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**PRODUCTION OF CARBON-NEUTRAL HYDROCARBONS FROM CO₂
AND H₂ IN LIEU OF CARBON CAPTURE AND SEQUESTRATION (CCS)**

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ABSTRACT: To ensure an environmentally sustainable future, the problem of CO₂ emissions must be addressed by implementing carbon-neutral energy systems. Carbon Capture and Storage (CCS) is a group of technologies designed to capture CO₂ emissions and sequester them in geological formations. However, CCS is currently hindered by high capital costs and technological challenges. This work discusses the potential to capture CO₂ emissions from power plants and chemically combine them with hydrogen from renewable sources to produce carbon-neutral products. Potentially useful reformed products include methane, methanol, and green biodiesel. Wind, solar, biomass, and nuclear sources show the most future promise as sources of renewable hydrogen. The technological and economic issues involved in the energy input required to produce H₂, capture CO₂, and create hydrocarbons is discussed.

INTRODUCTION

One of the top environmental issues humanity now faces is CO₂ emissions from fossil fuel combustion. The global climate change associated with the accumulation of CO₂ in the atmosphere poses serious long-term risks¹. To ensure an environmentally sustainable future, this problem must be addressed by developing and implementing carbon-neutral energy systems that do not increase atmospheric CO₂ levels². With fossil fuels currently being the most available and cost-effective energy sources, there are many economic, political, and technological barriers to achieving carbon-neutral status. Carbon Capture and Storage (CCS) is a group of technologies designed to capture CO₂ from entering the atmosphere. We discuss the potential for producing carbon-neutral hydrocarbons from CO₂ emissions rather than sequestering the emissions in geological formations, as well as methods of producing renewable hydrogen.

CARBON CAPTURE AND STORAGE

The goal of Carbon Capture and Storage (CCS), also known as carbon capture and sequestration, is to prevent carbon dioxide from being emitted to the atmosphere. The concept of CCS is to first trap the CO₂ released from power plants and industrial processes, to transport the CO₂ often using pipelines, and to inject the supercritical CO₂ for storage into geological formations several kilometers below ground.³ The geologic formations available for carbon sequestration include saline aquifers, depleted oil and gas reservoirs, and un-mineable coal seams.² CCS projects mainly focus on electricity production; the industry that accounts for about 38% of CO₂ emissions in the USA.⁴ The CCS process typically reduces power plant efficiency by about 20-30% to capture 85% of the plant's CO₂ emissions;⁵ and reduced power output increases the electricity cost. There are also safety concerns about CCS among the public and scientific communities.⁶

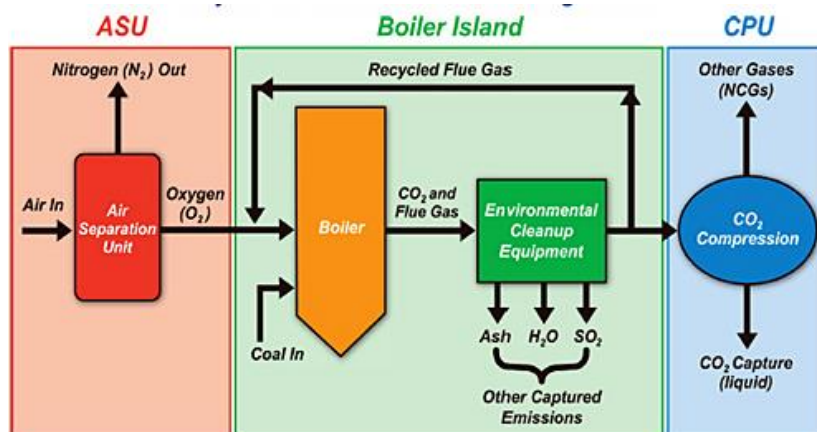


Figure 1. Proposed Oxy-Combustion clean-coal technology with Carbon Capture and Storage (CCS) for the Meredosia FutureGen 2.0 project in Illinois, USA. Source: FutureGen 2.0

