# Sustainable Energy Conversion Pathways for Solid Wastes

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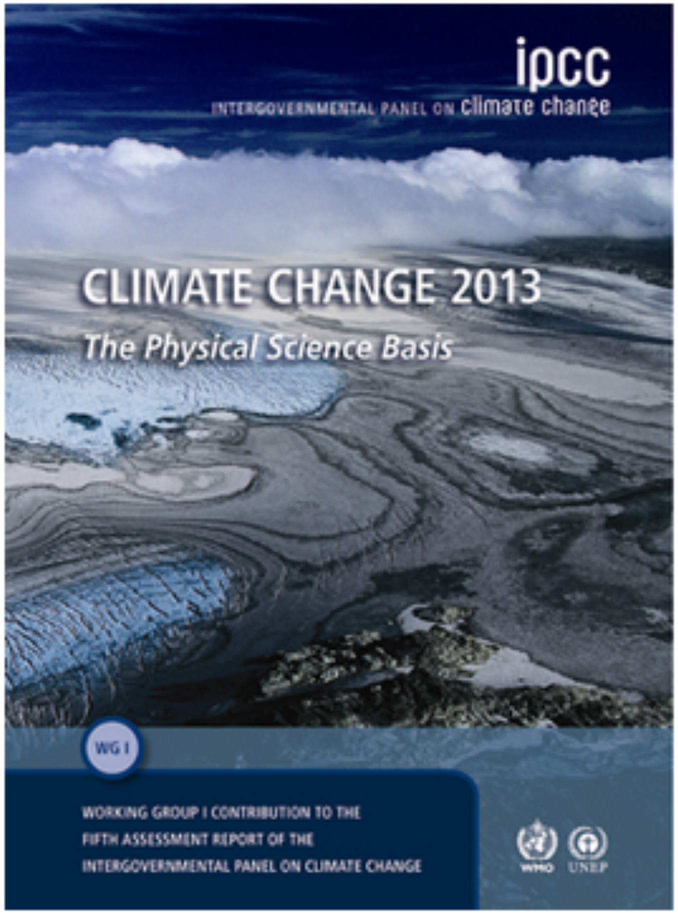
http://www.ipcc.ch/report/ar5/wg1/#.Uk0OXVO8ySo




Summary for Policymakers | Full Report

Quick Links

- Fifth Assessment Report (AR5)
- More on Working Group I (WGI) report
- More on AR5

## Report by Chapters

Technical Summary

- Introduction
- Observations: Atmosphere and Surface
- Observations: Ocean
- Observations: Cryosphere
- Information from Paleoclimate Archives
- Carbon and Other Biogeochemical Cycles
- Clouds and Aerosols
- Anthropogenic and Natural Radiative Forcing
- Evaluation of Climate Models
- Detection and Attribution of Climate Change: from Global to Regional
- Near-term Climate Change: Projections and Predictability
- Long-term Climate Change: Projections, Commitments and Irreversibility
- Sea Level Change
- Climate Phenomena and their Relevance for Future Regional Climate Change

Annex I: Atlas of Global and Regional Climate Projections
Annex II: Glossary
Annex III: Acronyms and Regional Abbreviations

Changes to the Underlying Scientific/Technical Assessment (IPCC-XXVI/Doc.4)

Complete Underlying Scientific/Technical Assessment (166MB)

### E.8 Climate Stabilization, Climate Change Commitment and Irreversibility

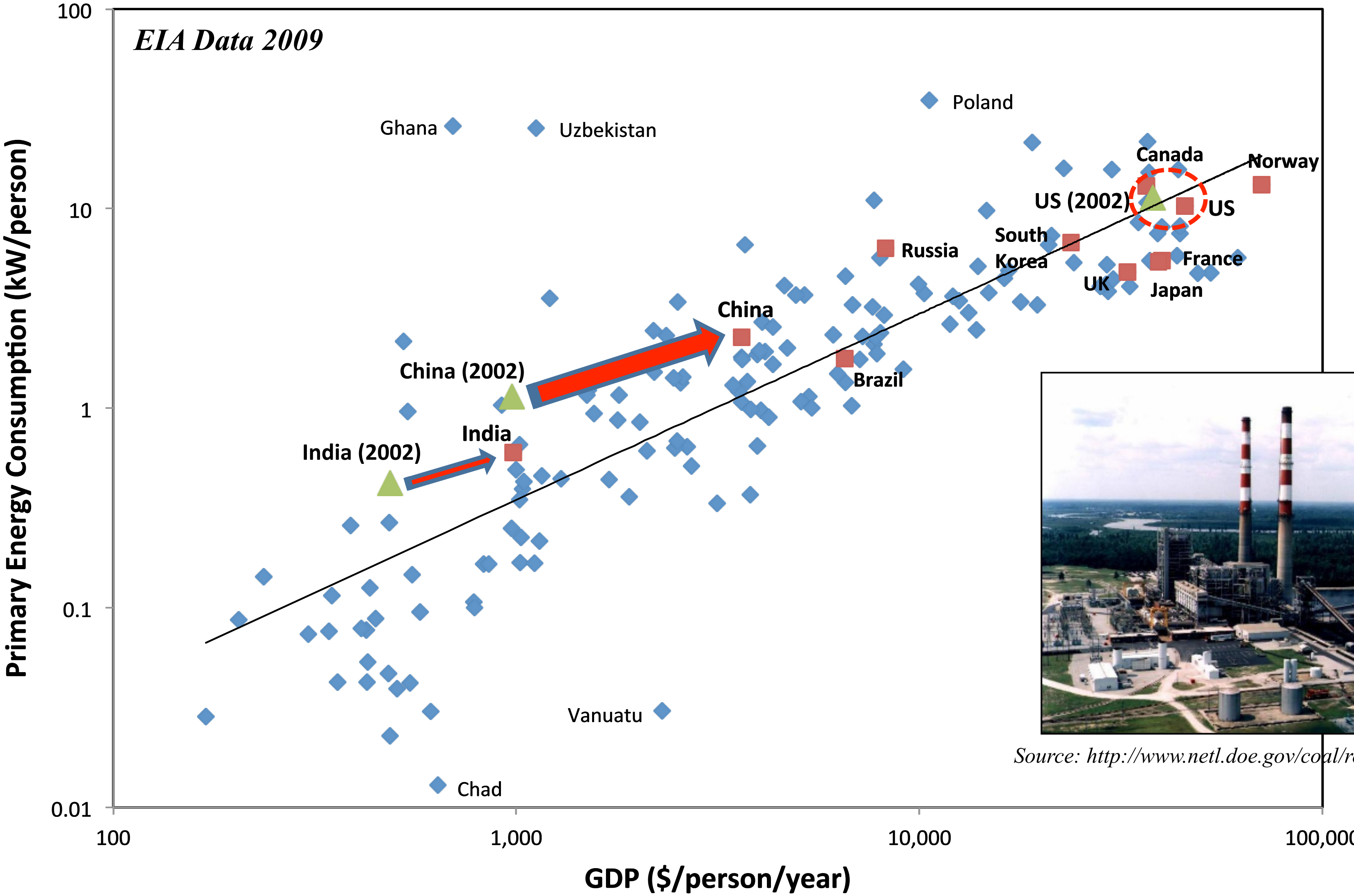
Cumulative emissions of $CO_2$ largely determine global mean surface warming by the late 21st century and beyond (see Figure SPM.10). Most aspects of climate change will persist for many centuries even if emissions of $CO_2$ are stopped. This represents a substantial multi-century climate change commitment created by past, present and future emissions of $CO_2$. {12.5}

- Methods that aim to deliberately alter the climate system to counter climate change, termed geoengineering, have been proposed. Limited evidence precludes a comprehensive quantitative assessment of both Solar Radiation Management (SRM) and Carbon Dioxide Removal (CDR) and their impact on the climate system. CDR methods have biogeochemical and technological limitations to their potential on a global scale. There is insufficient knowledge to quantify how much $CO_2$ emissions could be partially offset by CDR on a century timescale. Modelling indicates that SRM methods, if realizable, have the potential to substantially offset a global temperature rise, but they would also modify the global water cycle, and would not reduce ocean acidification. If SRM were terminated for any reason, there is *high confidence* that global surface temperatures would rise very rapidly to values consistent with the greenhouse gas forcing. CDR and SRM methods carry side effects and long-term consequences on a global scale. {6.5, 7.7}

**BECCS**

http://www.scientificamerican.com/article.cfm?id=latest-ipcc-climate-report-puts-geoengineering-in-the-spotlight

