, M. C., Gruber-Wölfler, H., and Kappe, C. O. 2017. "Design and 3D Printing of a Stainless Steel Reactor for Continuous Difluoromethylations using Fluoroform," *Reaction Chemisry & Engineering* 2: 919–927. doi: 10.1039/C7RE00176B.

Hoek, A. 2006. "The Shell GTL Process: Towards a World Scale Project in Qatar: the Pearl Project." Presented at the DGMK-Conference on Synthesis Gas Chemistry, Dresden, Germany, October 4–6.

Hoornweg, D., and Bhada-Tata, P. 2012. "What a Waste: A Global Review of Solid Waste Management." *Urban Development Series Knowledge Papers, World Bank*. Washington, D.C.: World Bank. No. 15 (March).

Ibendahl, G. 2017. "Predicting Fertilizer Prices." Kansas State University Department of Agricultural Economics, February. http://www.agmanager.info.

Ifp Energies nouvelles (IFPEN). 2016. "A Chemical Reactor Designed by Modeling and Manufactured by 3D printing–A Global First." *ifpEnergies nouvelles*. Accessed February 16, 2018. http://www.ifpenergiesnouvelles.com/News/Press-releases/A-chemical-reactor-designed-by-modeling-and-manufactured-by-3D-printing-A-global-first.

International Energy Agency. 2007. *Tracking Industrial Energy Efficiency and COE Emissions*. OECD/IEA. Paris: OECD/IEA. https://www.iea.org/publications/freepublications/publication/tracking_emissions.pdf.

International Energy Agency. 2013. "Technology Roadmap: Energy and GHG Reductions in the Chemical Industry via Catalytic Processes." OECD/IEA: Paris. https://www.iea.org/publications/freepublications/publication/technology-roadmap-energy-and-ghg-reductions-in-the-chemical-industry-via-catalytic-processes.html.

Iulianelli, A., Liguori, S., Wilcox, J., and Basile, A. 2016. "Advances on Methane Steam Reforming to Produce Hydrogen through Membrane Reactors Technology: A Review." *Catalysis Reviews* 58: 1–35. doi: 10.1080/01614940.2015.1099882.

Kalirai, S., Boesenberg, U., Falkenberg, G., Meirer, F., and Weckhuysen, B. M. 2015. "X-ray Fluorescence Tomography of Aged Fluid-catalytic-cracking Catalyst Particles Reveals Insight into Metal Deposition Processes." *ChemCatChem* 7: 3674–3682. doi: 10.1002/cctc.201500710.

Kalirai, S., Paalanen, P. P., Wang, J., Meirer, F., and Weckhuysen, B. M. 2016. "Visualizing Dealumination of a Single Zeolite Domain in a Real-Life Catalytic Cracking Particle." *Angewandte Chemie International Edition* 55: 11134–11138. doi: 10.1002/anie.201605215

Knight, J., and Mehlberg, R. 2011. "Maximize Propylene from your FCC Unit." https://www.uop.com/?document=uop-maximize-propylene-from-your-fcc-unit-paper&download=1.

Koepf, E., Alxneit, I., Wieckert, C., and Meier, A. 2017. "A Review of High Temperature Solar Driven Reactor Technology: 25 Years of Experience in Research and Development at the Paul Scherrer Institute." *Applied Energy* 188: 620–651. doi: 10.1016/j.apenergy.2016.11.088.

Lambert, N., Ogasawara, I., Abba, I., Redhwi, H., and Krug, K. 2016. "HS-FCC for Propylene: Concept to Commercial Operation." http://france.axens.net/en/component/axensdocuments/1199/hs-fcc-for-propylene-concept-to-commercial-operation/english.html.

LeViness, S., Deshmukh, S. R., Richard, L. A., and Robota, H. J. 2014, "Velocys Fischer-Tropsch Synthesis Technology—New Advances on the State of the Art." *Topics in Catalysis* 57:518. https://doi.org/10.1007/s11244-013-0208-x.

Lim, E. G., Dames, E. E., Cedrone, K. D., Acocella, A. J., Needham, T. R., Arce, A., and Cohn, D. R. 2016. "The Engine Reformer: Syngas Production in an Engine for Compact Gas-to-Liquids Synthesis." *The Canadian Journal of Chemical Engineering* 94: 623–635. doi: 10.1002/cjce.22443.

