

Hydrogen Generation with Limited Carbon Emissions



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Outline

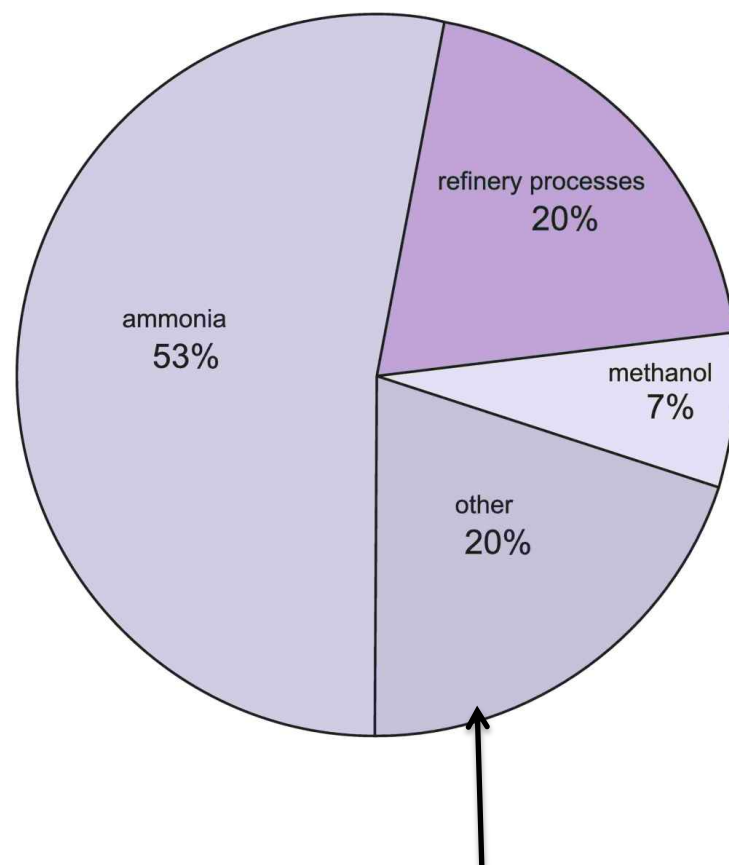
- Hydrogen production and uses
- Conversion of methane to hydrogen and graphite using iron ore catalysis

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Uses of Hydrogen

- Industrial chemistry
 - Production of ammonia: Haber process: $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$
- Petroleum Refineries:
 - Cracking long carbon chains into smaller ones by introducing hydrogen.
 - Lowering sulfur content of fuels by forming hydrogen disulfide (H_2S).
- Production of methanol.
 - Used as a feedstock for plastics and other applications.

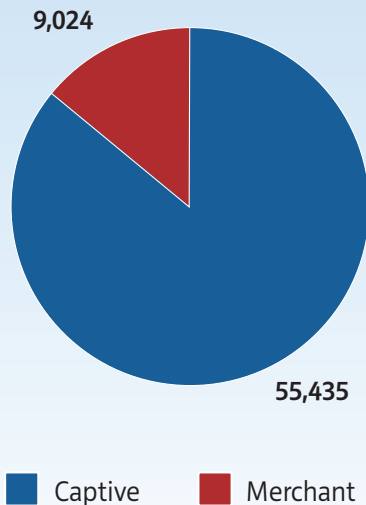


<5% used for energy applications (e.g. fuel cells)