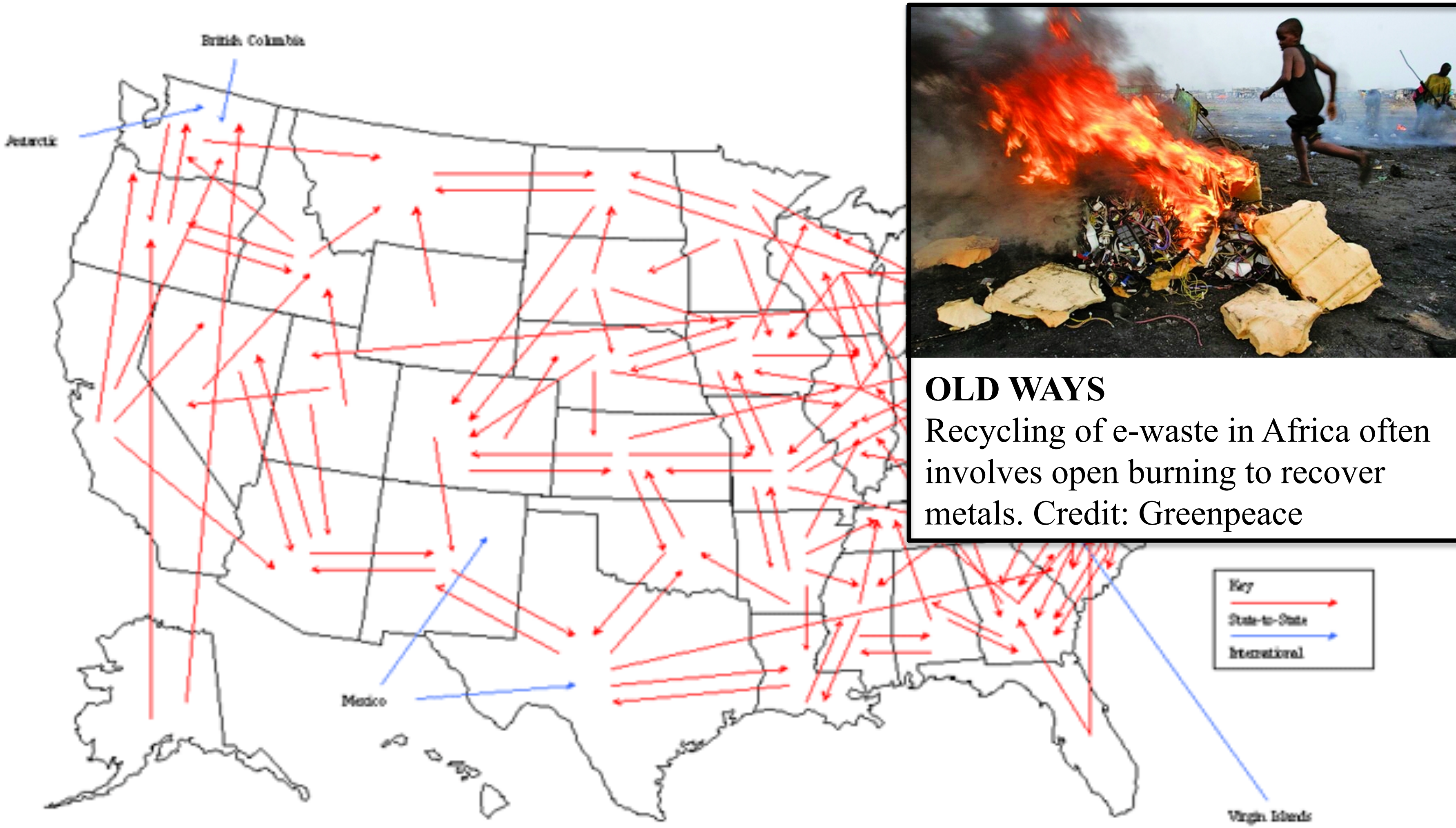
# Energy, Economic Growth and Quality of Life




Source: http://www.netl.doe.gov/coal/refshelf/ncp.pdf

# Interstate Transport of Municipal Solid Wastes

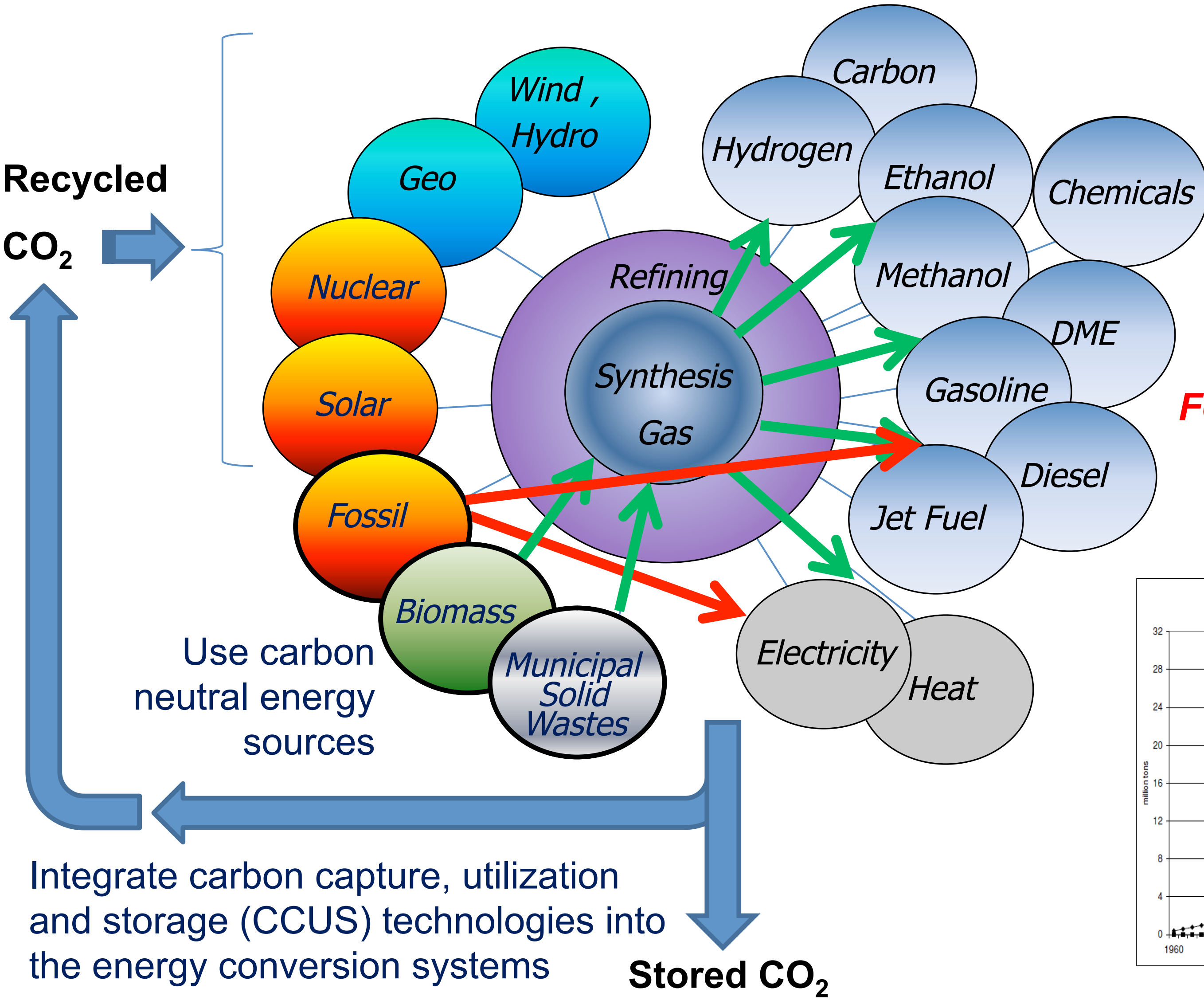
## (Congressional Research Service)




Interstate Shipment of Municipal Solid Waste in 2002 (CRS, 2002)
Note: Map does not include transactions with the District of Columbia

**OLD WAYS**
Recycling of e-waste in Africa often involves open burning to recover metals. Credit: Greenpeace

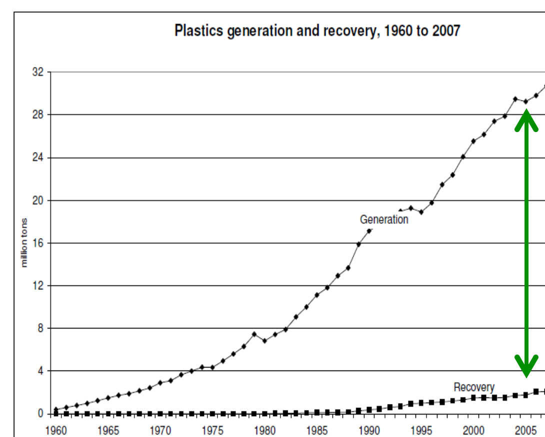
# Towards Sustainable Energy and Environment




Use domestic energy sources to achieve energy independence with environmental sustainability