The major expense of CCS lies in the large quantities of equipment needed to trap, condense, transport, and bury the CO₂. According to a 2012 paper from the USA Congressional Budget office, the Levelized Cost Of Energy (LCOE) of a new coal plant equipped with CCS is between \$90 to \$150 per megawatt-hour (MW.hr), or \$0.09 to \$0.15 per kilowatt-hour (kW.hr).⁷ Both the average capital cost and the LCOE of a coal plant with CCS would be 76% higher than a conventional plant.⁷ At this point in time, without government incentives and subsidies, CCS technology cannot become economically feasible.⁸

Approximately eight industrial-scale CCS projects are proceeding with federal support in the USA, including the \$200 million Illinois Industrial Carbon Capture and Storage project in Decatur, Illinois; the \$2.88 billion Kemper Integrated Gasification Combined Cycle plant in Kemper County, Michigan; the \$2.5 billion Texas Clean Energy Project in Penwell, Texas; the \$2.8 billion Hydrogen Energy California Project in Bakersfield, CA; and the \$1.65 billion FutureGen 2.0 project in Meredosia, Illinois.⁹ Considering the frequency of delays in these CCS

projects and the cancelations of prior projects such as FutureGen 1.0, it is uncertain if the plants will be operational by the projected completion dates in the coming decades.

CARBON NEUTRAL CONCEPT

For CCS to accomplish reductions in CO₂ emissions effectively it is important to focus on the goal of being near carbon-neutral, meaning able to capture 90% or more of the fossil carbon in the fuel.¹⁰ A carbon-negative project that is able to capture CO₂ directly from the air or from biomass, is an idealistic solution but will not be addressed in this work. Chalmers and Gibbons¹⁰ classify the capture CO₂ from gaseous and liquid fuel production (e.g., petroleum or natural gas refining) as carbon-positive, considering that the product fuel will probably release carbon emissions. These classes of CCS projects are important to distinguish, for long-term developments to be most beneficial.

Rapid actions must be taken if climate change is to be moderated. Assuming that the threshold for safe emission is an additional 500 to 1,000 Gigatons of CO₂, Chalmers and Gibbons¹⁰ suggest that this threshold can easily be overshoot with the volume of affordable fossil fuels that can be produced. In this light, the proposed use of CCS is complex in nature. By using CCS technology, fossil fuels can continue to be used, ideally preventing the accumulation of CO₂ emissions in the atmosphere.¹⁰ However, if the real solution to the environmental problem is to invest in renewable sources of energy, CCS is only a crutch to keep fossil fuels in use.

POTENTIAL HYDROCARBON PRODUCTS

A significant portion of the costly technology of CCS goes toward transporting and sequestering the CO₂ underground. Rather than attempting to store the emissions in geological formations, which is no guarantee against leaks that would release CO₂ into the atmosphere anyway, it may be possible to convert the CO₂ into useful products. For example, CO₂ can be reacted with hydrogen to create hydrocarbons. For instance, the Sabatier reaction could be used to create methane, CH₄. Ideally, the hydrogen would be generated from water using non-carbon sources as described later. Although the combustion of the product hydrocarbon would release the CO₂ back into the atmosphere, this creates a carbon-neutral, relatively clean-burning fuel cycle.

The Sabatier reaction shown in Eq. 1 ($\Delta H_{298} = -165$ kJ/mol) is a well-established process for producing methane by reacting CO₂ with H₂ over a metal catalyst, the most effective catalysts being nickel and ruthenium.¹¹



The Sabatier process is most commonly used for the purification of H₂ for ammonia manufacture and fuel cells, and also for removing CO₂ from confined spaces such as submarines and spacecraft. There has been consideration of the possible use of Sabatier methanation to reduce

power plants' CO₂ emissions. The main challenge with this application is the need for large volumes of economically-produced, renewably-sourced H₂.¹²