Liu, S. 2013. "Batch Reactor." In *Bioprocess Engineering, First Edition*. Elsevier, Chapter 4. doi: 10.1016/B978-0-444-59525-6.01001-5.

Liu, Y., Meirer, F., Krest, C. M., Webb, S., and Weckhuysen, B. M. 2016. "Relating Structure and Composition with Accessibility of a Single Catalyst Particle using Correlative 3-dimensional Micro-spectroscopy." *Nature Communications* 7: 12634. doi: 10.1038/ncomms12634.

Meirer, F., Kalirai, S., Morris, D., Soparawalla, S., Liu, Y., Mesu, G., Andrews, J. C., and Weckhuysen, B. M. 2015a. "Life and Death of a Single Catalytic Cracking Particle." *Science Advances* 1, e1400199. doi: 10.1126/sciadv.1400199.

Meirer, F., Morris, D. T., Kalirai, S., Liu, Y., Andrews, J. C., and Weckhuysen, B. M. 2015b. "Mapping Metals Incorporation of a Whole Single Catalyst Particle Using Element Specific X-ray Nanotomography." *Journal of the American Chemical Society* 137: 102–105. doi: 10.1021/ja511503d.

Milton, R. D., Cai, R., Abdellaoui, S., Leech, D., De Lacey, A. L., Pita, M., and Minteer, S. D. 2107. "Bioelectrochemical Haber-Bosch Process: An Ammonia-producing H_2/N_2 Fuel Cell." *Angewandte Chemie International Edition* 56: 2680–2683. doi: 10.1002/anie.201612500.

Mohandy, P. S., and Ramesh, S. 2013. "Depolymerization Processes, Apparatuses, and Catalysts for Use in Connection Therewith." U.S. Patent 20130317238 A1, filed December 8, 2011, and published November 28, 2013.

Manzano, J. S., Weinstein, Z. B., Sadow, A. D., and Slowing, I. I. 2017. "Direct 3D Printing of Catalytically Active Structures." *ACS Cataysis*. 7:7567–7577. doi: 10.1021/acscatal.7b02111.

NGNP Industry Alliance. 2010. "The High Temperature Gas-Cooled Reactor (HTGR)—Safe, Clean and Sustainable Energy for the Future." http://www.ngnpalliance.org/index.php/htgr.

Palma, V., Martino, M., Ricca, A., and Ciambelli, P. 2016. "Structured Catalysts and Support for Membrane Reactors." In *Membrane Reactor Engineering: Applications for a Greener Process Industry*, edited by Basile, A., De Falco, M., Centi, G., and Iaquaniello, G. Wiley.

Petrus, L., and Noordermeer, M. A. 2006. "Biomass to Biofuels, A Chemical Perspective." *Green Chemistry* 8: 861–867. doi: 10.1039/B605036K.

Philbrick, M., Hoffman, B., and Nieves, R. 2017. "Biofuels and Bioproducts from Wet and Gaseous Waste Streams: Challenges and Opportunities," DOE/EE-1472. Prepared for U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Bioenergy Technologies Office. January. https://energy.gov/eere/bioenergy/downloads/biofuels-and-bioproducts-wet-and-gaseous-waste-streams-challenges-and.

Pickard, P. 2008. "Sulfur-Iodine Thermochemical Cycle." Presented at the Department of Energy Hydrogen and Fuel Cells Program 2008 Annual Merit Review, Arlington, VA, June.

Ramesh, S., and Sibul, J. 2007. "Method of Recycling a Recyclable Plastic." U.S. Patent 20070083068, filed October 6, 2006, and published April 12, 2007.

Rezac, M. E. 2000. "Catalytic Membrane Reactors." In *Encyclopedia of Separations Sciences*, *First Edition*, edited by Wilson, I., C. Poole, and M. Cooke. Academic Press, pp. 1676–1682.

Ristanović, Z., Kerssens, M. M., Kubarev, A.V., Hendriks, F. C., Dedecker, P., Hofkens, J., Roeffaers, M. B. J., and Weckhuysen, B. M. 2015. "High-resolution Single-molecule Fluorescence Imaging of Zeolite Aggregates within Real-life Fluid Catalytic Cracking Particles." *Angewandte Chemie International Edition* 127: 1856–1860. doi: 10.1002/anie.201410236.