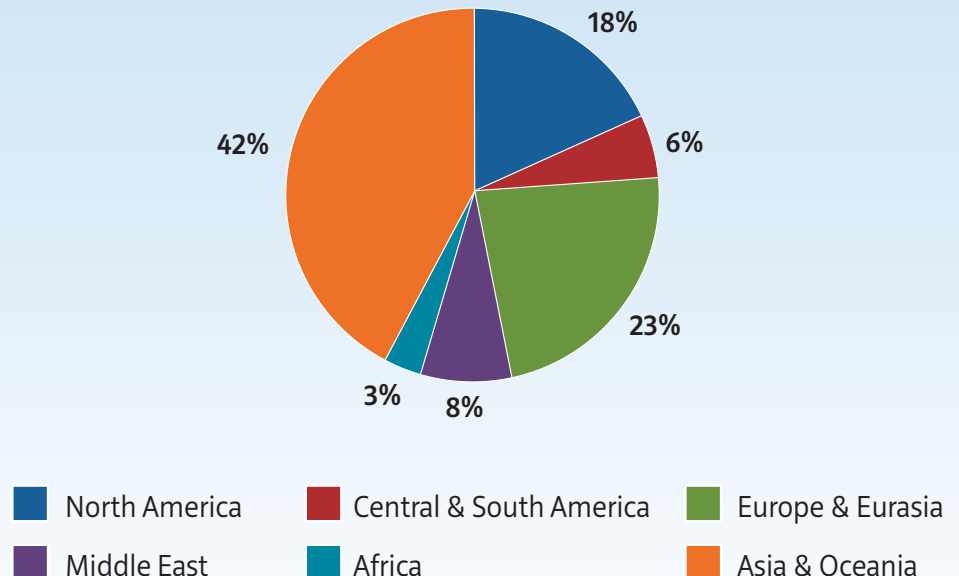
Hydrogen Market

- Current global hydrogen production: 65 million metric tons per year (1 metric ton = 1000 kg)
- Global hydrogen market is estimated to be worth over \$US100 billion in 2016 and growing to \$US152 billion by 2021.

Global Hydrogen Market (by distribution)
(million metric tonnes, 2014)

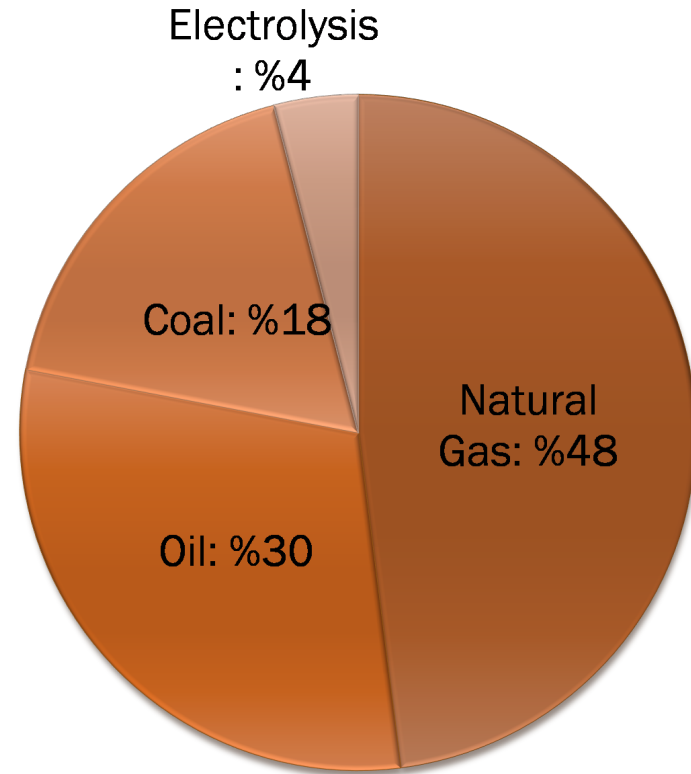


Global Hydrogen Production (by region)
2014 (est)



Current Hydrogen Production

- Steam methane reform (SMR) or natural gas reforming
 - Most common method of producing bulk hydrogen (95%)
 - Taken from natural gas (i.e. methane) procured from mining or from coal and oil.
- Sources of methane:
 - Natural gas
 - Breakdown of coal and oil in chemical processes.



Sources of World H₂ Production

- Electrolysis – water splitting to form hydrogen and oxygen.
 - Only for specific point of use application