***Fossil fuels are fungible…***

Energy from Waste




EPA 2007

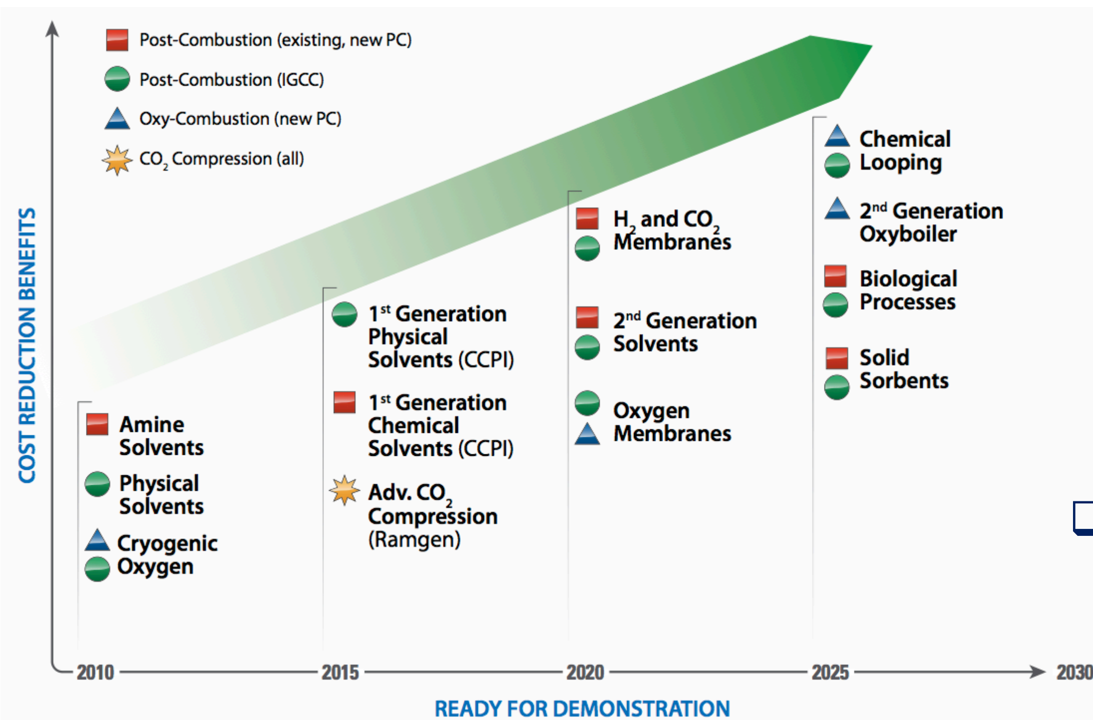
# Post-Combustion $CO_2$ Capture

# Carbon Capture, Utilization and Storage Technologies (CCUS)

Utilization ← Capture → Storage

↓

## Carbon Capture Technologies




(NETL, 2010)

## ❑ Required characteristics for CCS

- Capacity and economic feasibility
- Environmental benign fate
- Long term stability

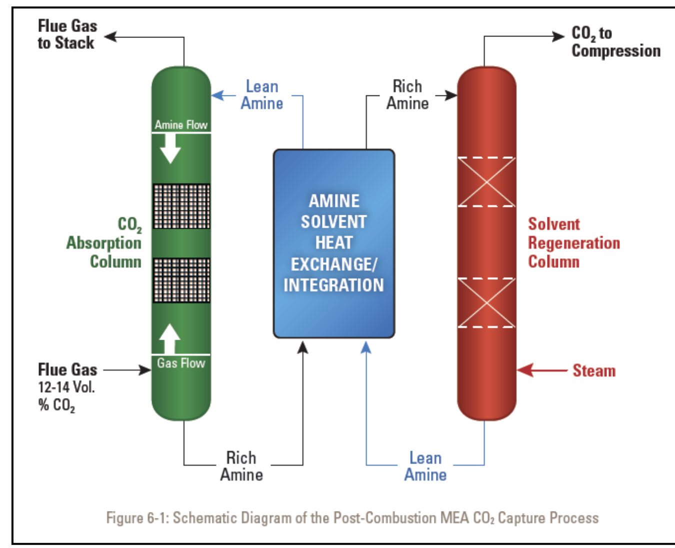


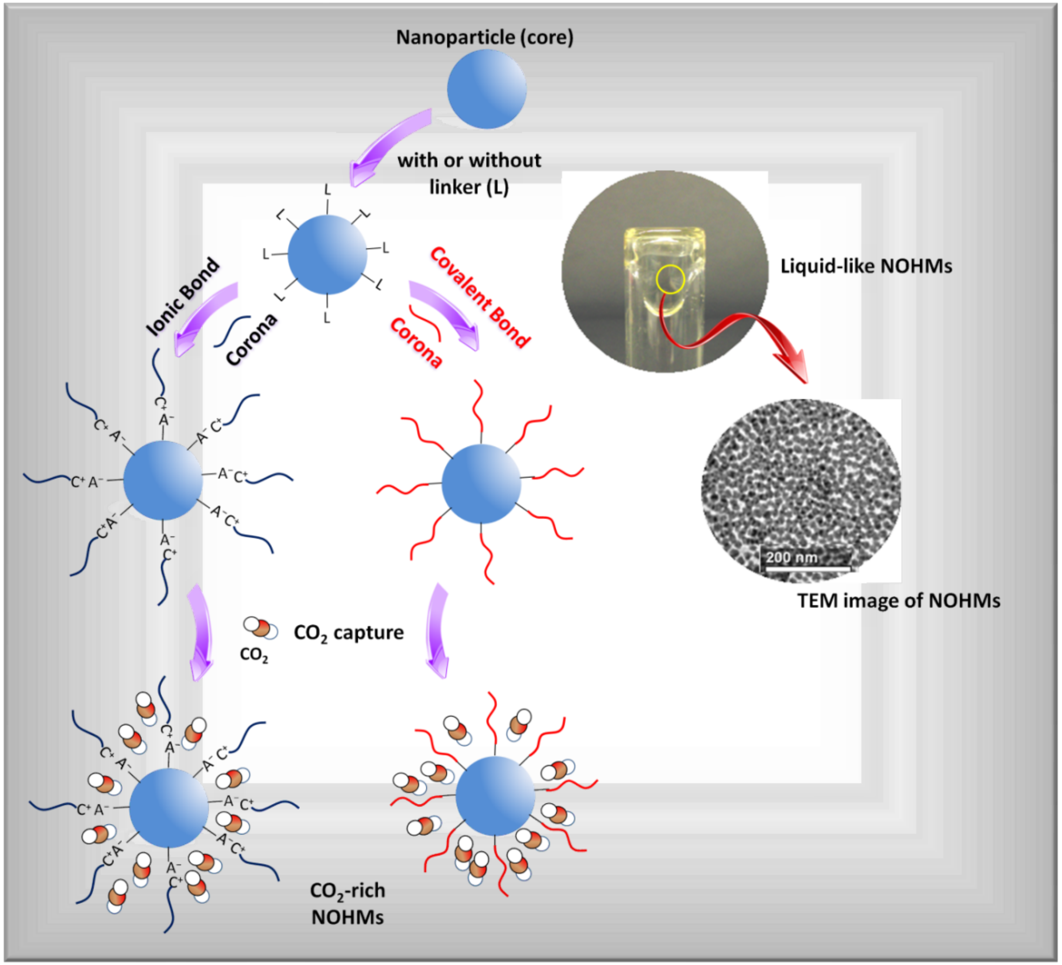

Figure 6-1: Schematic Diagram of the Post-Combustion MEA $CO_2$ Capture Process

(NETL, 2011)

## ❑ MEA Challenges

- Corrosion and solvent degradation
- High capital and operating costs
- High parasitic energy penalty

# Nanoparticle Organic Hybrid Materials (NOHMs)

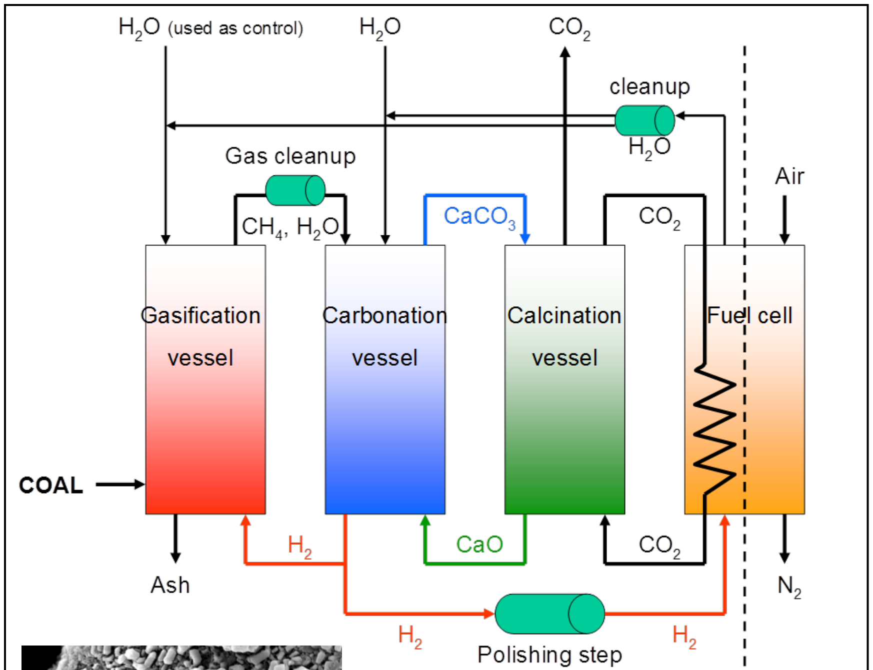



- Solvent-free liquid-like hybrid systems
  - Solvent tethered to nanoparticle cores
  - Zero-vapor pressure and improved thermal stability
- Tunable chemical and physical properties
  - Liquid, solid, gel
  - Solvation in NOHMs driven by both entropic and enthalpic interactions
- Straightforward synthesis
  - Easy to scale up