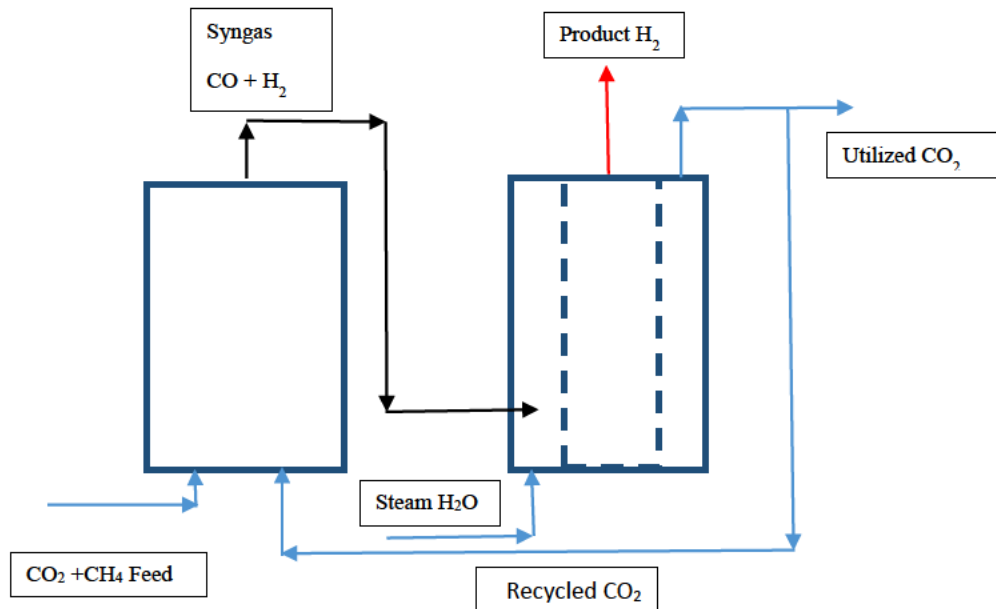


Figure 2. Hydrogen production using the CO₂ dry reforming process

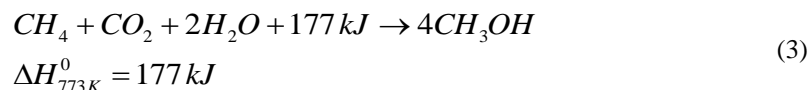
METHANOL PRODUCTION

Another potentially useful product that could be made from reformed CO₂ is methanol, CH₃OH. Methanol is an important chemical feedstock and alternate fuel source, with fewer toxic emissions than gasoline. Although methanol is typically generated from CO, CO₂, and H₂ over a Cu/ZnO/Al₂O₃ catalyst, CO₂ can be directly hydrogenated to methanol in a one-step conversion.¹³ Researchers at the University of Texas at Arlington generated methanol directly from CO₂ with a 95% efficiency, using sunlight and copper oxide nanorods.¹⁴ Another research group at the Universidade Federal do Paraná in Brazil designed and simulated a methanol plant that would use CO₂ captured from flue gases of a coal power plant and hydrogen generated from water electrolysis.¹³ This plan could be retrofitted (at great cost) to existing coal power plants, although CO₂ capture units significantly decrease plant efficiencies.⁸ At the present time conversion of CO₂ to methanol seems uneconomic;¹⁵ however, the proposal for using existing fossil fuel supplies with less environmental harm is promising.³⁰⁻³²

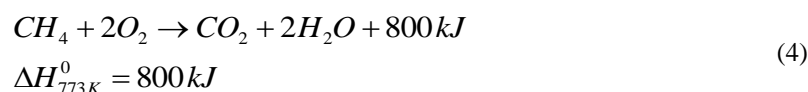
A first step involves the formation of synthesis gas via the combined steam and CO₂ reforming of CH₄:



Following the reforming step, methanol is synthesized by reacting the resultant synthesis gas. The overall process can be described as:



At a heat efficiency of the system of 80 percent, the energy needed to drive the reaction increases to 221 kJ. For 1 mole of CO₂ to be consumed a heat input of 221 kJ is needed from an external source by burning natural gas:



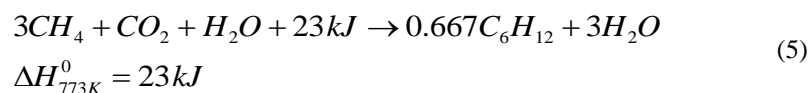
In this case 0.34 moles of CO₂ will be released so as to provide the required energy to drive the overall methanol synthesis reaction. The overall amount of CO₂ consumed in the methanol synthesis process is 0.66 moles per mole of CO₂ consumed by the initial reforming of CH₄.