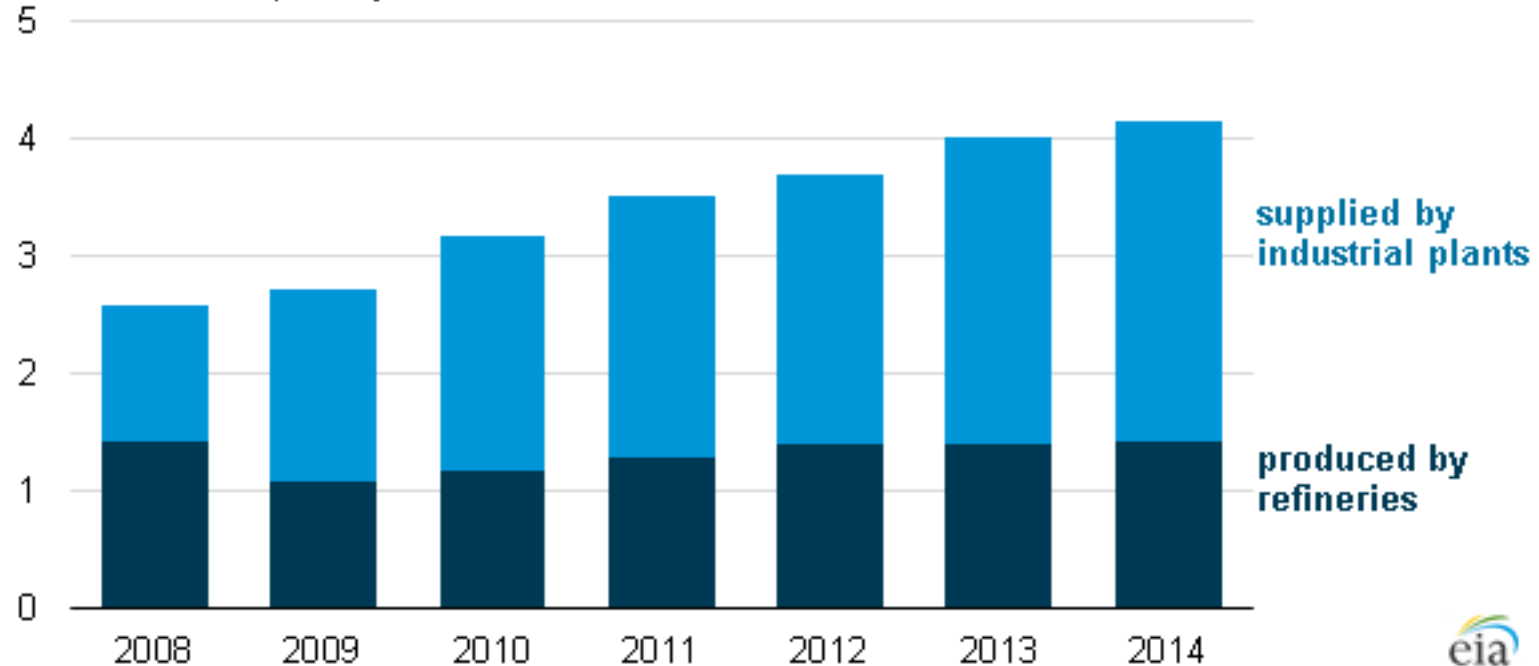
Steam methane reform

- Reaction #1: Gasification:
 - $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$
 - High temperature (700 – 1100 C)
 - Nickel catalyst.
 - Endothermic reaction: $\Delta H_r = 206 \text{ kJ/mol}$
- Reaction #2: Water gas shift reaction:
 - $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$
 - Moderate temperature (360C)
 - Iron ore catalyst.
 - Exothermic reaction: $\Delta H_r = -41 \text{ kJ/mol}$
- Net reaction requires energy input

U.S. Refinery Demand of Hydrogen

U.S. refinery demand for hydrogen (2008–14)