**ZERO VAPOR PRESSURE+ TUNABLE PROPERTIES**

# Solid Sorbents & Chemical Looping Technologies

## Carbonation / Calcination cycle





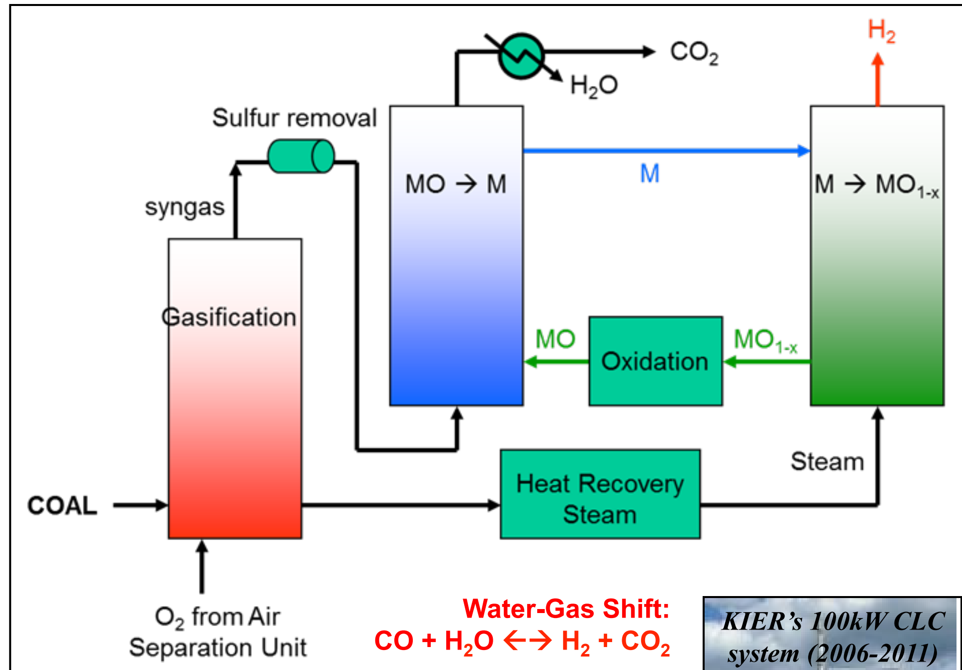
$$MO + CO_2 \rightarrow MCO_3$$

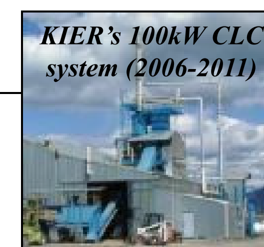
$$MCO_3 \rightarrow MO + CO_2$$

e.g., ZECA process

(Los Alamos National Lab)

## Oxidation / Reduction cycle




$$MO + CO \rightarrow M + CO_2$$

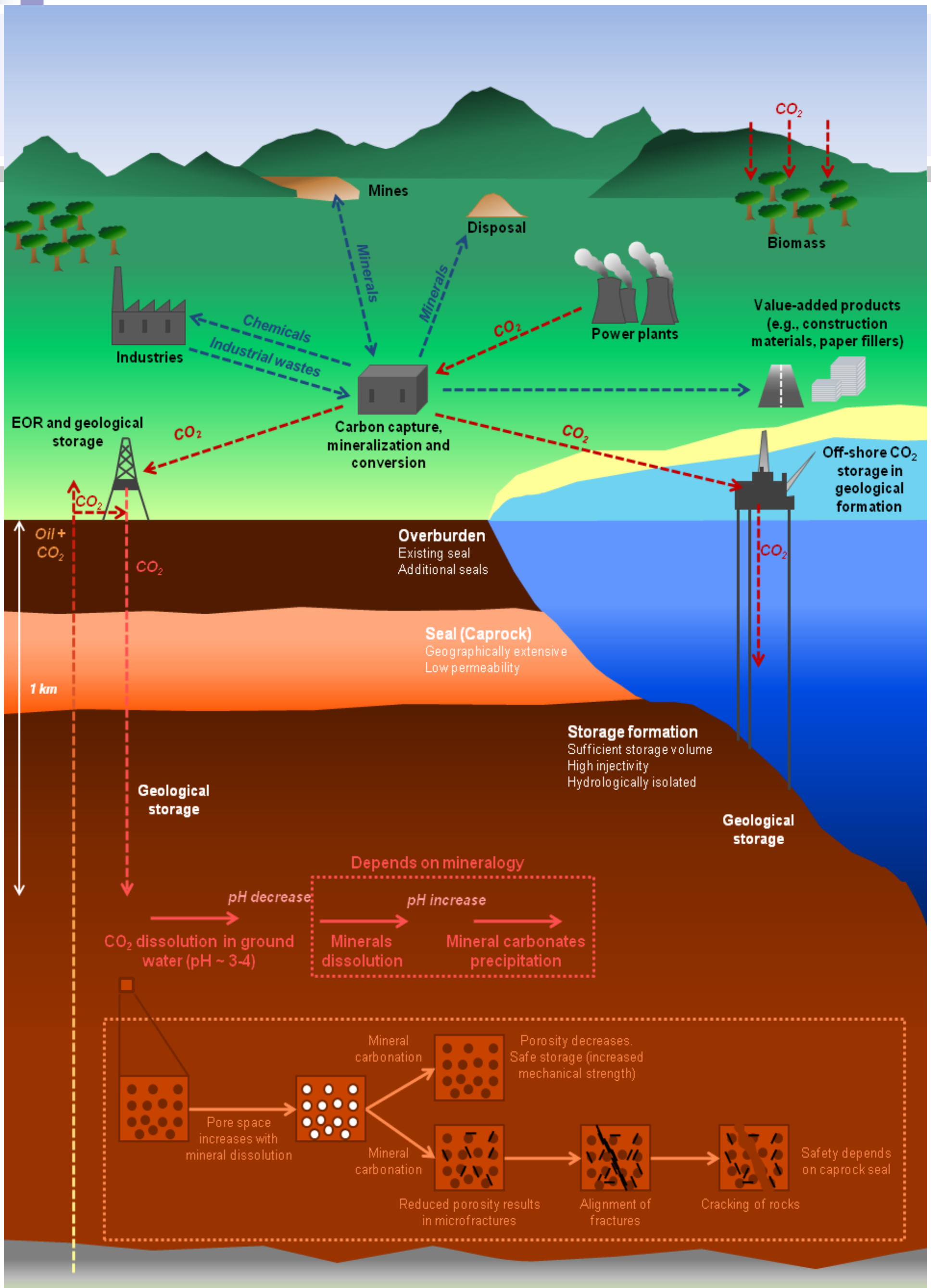
$$M + H_2O \rightarrow MO + H_2$$

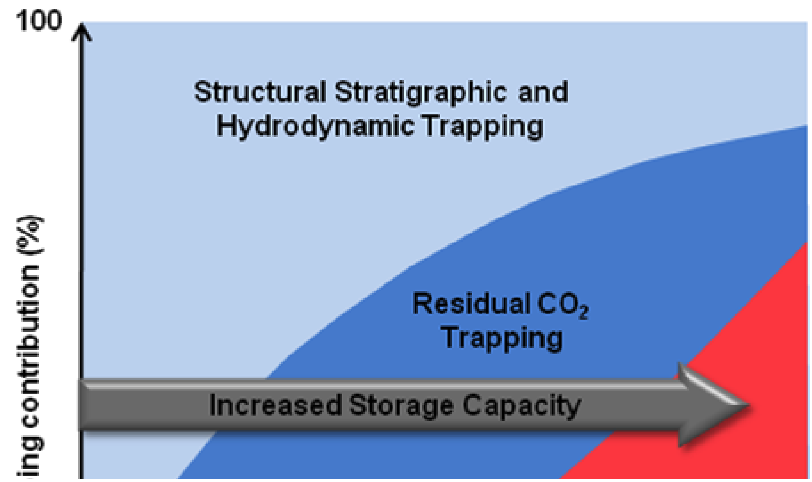
e.g., Chemical Looping process for $H_2$ production

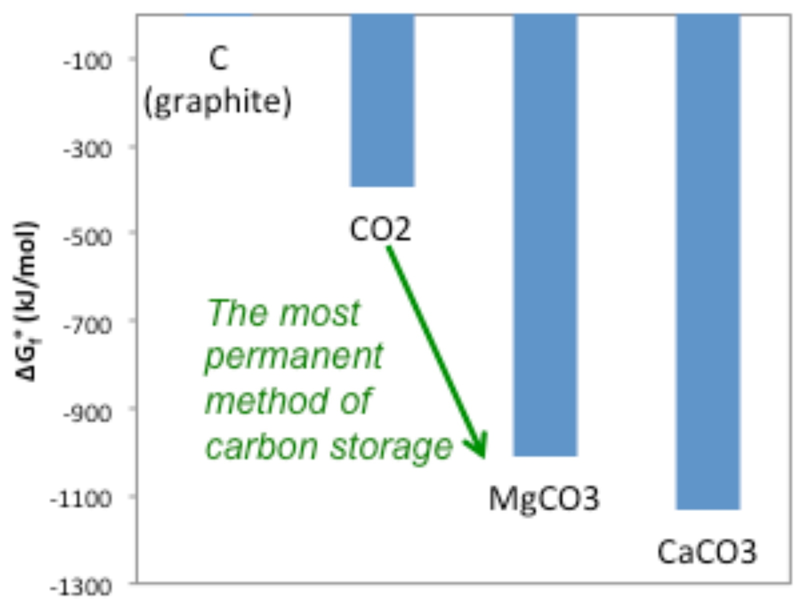
(Ohio State Univ.: U.S. Patent No. 11/010,648 (2004))