Methanol is a useful commodity with a worldwide annual production of 30 x 10⁶ million metric tonnes. Methanol is synthesized in a process where synthesis gas is produced solely by the steam reforming of CH₄. If all the methanol production in the world were to be shifted to a process which combined CO₂ and steam reforming, 10 million tonnes of CO₂ could be consumed corresponding to the mitigation of 6.6 x 10⁶ metric tonnes of CO₂ annually. Unfortunately, this amount is insignificant in comparison to the global CO₂ emissions. Excluding deforestation and land use change, CO₂ emissions amounted to 23.9 x 10⁹ metric tonnes in 1996.

SULFUR-FREE GREEN DIESEL FUEL

To take the methanol product a step further, methanol can be utilized for the production of biodiesel. Biodiesel, which is synthesized by trans-esterification of vegetable oils with methanol to form fatty acid methyl esters, is a renewable diesel fuel substitute.¹⁶ Biodiesel yields 93% more energy than the amount invested in its production, and biodiesel emits only 1.0%, 8.3%, and 13% of the agricultural nitrogen, phosphorus, and pesticide pollutants, respectively, per net energy gain as compared to ethanol.¹⁷ Because biodiesel production is limited by the high cost of the vegetable oils, the additional energy required to produce the methanol from CO₂ is most likely cost prohibitive.³⁰⁻³²

The first step involves the reforming of CH₄ to produce synthesis gas while in the second step the resulting synthesis gas is reacted to produce the diesel fuel:



With an energy efficiency of 80 percent, the energy required to drive the reaction is 28.8 kJ. This energy can be supplied by burning CH₄ at the expense of 0.05 moles of CO₂ per mole of CO₂ consumed in the Fischer-Tropsch process.

RENEWABLE HYDROGEN SOURCES

Currently, about 95% of hydrogen production is powered by non-renewable, carbon-based sources.¹⁸ We describe and compare a few methods for producing hydrogen from renewable sources.

A 2007 study by the USA Department of Energy's National Renewable Energy Laboratory (NREL) concluded that wind, solar, and biomass resources in the USA could be used to produce about 1 billion metric tons of hydrogen per year. In the Great Plains region and central USA states, wind is the leading resource for hydrogen production, whereas solar is the dominant resource in most other regions, especially in the Southwest. A few population-dense counties, such as the Miami and New York City areas, have high potential to produce hydrogen from biomass due to the greater generation of waste. The research study proposes that renewable hydrogen can potentially displace gasoline consumption in most USA states. However, many challenges must be overcome to achieve sustainable hydrogen-based transportation. The USA lacks an infrastructure to support country-wide use of hydrogen fuel. Areas with high energy demand would need to rely on resources from other locations. Another important concern is that renewably-sourced hydrogen production comes with multiple technical and economic difficulties.¹⁹

Electrolysis involves passing electricity between two electrodes to break water molecules into H₂ and O₂. Electrolysis produces a clean fuel because no CO₂ or NO_x is produced;²⁰ however, electrolysis is quite expensive, costing approximately 80% of the operating cost of hydrogen production.²¹ A few types of electrolytic cells have been developed. Solid Oxide Electrolysis Cells (SOEC's) perform high temperature electrolysis, operating at high temperatures near 800 °C and using thermal energy from concentrated solar, nuclear power, or industrial waste heat.²² Polymer Electrolyte Membrane cells (PEM's) are relatively simple, operate below 100 °C, and accept a range of voltage inputs; thus, PEM's are ideal for renewables like wind or solar photovoltaic.²³ The third kind is Alkaline Electrolysis Cells (AEC's) that use high concentrations of electrolytes and operate at high temperatures near 200 °C.²³

If the electricity used to power electrolysis is renewable, the hydrogen can be considered as renewably produced.²⁴ In particular, wind and biomass are promising sources of electricity for electrolytic hydrogen production.