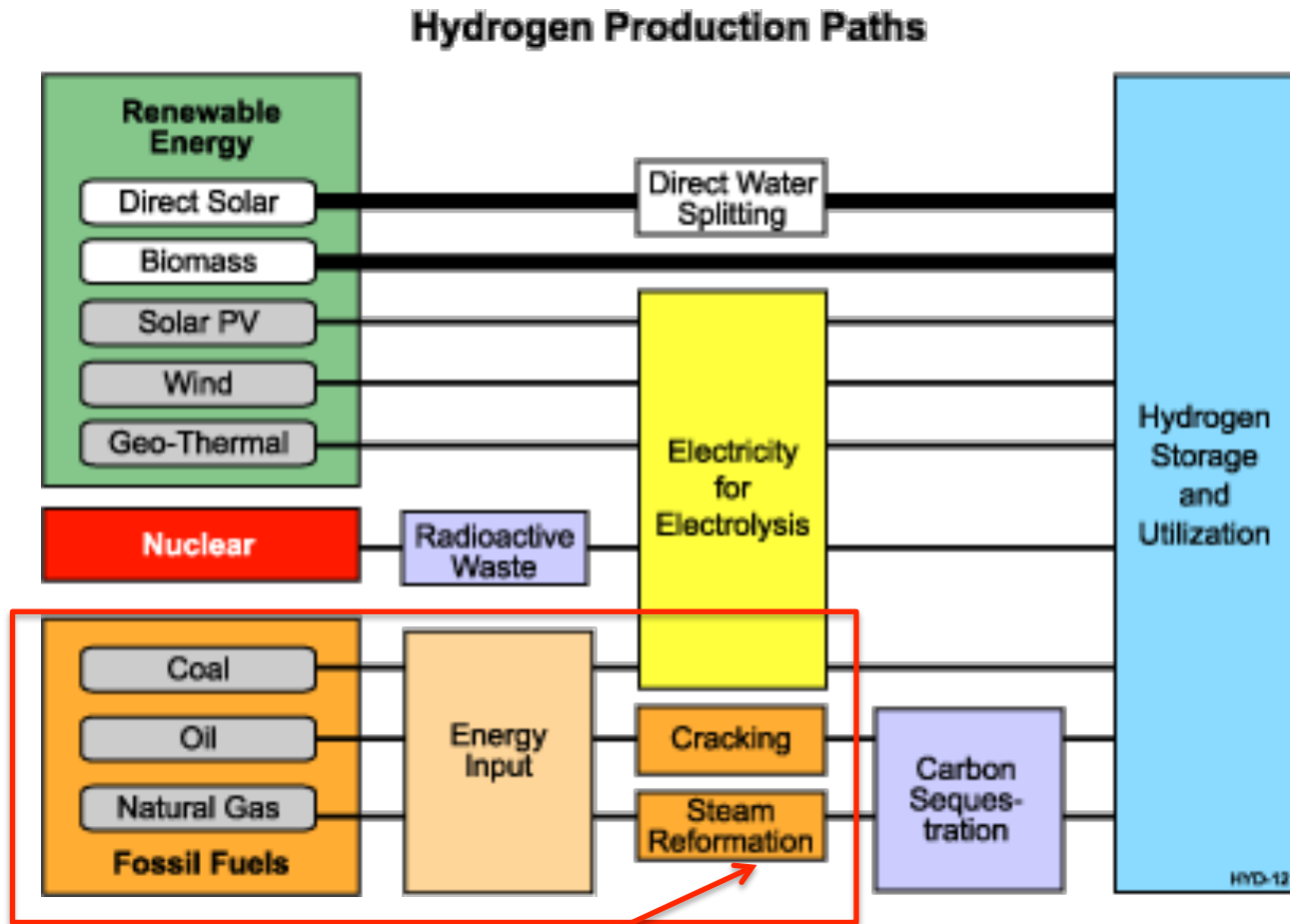
billion cubic feet per day



- Negligible change in H₂ production by refineries.
- Increased demand from industrial plants.