# Can we combine $CO_2$ capture and storage?

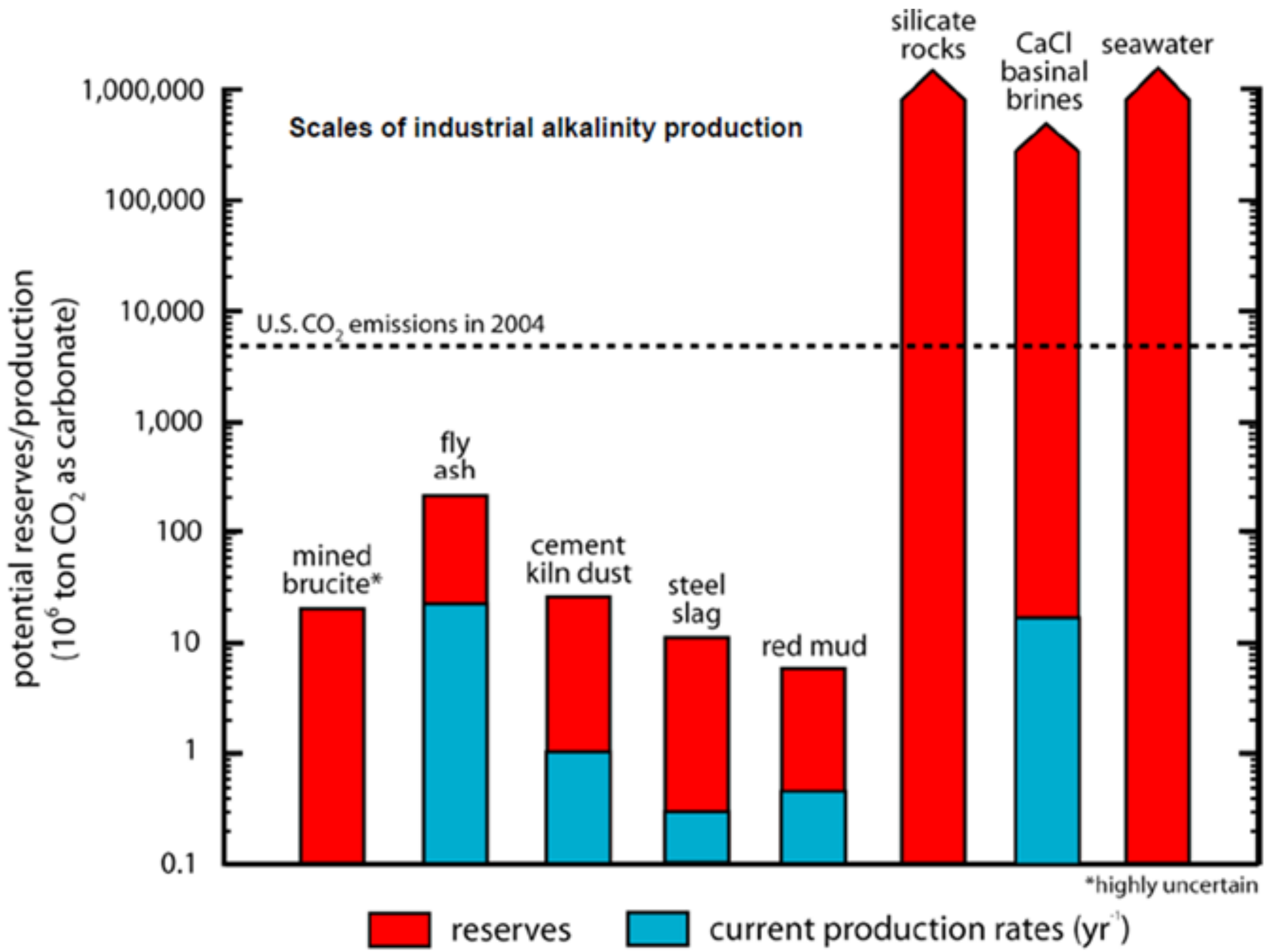
# Carbon Storage in Geologic Formations



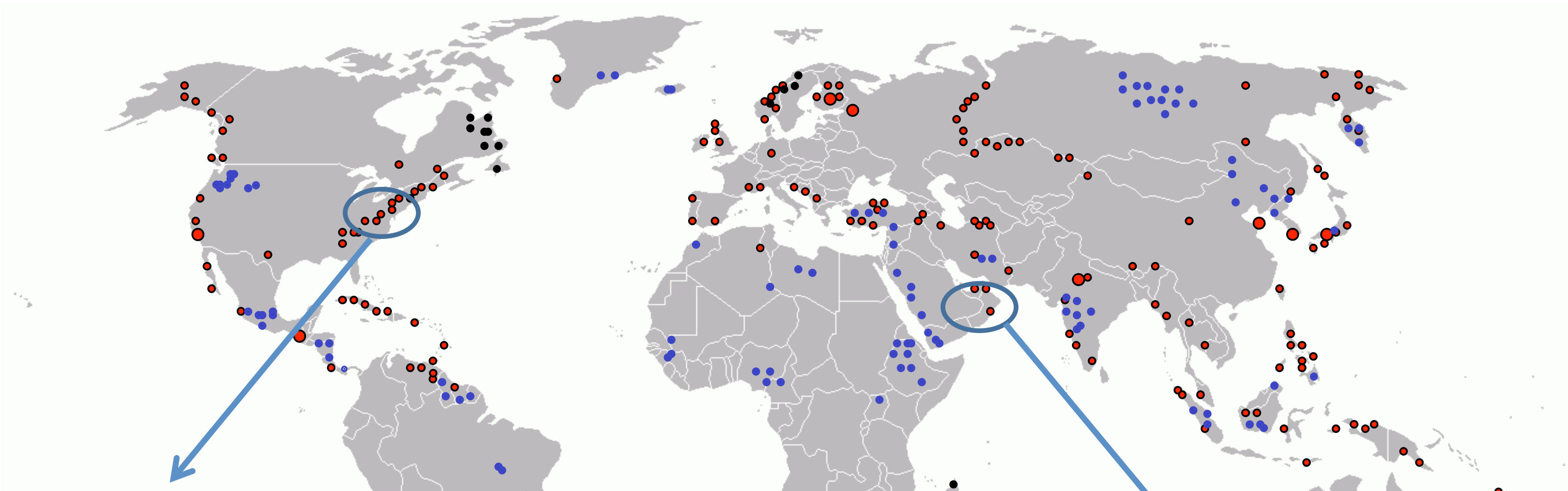



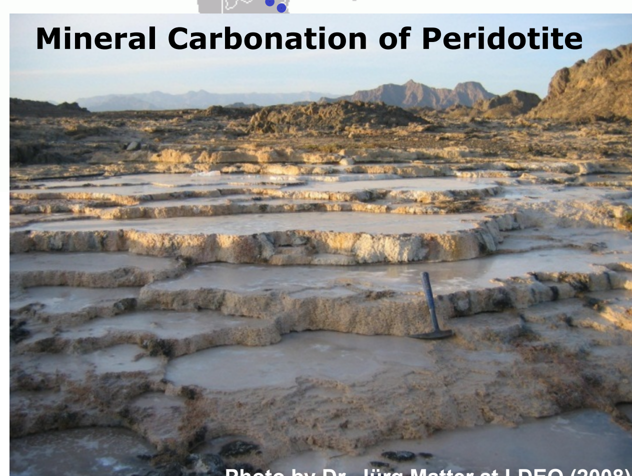



# Availability of Industrial Wastes



# Availability of Minerals

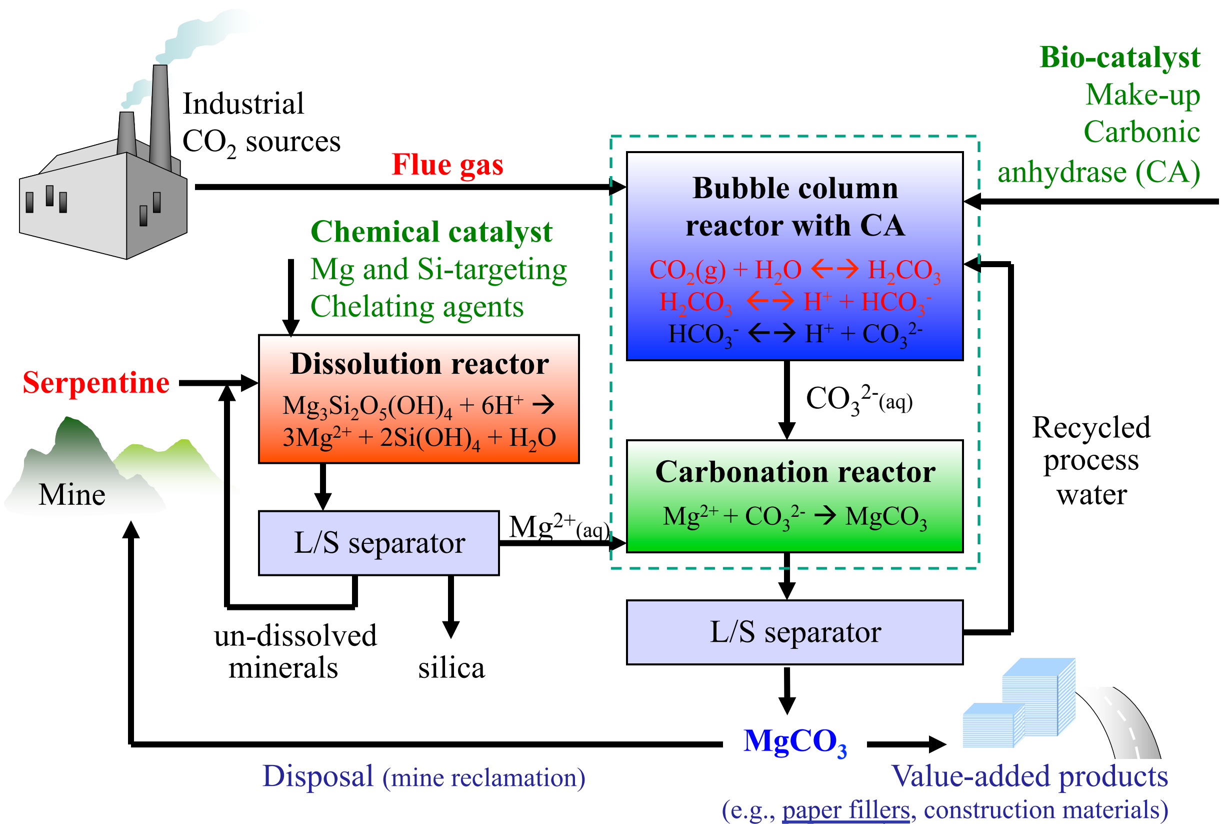


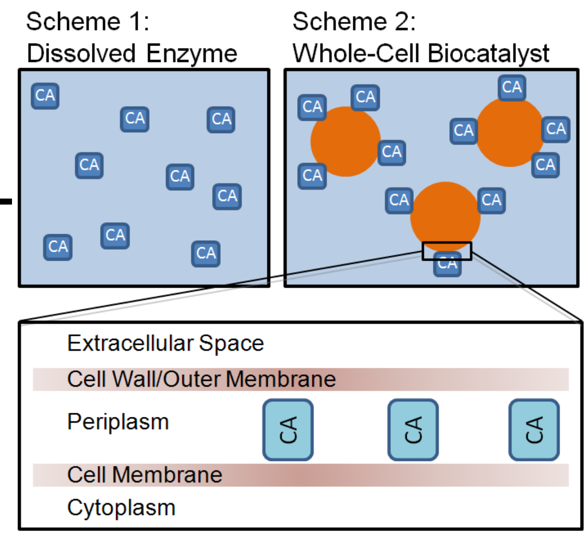





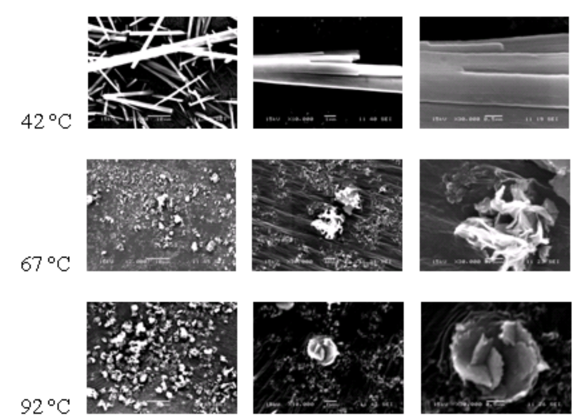
- Basalt
- Labradorite
- Magnesium-based Ultramafic Rocks (Serpentine, Olivine)

# Chemical and Biological Catalytic Enhancement of Weathering of Silicate Minerals as Novel Carbon Capture and Storage Technology

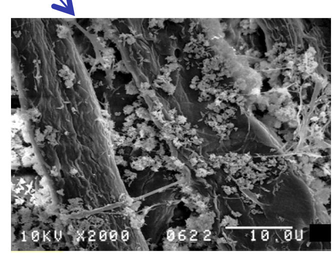