Ro, K. S., Cantrell, K. B., and Hunt, P. G. 2010. "High-temperature Pyrolysis of Blended Animal Manures for Producing Renewable Energy and Value-added Biochar." *Industrial and Engineering Chemistry Research* 49: 10125–10131. doi: 10.1021/ie101155m.

Roeb, M., Neises, M., Monnerie, N., Sattler, C., and Pitz-Paal, R. 2011. "Technologies and Trends in Solar Power and Fuels." *Energy and Environmental Science* 4: 2503–2511. doi: 10.1039/C1EE01128F.

Coker, E. N., Rodriguez, M. A., Ambrosini, A., Stumpf, R. R., Stecherl, E. B., Wolverton, C., and Meredit, B. 2008. *Fundamental Materials Issues for Thermochemical H2O and CO2 Splitting.* SAND2008-7655. Sandia National Laboratories. Albuquereque, NM: Sandia National Laboratories. http://prod.sandia.gov/techlib/access-control.cgi/2008/087655.pdf.

Sandia (Sandia National Laboratories). 2009. "Sunshine to Petrol," SAND2009-5796P. Sandia National Laboratories Energy, Climate and Infrastructure Security. http://energy.sandia.gov/wp-content/gallery/uploads/S2P_SAND2009-5796P.pdf.

Saric, M., den Exter, M., Motelica, A., Palo, E., Iaquaniello, G., Shabtai, K., and Ricca, A. 2015. "Design and Test Results of Catalytic Membrane Reactors for Steam Methane Reforming." Presented at the Catalytic Membrane Reactors: What's Next? ISPT and CARENA Joint Workshop, Petten, Netherlands, April.

Sattler, C., Monnerie, N., Roeb, M., and Lange, M. 2016. "Solar Thermal Water Decomposition." In *Hydrogen Science and Engineering Materials Processes, Systems, and Technologies, First Edition*, edited by Stolten, D., and Emonts, B. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co.

Schlögl, R. 1991. In *Catalytic Ammonia Synthesis: Fundamentals and Practice*. Edited by Jennings, J. R. Berlin: Springer, p. 19.

Schnitkey, G. 2016. "Anhydrous Ammonia, Corn, and Natural Gas Prices Over Time." Farmdocdaily. University of Illinois at Urbana-Champaign. http://farmdocdaily.illinois.edu/2016/06/anhydrous-ammonia-corn-and-natural-gas-prices.html.

Schrauzer, G. N., and Guth, T. D. 1977. "Photocatalytic Reactions. 1. Photolysis of Water and Photoreduction of Nitrogen on Titanium Dioxide." *Journal of the American Chemical Society* 99: 7189–7193. doi: 10.1021/ja00464a015.

Shell Global. 2017. "Pearl GTL—Overview." http://www.shell.com/about-us/major-projects/pearl-gtl/pearl-gtl-an-overview.html.

Shell Qatar. 2017. "Introduction to Pearl GTL." http://www.shell.com.qa/en_qa/projects-and-sites/pearl-gtl.html.

Simako, D. S. A., Wright, M. M., Ahmed, S., Mokheimer, E. M. A., and Román-Leshkov, Y. 2015. "Solar Thermal Catalytic Reforming of Natural Gas: A Review on Chemistry, Catalysis and System Design." *Catalysis Science & Technology* 5: 1991–2016. doi: 10.1039/C4CY01333F.

Smith, R. 2016. *Chemical Process Design and Integration*. West Sussex, UK: Wiley and Sons, Ltd.

Solar EIS (Solar Energy Development Programmatic EIS Information Center). 2017. "Concentrating Solar Power (CSP) Technologies." Website for public information and involvement in the Programmatic Environmental Impact Statement (PEIS) for Solar Energy Development in Six Southwestern States. http://solareis.anl.gov/guide/solar/csp/.

Steinfeld, A. 2005. "Solar Thermochemical Production of Hydrogen." *Solar Energy* 78: 603–615. doi: 10.1016/j.solener.2003.12.012.

Steinfeld, A., and Weimer, A. W. 2010. "Thermochemical Production of Fuels with Concentrated Solar Energy." *Optics Express* 18: A100–A111. doi: 10.1364/OE.18.00A100.