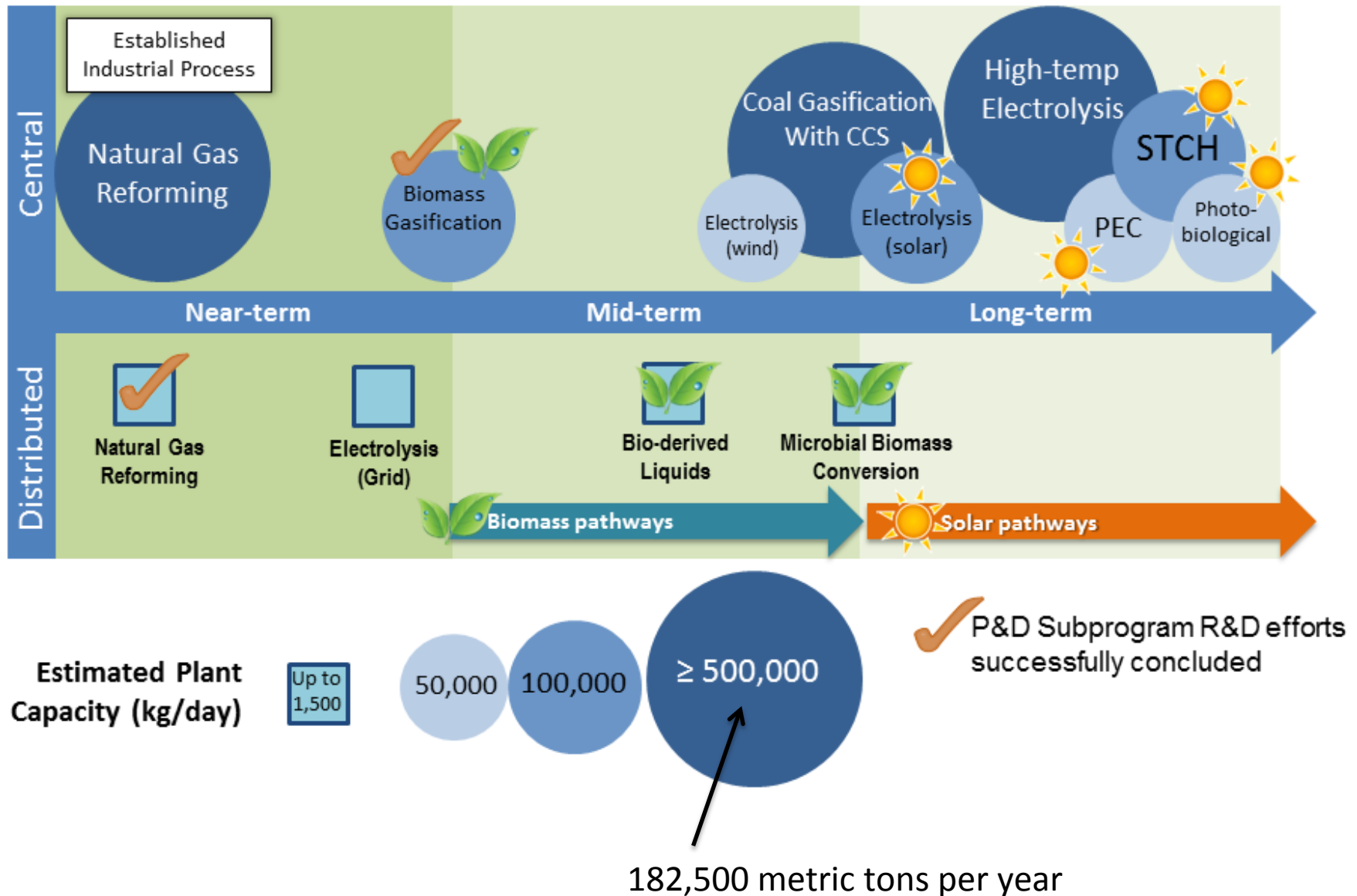
4 billion cubic feet = 9,450 metric tons per day =
3,450,000 metric tons per year = 3.45 million metric tons per year