## Controlled Formation of Precipitated Magnesium Carbonates



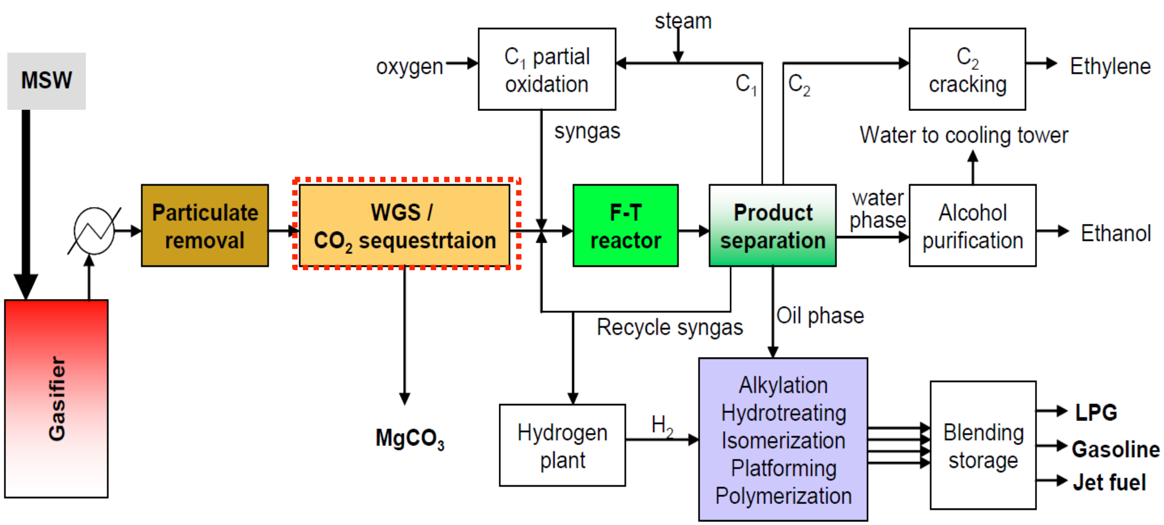

- No need for the solvent regeneration and $CO_2$ compression, straightforward MVA
- Alternative $CO_2$ utilization option with improved economic feasibility



# Synthetic Liquid Fuels from Solid Wastes with integrated CCS

# Energy Conversion with CCS

## Sustainable Waste-to-Liquid Fuel Scheme



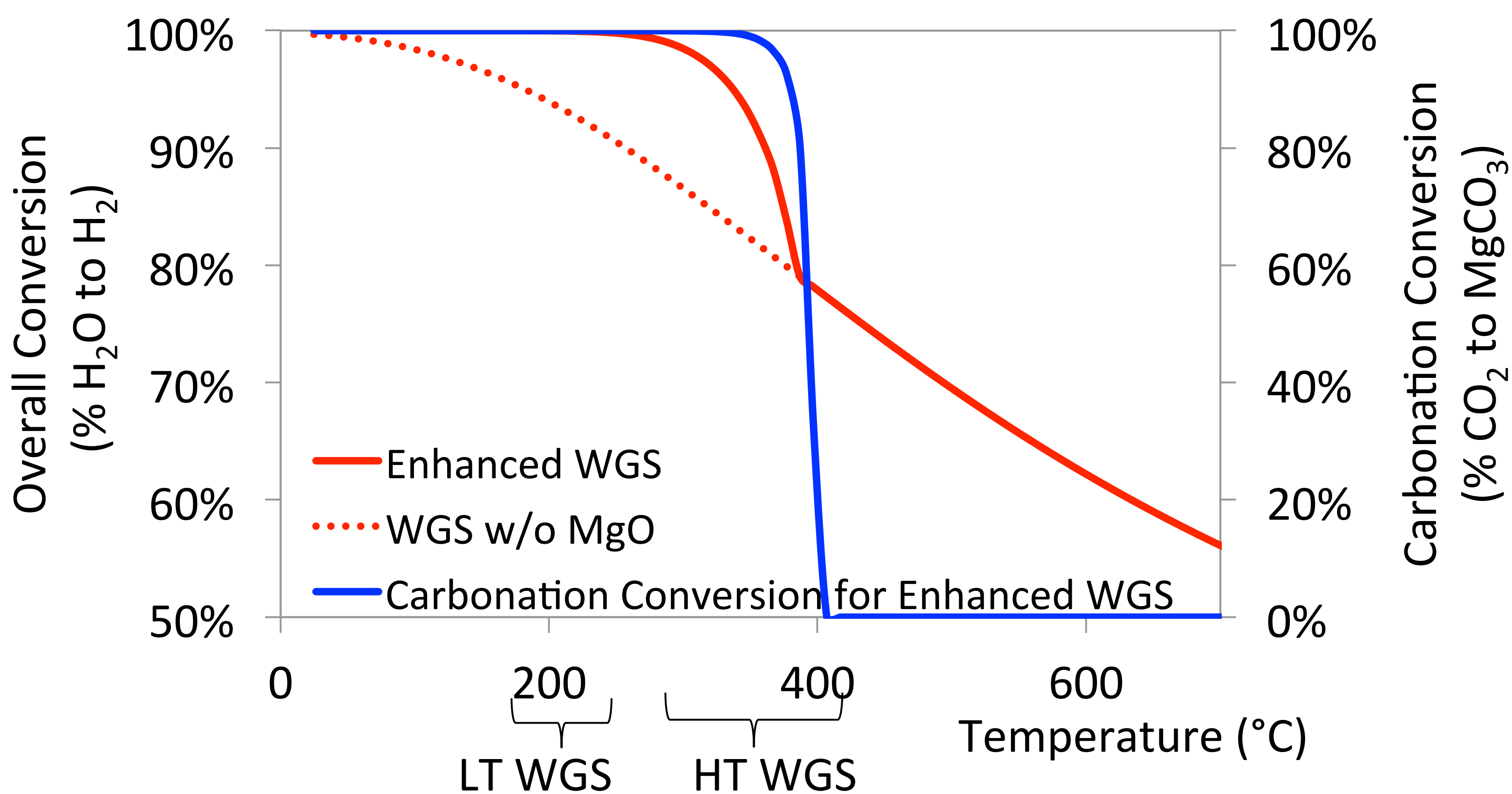

X-to-Liquids processes have high carbon footprint

$$Mg(OH)_{2(s)}$$
$$+$$
$$H_2O_{(g)} + CO_{(g)} \xleftrightarrow[\text{\& multi-stage}]{\text{catalyst}} CO_{2(g)} + H_{2(g)}$$
$$\downarrow$$
$$MgCO_{3(s)} + H_2O_{(g)}$$