Advances in wind power have reduced the cost of utility-scale wind electricity to 3-7 cents per kW.hr, making wind electrolysis an attractive option.²⁴ Wind electrolysis involves the wind turning a wind turbine containing an electrical generator, which can power an electrolyzer to dissociate water into O₂ and H₂. A potential advantage of wind electrolysis systems is the improved ability to dispatch electricity; that is, the wind turbine can produce hydrogen to store energy, later using a fuel cell to create electricity in high-demand periods. For wind electrolysis to become cost-effective, there will need to be a decrease in wind electricity prices, increase in electrolyzer efficiency, and an increased effort to integrate wind/electrolyzer systems.²⁴

According to the National Renewable Energy Laboratory (NREL), biomass is one of the favorable options for the near-term renewable production of hydrogen.²⁴ Biomass resources from agriculture, forests, and consumer wastes are plentiful in the USA. The thermochemical processes of gasification and pyrolysis are used to break down the cellulose, hemicellulose, and lignin in the resources to produce hydrogen. Gasification involves vaporizing the volatile biomass components to yield CO₂ and H₂. Pyrolysis involves anaerobic degradation of the biomass to char, bio-oil, and gases, followed by steam reforming of the bio-oil and gases to form CO₂ and H₂. NREL is working to demonstrate pyrolysis and gasification, which are currently not cost-competitive, for large-scale applications.²⁴

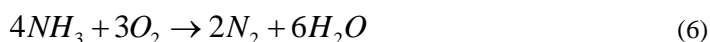
Nuclear energy can produce both electricity and hydrogen. The Very High Temperature Reactor (VHTR) reactor design that can be utilized for the manufacture of hydrogen. The VHTR is a Generation IV reactor concept being developed by the Idaho National Engineering and Environmental Laboratory (INEL). The VHTR is a helium-cooled and graphite-moderated thermal neutron spectrum reactor. High output temperatures of 1,000°C or higher allow for process heat or hydrogen production applications. Hydrogen production by the VHTR could efficiently be accomplished by applying the heat to a thermochemical sulfur-iodine cycle.²⁵

The cost of renewable hydrogen is currently high, and it will take several decades to significantly reduce it to the point of being cost-competitive with carbon-based hydrogen production. However, wind, solar, biomass, and nuclear sources are strong options for renewable, carbon-free hydrogen production.

USE OF AMMONIA IN A NITROGEN-BASED ECONOMY

As 78% of dry air is composed of nitrogen gas, the concept of a nitrogen economy rather than a hydrogen economy is worth consideration. Nitrogen, like hydrogen, is a plentiful gas that can be used as an energy carrier. Separating nitrogen from the air typically involves cooling air to about -196 °C / -320 °F in order to liquefy it.²⁶ By fractional distillation processes, liquid nitrogen can be isolated from the other components of air, based on boiling points levels.

A useful nitrogen-containing chemical is ammonia, NH₃. A steam cycle system can utilize ammonia to drive a turbine and generate electricity²⁷. Ammonia could also be directly combusted for fuel to release energy in internal combustion engines as in Eq. 2, ($\Delta H^\circ = -1,267.20 \text{ kJ/mol}$).²⁸



A nitrogen economy could have advantages over a hydrogen-based economy. Delivering energy using hydrogen typically relies on expensive hydrogen fuel cells. In contrast, nitrogen can potentially deliver energy in ammonia steam cycles or internal combustion engines. Storage and transportation may be easier for ammonia than hydrogen, as ammonia can be stored in solutions and as liquid anhydrous ammonia. Although both ammonia and hydrogen are highly reactive, ammonia is a more stable compound than hydrogen. However, aqueous and gaseous ammonia are classified as highly corrosive and toxic, which makes containment and safety precautions very important.²⁹ Overall a nitrogen economy concept may have potential benefits.