Alternative Hydrogen Production Paths



Conventional steam reformation is the one current large scale method of hydrogen production.

Hydrogen Production



Outline

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- Conversion of methane to hydrogen and graphite using iron ore catalysis

Hazer Process to Form Hydrogen

- Alternative Reaction: Decomposition
 - $\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$
 - Catalyst: Unprocessed iron ore
 - Moderate temperatures (800-900 C)
 - Moderate pressures (0 – 8 bar).
 - Endothermic: $\Delta H_r = 74.81 \text{ kJ/mol}$
- Primary benefits:
 - Limited CO_2 production
 - Disposable catalyst – don't need to chemically remove graphite from iron ore to reuse catalyst.
- Other considerations: Still requires fossil fuels as feedstock to produce hydrogen and graphite.

Hazer Process to Form Hydrogen – Patent Application

- Previous methods:
 - Conversion efficiency to carbon is low.
 - Catalysts are quickly deactivated, stopping the reaction.
 - Catalyst lifetime is only a few hours.
 - The higher the conversion efficiency, the quicker the catalyst is depleted.
 - Carbon generated is amorphous and not useful and hard to dispose of.

Hazer Process to Form Hydrogen – Patent Application

- New method:
 - Use iron oxide catalysts under different temperature and pressure conditions.
 - Product #1: Hydrogen
 - Product #2: Carbon comprising graphitic particles including spherical and onion-like graphitic particles which can disassociate from the catalyst during the conversion process → reduces buildup of carbon product on catalyst to stop reaction.
 - Conversion efficiency sustainable for > 50 hours.
- 1 metric ton of iron ore used as a catalyst can produce 10 metric tons of hydrogen.
 - Iron ore 2016 US price: \$50-60 per dry metric ton
 - Nickel 2016 US price: \$9,000 to \$10,000 per metric ton

<http://patents.com/us-20160156051.html>

<https://www.theguardian.com/sustainable-business/2016/jul/22/cheap-and-clean-australian-company-creates-hydrogen-with-near-zero-emissions>

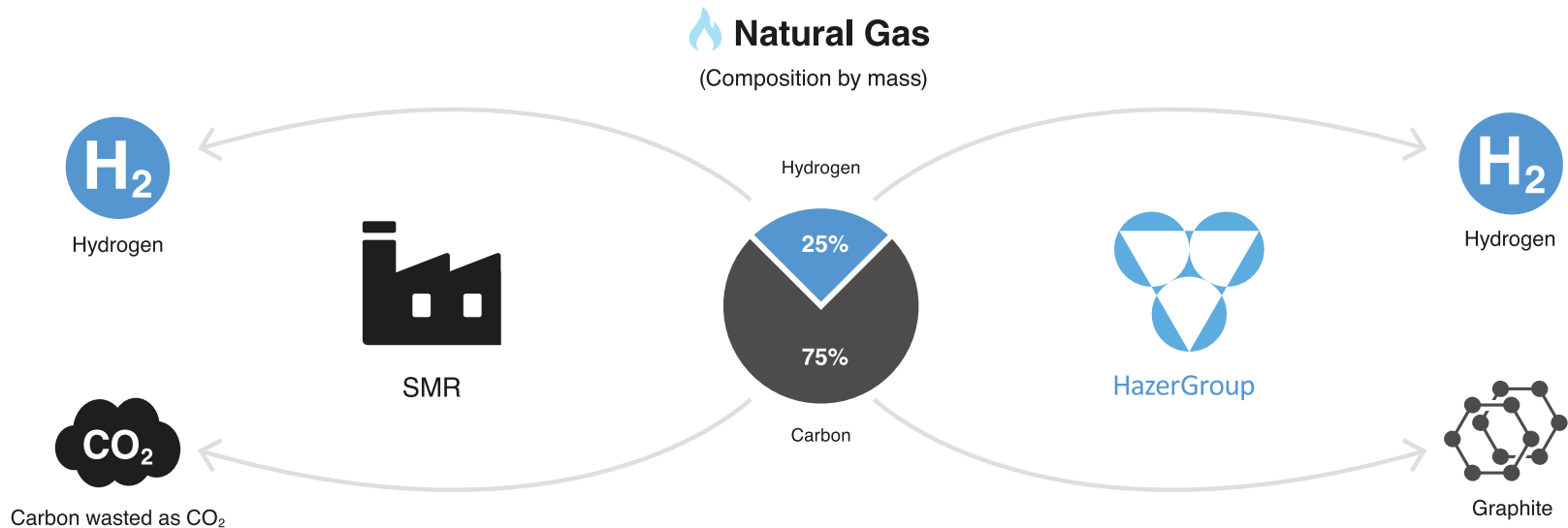
<http://www.indexmundi.com/commodities/?commodity=iron-ore>