Stolze, P. 1995. In *Ammonia: Catalysis and Manufacture*. Edited by Nielsen, A. Berlin: Springer, p. 17.

Summers, W. A. 2008. "Hybrid Sulfur Thermochemical Process Development." Presented at the Department of Energy Hydrogen and Fuel Cells Program 2008 Annual Merit Review, Arlington, VA, June.

Taboada, S. 2015. "Small-Scale GTL Technologies on the Brink of Commercialization." http://www.nexant.com/resources/small-scale-gtl-technologies-brink-commercialization.

Tamaru, K. 1991. In *Catalytic Ammonia Synthesis: Fundamentals and Practice*. Edited by Jennings, J. R. Berlin: Springer, p. 1.

Urban, Z. 2016. "Modular and Scalable Fischer-Tropsch Reactor for Small-scale Gas-to-Liquid Production." *Chemical Engineering & Technology* 39: 2142–2150. doi: 10.1002/ceat.201600283.

U.S. Department of Agriculture. 2015. *Biogas Opportunities Roadmap Progress Report*. Joint report from the USDA, EPA, and DOE. https://www.rd.usda.gov/files/Biogas-Roadmap-Progress-Report-v12.pdf.

U.S. Department of Energy, Advanced Manufacturing Office. 2014. *Bandwidth Study on Energy Use and Potential Energy Saving Opportunities in U.S. Chemical Manufacturing*. https://energy.gov/sites/prod/files/2015/08/f26/chemical_bandwidth_report.pdf.

U.S. Department of Energy, Energy Information Administration. 2018. "Natural Gas Prices." https://www.eia.gov/dnav/ng/ng_pri_sum_dcu_nus_a.htm.

U.S. Department of Energy, Office of Science. 2016. "Sustainable Ammonia Synthesis." Roundtable Discussion held by the DOE Office of Science, Dulles, Virginia. February. https://science.energy.gov/~/media/bes/pdf/reports/2016/SustainableAmmoniaReport.pdf.

U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy. 2018. "Hydrogen Production: Thermochemical Water Splitting." https://energy.gov/eere/fuelcells/hydrogen-production-thermochemical-water-splitting

U.S. Environmental Protection Agency, Office of Air and Radiation. 2017. "Energy Efficiency and Cost Saving Opportunities for Ammonia and Nitrogenous Fertilizer Production." Document No. 430-R-17002, Washington, D.C. https://www.energystar.gov/sites/default/files/tools/Fertilizer_guide_170418_508.pdf.

U.S. Geological Survey. 2016. Mineral Commodity Summaries, January. https://minerals.usgs.gov/minerals/pubs/commodity/nitrogen/mcs-2016-nitro.pdf.

Velocys. 2017a. "Microchannel Reactors." http://www.velocys.com/our_technology_core_technologies_reactors.php

Velocys. 2017b. "Super-active Catalysts." http://www.velocys.com/our_technology_core_technologies_catalysts.php

Visvanathan, C. 2010. "Bioenergy Production from Organic Fraction of Municipal Solid Waste (OFMSW) through Dry Anaerobic Digestion." In *Bioenergy and Biofuel from Biowastes and Biomass*, edited by Khanal, S. K., Surampalli, R. Y., Zhang, T. C., Lamsal, B. P., Tyagi, R. D., and Kao, C. M. Reston, VA: American Society of Civil Engineers. doi:10.1061/9780784410899.ch04.

Voegele, E. 2017. "Velocys, British Airways partner on proposed biojet project." *Biomass Magazine*. http://biomassmagazine.com/articles/14688/velocys-british-airways-partner-on-proposed-biojet-project.

Weber, R. S. 2017. Internal document. Pacific Northwest National Laboratory (PNNL).

Weimer, A. 2006. "Development of Solar-powered Thermochemical Production of Hydrogen from Water." Presented at the Department of Energy Hydrogen and Fuel Cells Program 2006 Annual Merit Review, Arlington, VA, May.