CONCLUSIONS

Economics will play an important role in shaping the energy sources of the future. While carbon-based energy sources are foreseeably the most economically available in the near- to mid-term future, concern for the environmental impact is growing. In order to allow the continued use of fossil fuels with less detriment, technologies such as Carbon Capture and Storage (CCS) are being developed at high capital costs and with great technological challenges. Although currently cost-prohibitive, it is possible to capture CO₂ emissions from power plants and chemically combine them with renewable hydrogen to produce carbon-neutral products. Potentially useful reformed products include methane, methanol, and biodiesel. Technological hurdles involve the challenge is the development of an economic and stable catalyst suitable for use in commercial scale plants. An important issue is the cost effective capturing of CO₂ from 24 x 10⁶ metric tons of gas emissions each year from fossil fuels.

If current CO₂ capturing cost could be reduced by 35-40 percent CO₂ and natural gas reforming can be potentially sustainable from CO₂ recovered from flue gases. Wind, biomass, and nuclear show the most future promise as sources of renewable hydrogen. Due to the energy input required to produce H₂, capture CO₂, and create hydrocarbons, this proposal has admittedly a net energy loss. Ultimately, if the cost of renewables can compete with the cost of carbon energy using CCS methods, the departure from fossil fuel dependence will happen all the more rapidly.

REFERENCES

1. Veziroglu, T. N., "Hydrogen Technology for Energy Needs of Human Settlements," *International Journal of Hydrogen Energy*, Vol. 12, pp. 99–129, 1987.
2. Muradov N. Z., and Veziroglu T. N., "Green Path from Fossil-Based to Hydrogen Economy: An Overview of Carbon-Neutral Technologies," *International Journal of Hydrogen Energy*, Vol. 33, No. 23, pp. 6804-6839, Dec. 2008.
3. United States Environmental Protection Agency (EPA), "Carbon Dioxide Capture and Sequestration," Sept. 2013. <http://www.epa.gov/climatechange/ccs/>

4. United States Environmental Protection Agency (EPA), "Overview of Greenhouse Gases," Sept. 2013, <http://www.epa.gov/climatechange/ghgemissions/gases/co2.html>
5. International Energy Agency, IEA Energy Technology Essentials, vol. ETE01, Dec. 2006.
6. Steinberg, M., "Fossil fuel Decarbonization Technology for Mitigating Global Warming," *International Journal of Hydrogen Energy*, Vol. 24, pp. 771, 1999.
7. Congress of the United States Congressional Budget Office, "Federal Efforts to Reduce the Cost of Capturing and Storing Carbon Dioxide," Pub. No. 4146, June 2012.
8. Integrated CO₂ Network, "10 Things You Should Know About Carbon Capture and Storage (CCS)," Nov. 2011.
9. Jacobsen, L., "Despite Notable Hurdles, Plants That Sequester Carbon Are Advancing," *Politifact*, Dec. 2012.
10. Chalmers H. and Gibbins J., "Carbon Capture and Storage: More Energy or Less Carbon?" *Journal of Renewable & Sustainable Energy*, Vol. 2, Issue 3, pp. 031006, May 2010.
11. Yaccato *et al.*, "Competitive CO and CO₂ Methanation Over Supported Noble Metal Catalysts in High Throughput Scanning Mass Spectrometer," *Appl. Catal. A-Gen.*, Vol. 296, pp. 30–48, 2005.
12. Hoekman, S. K., Broch, A., Robbins, C., and Purcell, R., "CO₂ Recycling by Reaction With Renewably-Generated Hydrogen," *International Journal of Greenhouse Gas Control*, Vol. 4, No. 1, pp. 44-50, 2010.
13. Van-Dala, E. S., and Bouallou, C., "Design and Simulation of a Methanol Production Plant From CO₂ Hydrogenation," *Journal of Cleaner Production*, Vol. 57, pp. 38-45, Oct. 2013.
14. Govers, F. X., "Simpler, cheaper way to make liquid methanol fuel using CO₂ and sunlight," *Gizmag*, April 2013.
15. Cifre, P. G., Badr, O. "Renewable Hydrogen Utilization for the Production of Methanol," *Energy Convers. Management*, Vol. 48, pp. 519–527, 2007.
16. Ma, F., Hanna, M. A., "Biodiesel Production: A Review," *Bioresour. Technol*, vol. 70, pp. 1–15, 1999.
17. Hill, J., Nelson, E., Tilman, D., Polasky, S., Tiffany, D., "Environmental, Economic, and Energetic Costs and Benefits of Biodiesel and Ethanol Biofuels," *Proceedings of the National Academy of Sciences of the United States*, Vol. 103, No. 30, July 2006.
18. Ogden J. M., "Prospects for Building a Hydrogen Energy Infrastructure," *Annual Review of Energy and the Environment*, Vol. 24, pp. 227–279, 1999.
19. Milbrandt, A., and Mann, M., "Potential for Hydrogen Production from Key Renewable Resources in the United States," National Renewable Energy Laboratory Technical Report NREL/TP-640-41134, Feb. 2007.
20. Armor, J. N., "The Multiple Roles for Catalysis in the Production of H₂," *Applied Catalysis A: General*, Vol. 176, pp. 159–176, 1999.
21. Chaubey R. *et al.*, "A Review on Development of Industrial Processes and Emerging Techniques for Production of Hydrogen from Renewable and Sustainable Sources," *Renewable & Sustainable Energy Reviews*, Vol. 23, pp. 443-462, July 2013.
22. Hauch, A., Ebbesen, S. D., Jensen, S. H., and Mogensen, M., "Highly Efficient High Temperature Electrolysis," *Journal of Materials Chemistry*, Vol. 18, No. 20, pp. 2331–2340, 2008.