<http://www.indexmundi.com/commodities/?commodity=nickel>

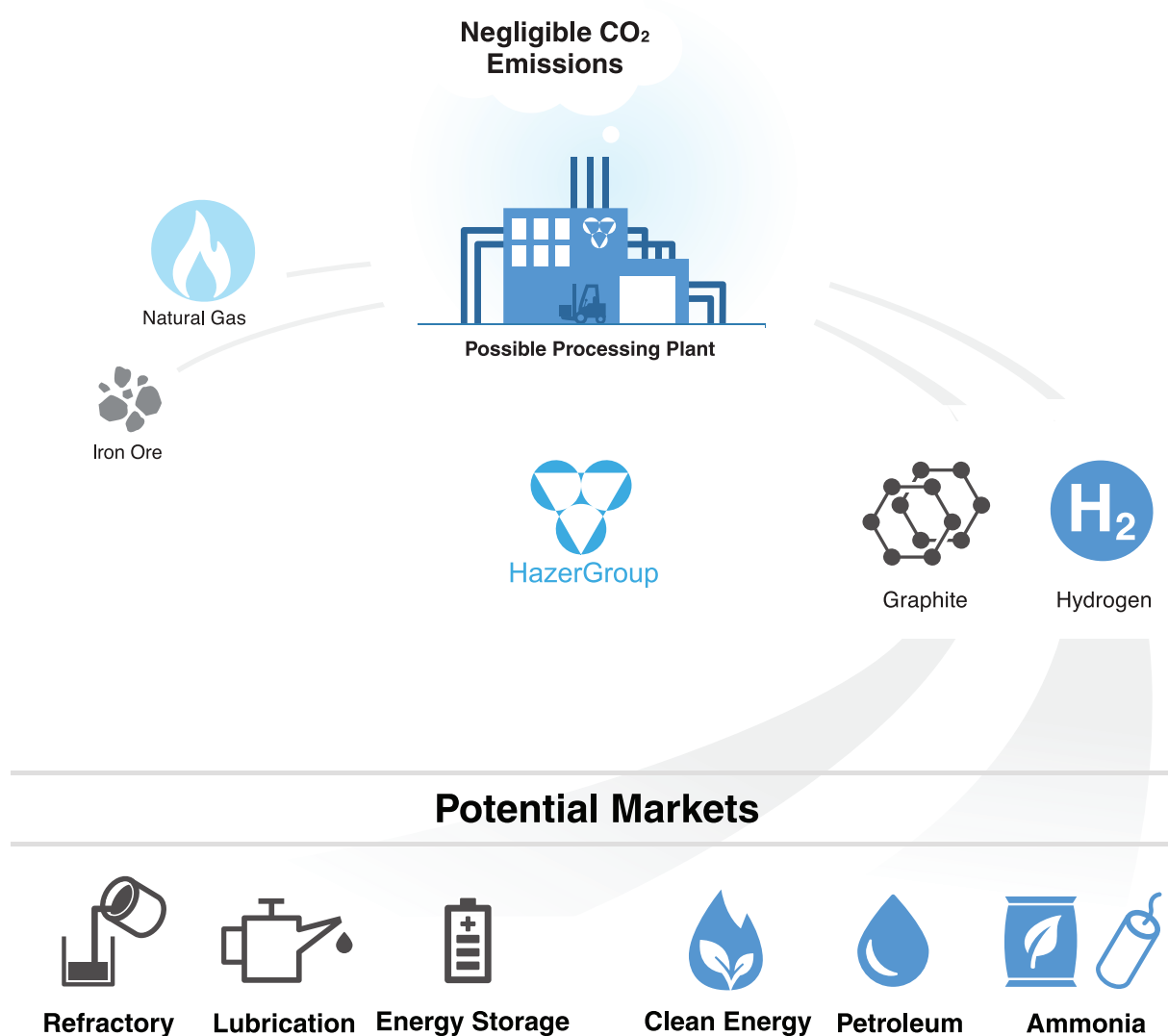
HazerGroup Ltd Business Plan

- Uses natural gas and unprocessed iron ore to form hydrogen and synthetic graphite.
- **Goal #1: halving the cost of hydrogen production from \$1 to \$1.50, down to \$0.50 to \$0.75 per kg.**
- The graphite produced is high purity (~86%wt), highly crystalline 'synthetic' graphite.
- W/single stage chemical purification, achieved 99% purity.
- The Hazer Process can be tailored to create a range of graphite morphologies, potentially enabling Hazer to target multiple specialized markets and end user applications.
- **Goal #2: Graphite can be sold for use in lithium ion batteries, lubrication, and industrial applications.**

Conventional Methods vs. Hazer Process

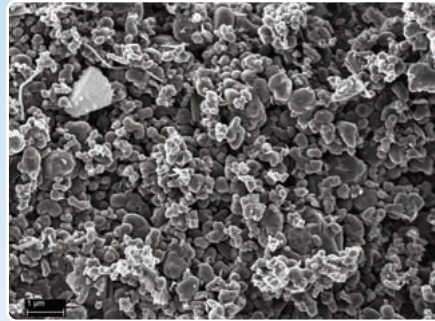


HazerGroup Ltd Production Plan

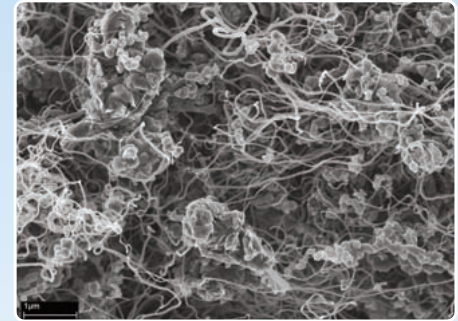


HazerGroup Graphite Production

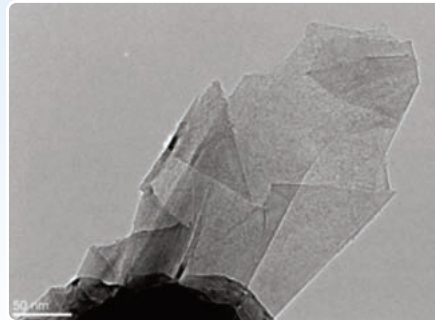
- Graphite Market: US\$1,000 per metric ton.
- Globally, the graphite market is worth around US\$13bn annually.
- Specialized graphite:
 - Spherical graphite: Li-ion batteries.
 - Graphene: flexible, transparent, great conductor.
 - Carbon Nano-Onions: super capacitors