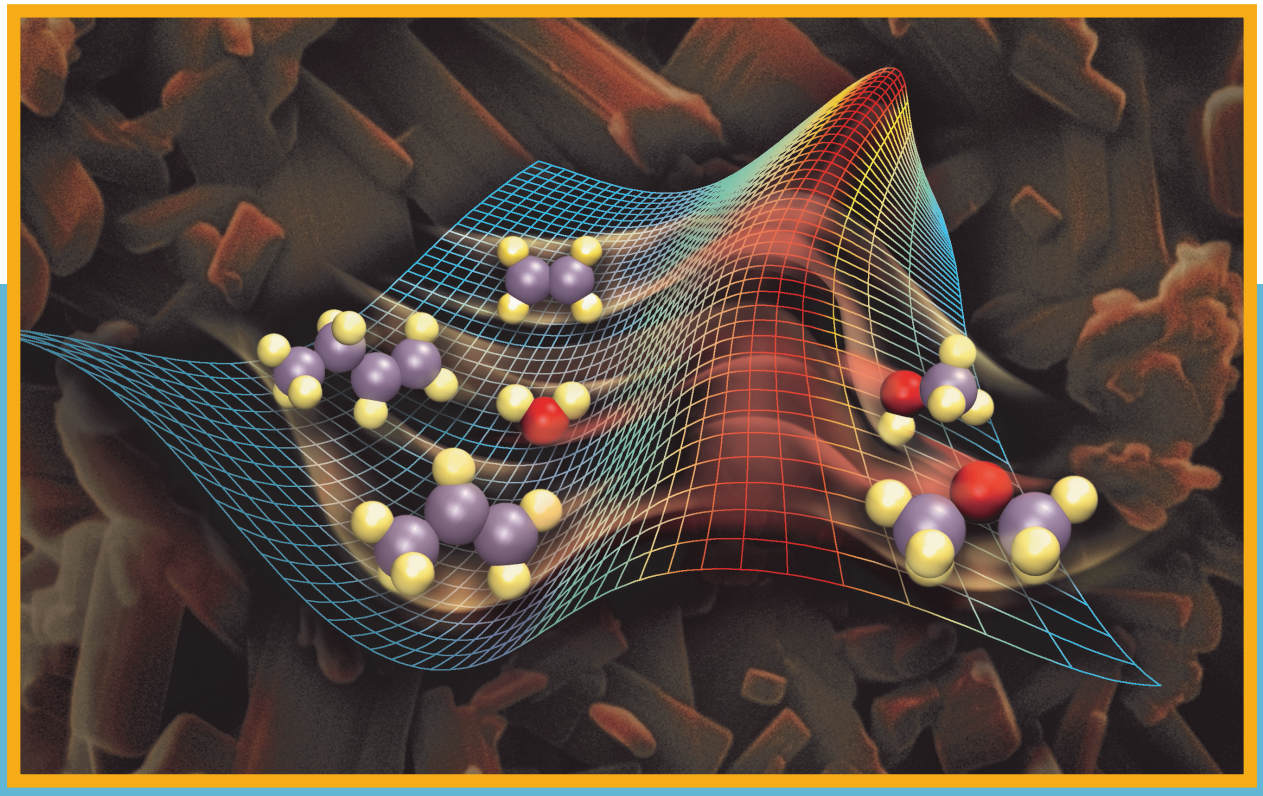
Weisz, P. B. 1982. "The Science of the Possible." *ChemTech* 12: 424–425.

Werpy, T., and Petersen, G. (Editors). 2004. *Top Value Added Chemicals from Biomass. Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas*. NREL/TP-510-35523. By Pacific Northwest National Laboratory (PNNL) and National Renewable Energy Laboratory (NREL). Golden, CO: NREL.

Williams, R., Jr. 1947. "Six-tenths Factor Aids in Approximating Costs." *Chemical Engineering* 54: 24–125.

Wu, H., Liang, Y., Shi, J., Wang, X., Yang, D., and Jiang, Z. 2013. "Enhanced Stability of Catalase Covalently Immobilized on Functionalized Titania Submicrospheres." *Materials Science and Engineering C* 33: 1438–1445. doi:10.1016/j.msec.2012.12.048.

Zheng, R., Diver, R., Caldwell, D., Fritz, B., Cameron, R., Humble, P., TeGrotenhuis, W., Dagle, R., and Wegeng, R. 2005. "Integrated Solar Thermochemical Reaction System for Steam Methane Reforming." *Energy Procedia* 69: 1192–1200. doi: 10.1016/j.egypro.2015.03.204.



DISCLAIMER: This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government.

U.S. DEPARTMENT OF ENERGY | Office of Science