23. Clarke, R. E., Giddey, S., Ciacchi, F. T., Badwal, S. P., Paul, B., and Andrews, J., "Direct Coupling of an Electrolyzer to a Solar PV System for Generating Hydrogen," *International Journal of Hydrogen Energy*, Vol. 34, No. 6, pp. 2531–2542, 2009.
24. National Renewable Energy Laboratory, "New Horizons for Hydrogen," National Renewable Energy Laboratory 2003 Research Review, Issue 2, pp. 2–9. April 2004.
25. Ragheb, M. "Fourth Generation Reactor Concepts," Nuclear, Plasma and Radiation Science - Inventing the Future, pp. 4-6, Mar 2013, [http://www.mragheb.com/NPRE 402 ME 405 Nuclear Power Engineering/index.htm](http://www.mragheb.com/NPRE_402_ME_405_Nuclear_Power_Engineering/index.htm).
26. National Center for Biotechnology Information, "Nitrogen – Compound Summary," PubChem, <http://pubchem.ncbi.nlm.nih.gov/summary/summary.cgi?cid=947>, 2009.
27. Erickson, D. C., "Water Conserving Steam-Ammonia Power Cycle," Energy Concepts Co, DOE SBIR Phase II Project, DE-FG02-05ER84201, Oct. 2008.
28. Greenwood N. N., and Earnshaw, A., "Chemistry of the Elements." Oxford: Pergamon Press. pp. 485, 1984.
29. Agency for Toxic Substances and Disease Registry, "Toxic FAQ Sheet for Ammonia," <http://www.atsdr.cdc.gov/tfacts126.pdf>, Sept. 2004.
30. Aresta, M. and Tommasi, I., "Energy Conversion Management," 38, S373, 1997.
31. Tijm, P. J. A., Waller, F. J., and Brown, D. M., "Methanol Technology Developments for the New Millennium," *Appl. Catal. A: Gen.*, 221, 275, 2001.
32. Treacy, D., and Ross, Julian R. H. "The Potential of the CO₂ Reforming of CH₄ as a Method of CO₂ Mitigation. A Thermodynamic Study," *Am. Chem. Soc., Div. Fuel Chem.*, 49(1), 127, 2004.