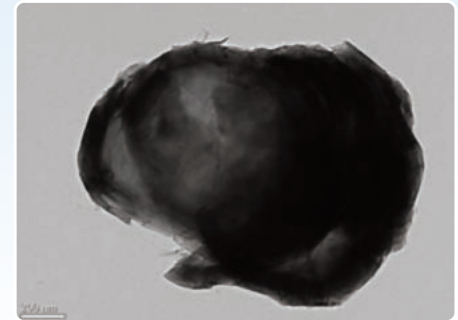
Carbon Nano Onions



Carbon Nanotubes



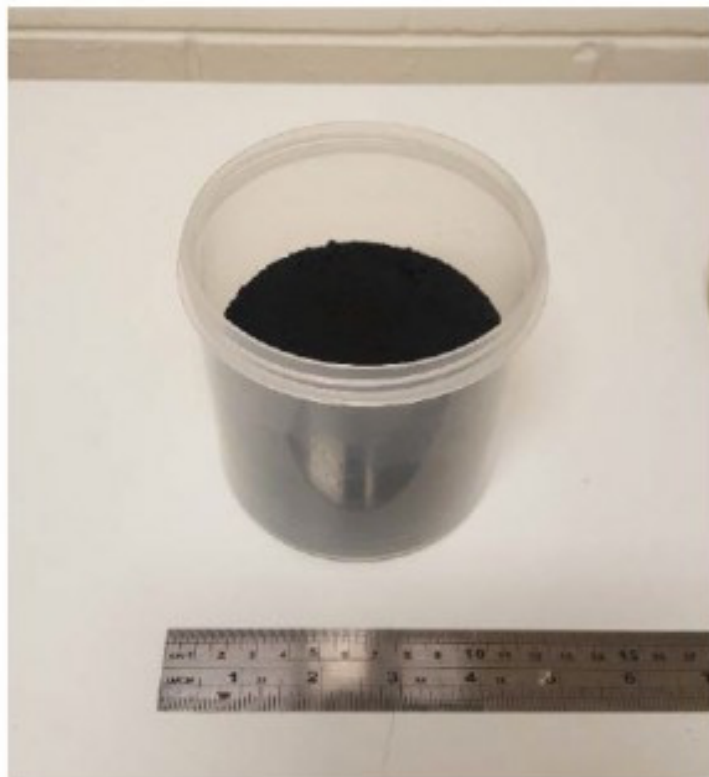
Graphene



Carbon Micro Shells

Range of carbon morphologies produced via Hazer Processs

HazerGroup Graphite Production



Hazer – graphite sample



HazerGroup Timeline

- 2006: Research begins at University of Western Australia that leads to discovery of Hazer Process.
- 2010: Hazer Group formed.
- 2015: First IPO of company.
- Current Test Reactors:
 - Static Bed Reactor
 - Can operate at pressures exceeding 10 bars.
 - 150 times the capacity of pre-IPO reactors.
 - Can test different temperatures and pressures to produce different types of graphite.
 - Fluidised Bed Reactor
 - Runs at atmospheric pressure.
 - 1 kg of graphite per day, over 3,000 times the amounts able to be produced using pre-IPO reactors.

HazerGroup Prospectus, September 30, 2015.

<https://fuelcellsworks.com/news/novel-hydrogen-production-company-hazer-group-announces-commercialization-update>

<http://www.azocleantech.com/article.aspx?ArticleID=611>

HazerGroup Timeline

- 2017-2018: Pilot plant capable of producing tens to hundreds of kilograms of hydrogen per day, or about 30 metric tons per year.

Industrial scale: Need plants that produce more than 10,000 metric tons of hydrogen per year.



<https://www.theguardian.com/sustainable-business/2016/jul/22/cheap-and-clean-australian-company-creates-hydrogen-with-near-zero-emissions>

<http://www.azocleantech.com/article.aspx?ArticleID=611>

Conclusions and questions

Conclusions:

- Hazer process is a clean alternative to standard methods of producing hydrogen from methane.
- Process still requires methane as feedstock, though methane can come from bio-gas in addition to fossil fuels.
- Clean hydrogen can promote fuel cells and cheaper graphite can promote Li-ion battery technology.

Questions:

- Can this process overtake conventional methods of producing hydrogen? How long would this take?
- Will this process promote hydrogen as a fuel for cars and other vehicles?
- Will this process promote the use of electric vehicles via graphite for Li-ion batteries?

Questions?



Hazer Process Fluidised Bed Reactor system, University of Sydney

References – links #1

Mahler Advanced Gas Systems: Hydrogen generation plant based on steam reforming

<http://www.mahler-ags.com/hydrogen/hydroform-c.htm>

The Essential Chemistry Industry Online: Hydrogen

<http://www.essentialchemicalindustry.org/chemicals/hydrogen.html>

Cheap and clean: Australian company creates hydrogen with near-zero emissions

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Producing Clean Hydrogen with Near-Zero Carbon Emissions using The Hazer Process

<http://www.azocleantech.com/article.aspx?ArticleID=611>

Pages: Welcome to the Wikid Energy Funhouse: Hydrogen Fuel Cells: Hydrogen Production

<https://wiki.uiowa.edu/display/greenergy/Hydrogen+Production>

ENERGY.GOV: Office of Energy Efficiency & Renewable Energy: HYDROGEN PRODUCTION: NATURAL GAS REFORMING

<http://energy.gov/eere/fuelcells/hydrogen-production-natural-gas-reforming>

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https://en.wikipedia.org/wiki/Electrolysis_of_water

References – links #2

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<http://www.eia.gov/todayinenergy/detail.php?id=24612>

Florida Solar Energy Center: Hydrogen Basics: Production

<http://www.fsec.ucf.edu/en/consumer/hydrogen/basics/production.htm>

U.S. Energy Information Administration: Hydrogen Explained: Production of Hydrogen

http://www.eia.gov/energyexplained/index.cfm?page=hydrogen_production

United States Patent Application 20160156051: PROCESS FOR PRODUCING HYDROGEN FROM HYDROCARBONS

<http://patents.com/us-20160156051.html>

IndexMundi: Commodity Prices: Iron ore

<http://www.indexmundi.com/commodities/?commodity=iron-ore>

IndexMundi: Commodity Prices: Nickel

<http://www.indexmundi.com/commodities/?commodity=nickel>

FuelCellsWorks: Novel Hydrogen Production Company Hazer Group Announces Commercialization Update

<https://fuelcellsworks.com/news/novel-hydrogen-production-company-hazer-group-announces-commercialization-update>