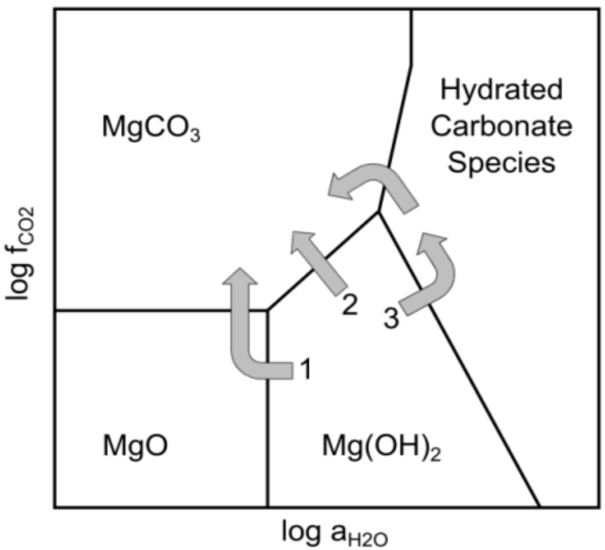
- ✓ Shifts equilibrium to products
- ✓ Provides Water
- ✓ Economic prospects

# Water Gas Shift with *in-situ* Carbon Capture: Theoretical Enhancement

| | | ΔHrxn |
|---|---|---|
| $Mg(OH)_2 \rightarrow MgO + H_2O$ | | ~ 80 kJ/mol |
| $MgO + CO_2 \rightarrow MgCO_3$ | | ~ -100 kJ/mol |
| $H_2O + CO \leftrightarrow CO_2 + H_2$ | | ~ -40 kJ/mol |

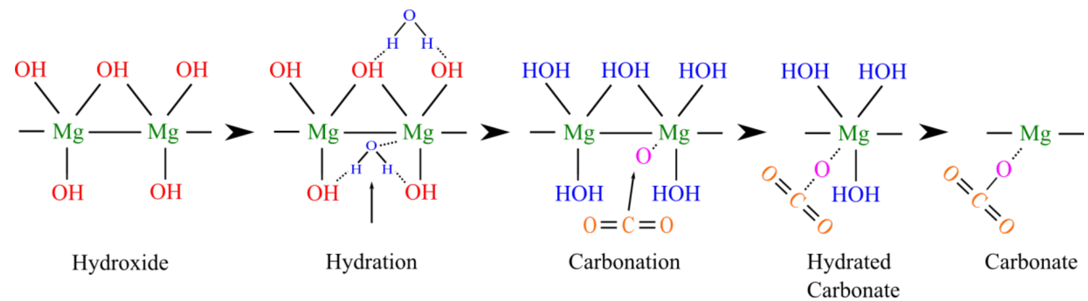


# Reaction Pathways in $Mg(OH)_2$ Carbonation



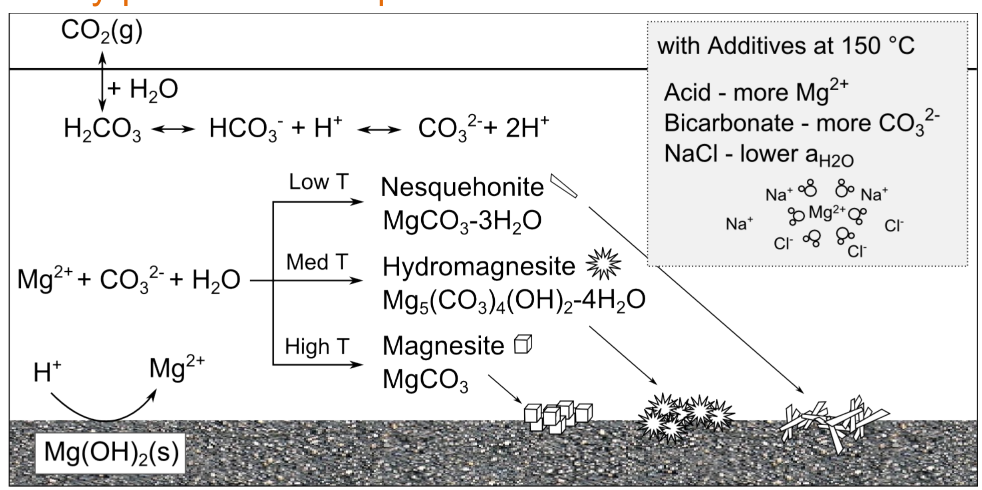

Geochemists Work Bench software (Release 7.0.2) at T = 300 °C and $P_{total}$ = 1 atm (basis, Magnesite activity = 1).

## Proposed gas-solid reaction pathway:




Adapted from Schaef *et al.* 2011

## Slurry-phase reaction phenomena:

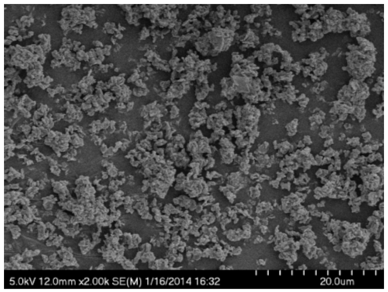


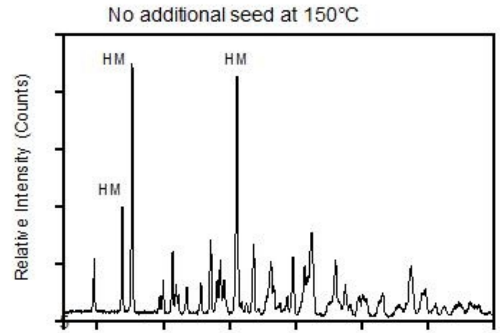

Schaef, H. T.; Windisch, C. F.; McGrail, B. P.; Martin, P. F.; Rosso, K. M., Brucite [Mg(OH2)] Carbonation in Wet Supercritical CO2: An in situ High Pressure X-Ray Diffraction Study. *Geochimica et Cosmochimica Acta* **2011**.
Fricker, K.; Park, A. H., Effect of H2O on the Carbonation of Mg(OH)2 for Combined CO2 Capture and Storage. *Chemical Engineering Science* **2013,** *100, 332-341,* http://dx.doi.org/10.1016/j.ces.2012.12.027
Fricker, K.; Park, A.-H. A., Investigation of the Temperature Effect on Carbonate Phase Formation in $Mg(OH)_2$ Slurry Carbonation **2014,** *In Preparation*.

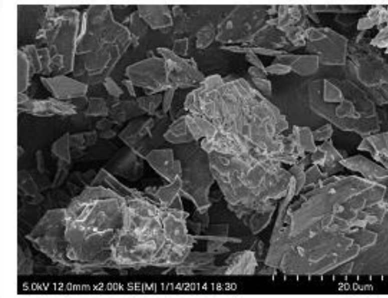
# Effect of Seeds on Slurry Carbonation Experiments at 150 $^oC$

Carbonation at 150 $^oC$ for 120 min

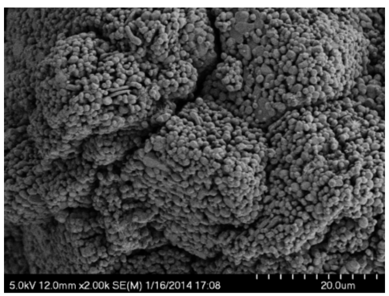
$Mg(OH)_2$

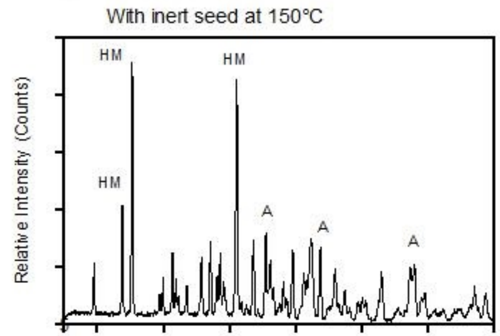


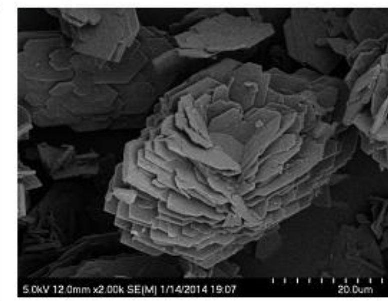



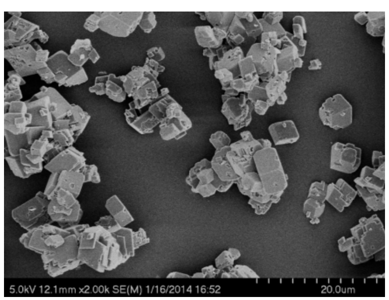

$Al_2O_3$

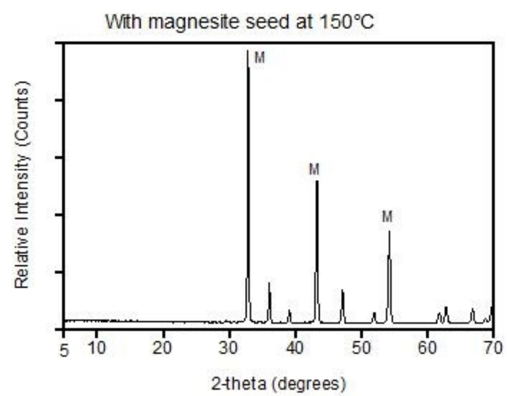


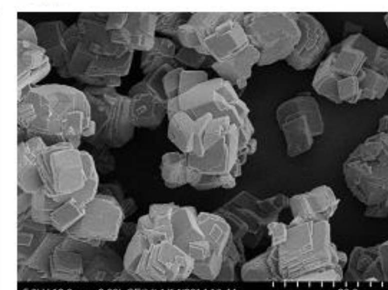




$MgCO_3$



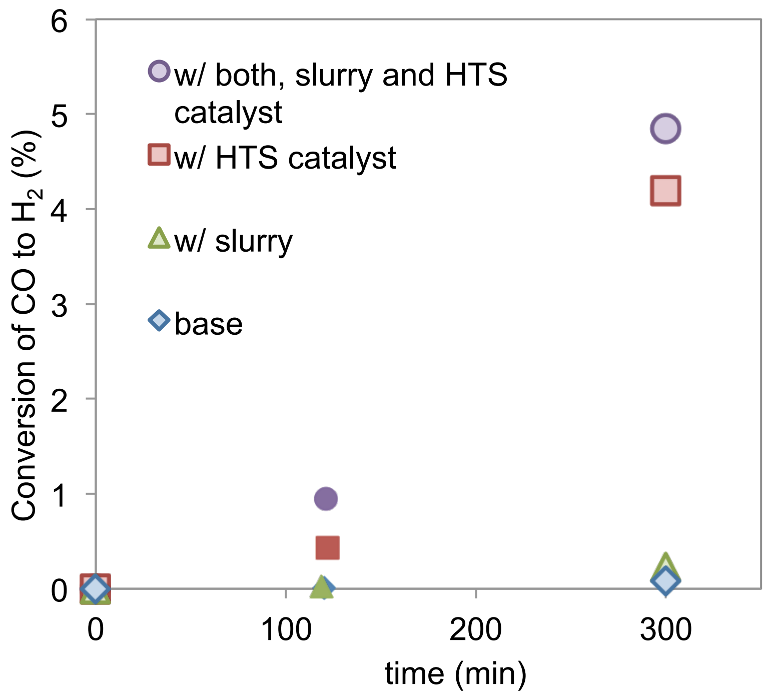



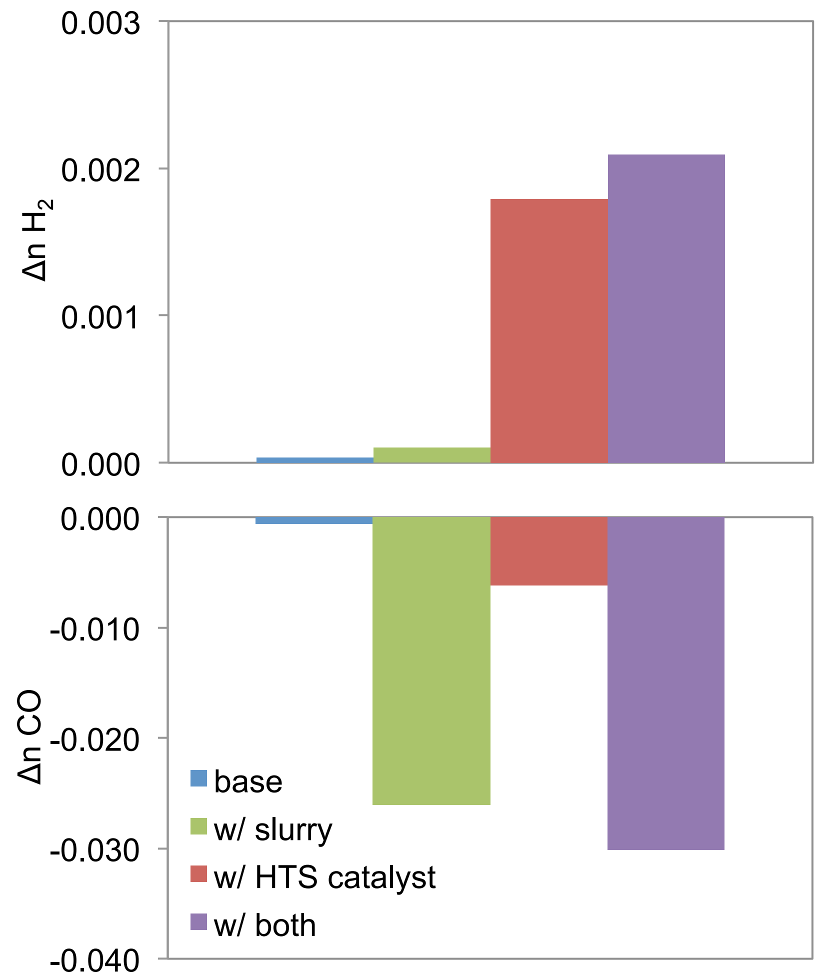

Starting materials

Swanson, E.J.; Fricker, K.J.; Sun, M.; Park, A.-H. A., Directed Precipitation of Hydrated and Anhydrous Magnesium Carbonates. **2014,** *In Preparation*.

# Effect of in-situ $Mg(OH)_2$ Slurry Carbonation on WGS

*Max conversion possible calculated using $K_{eq}(T)$*



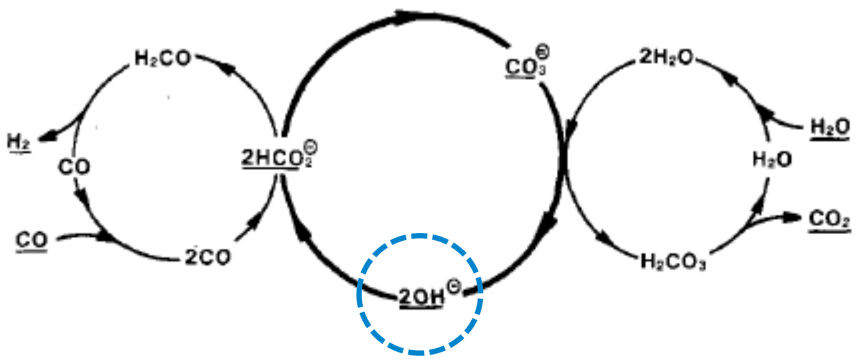



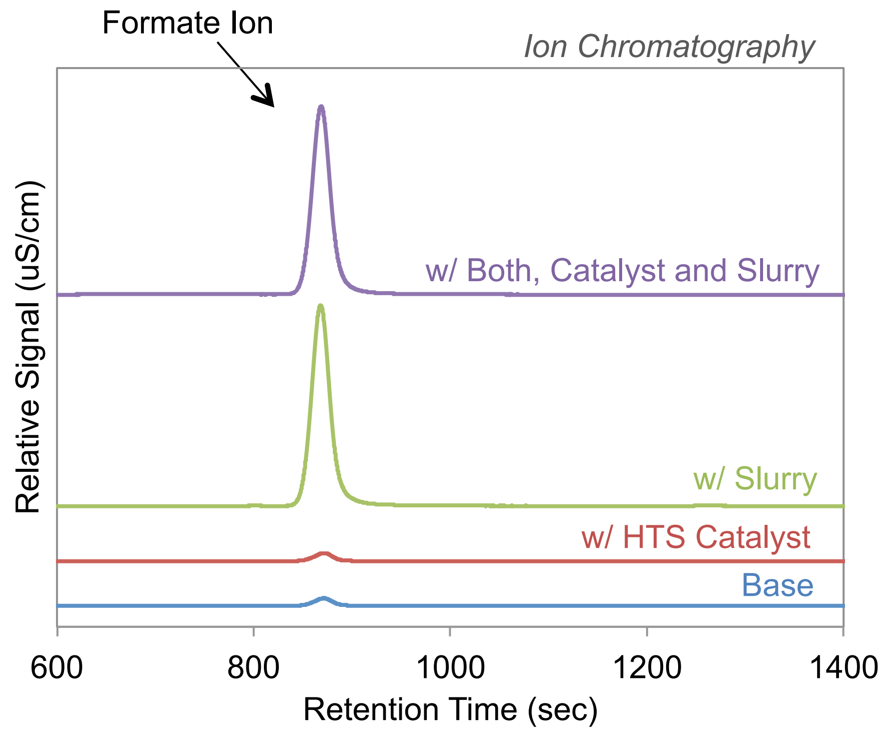

Relatively low conversion of CO to $H_2$

Mole imbalance, reaction is 1 to 1

# Investigating the Molar Imbalance

Eliott et al. (1983) found $OH^-$ producers (specifically alkali and alkaline carbonates) to catalyze a high pressure aqueous WGS System




$CO + OH^- \rightarrow HCO_2^-$ (formate)
$2HCO_2^- \rightarrow CO_3^{2-} + H_2CO$ (formaldehyde) [*slow*]
$H_2CO \rightarrow$ **$H_2$(g)** + CO [*fast*]

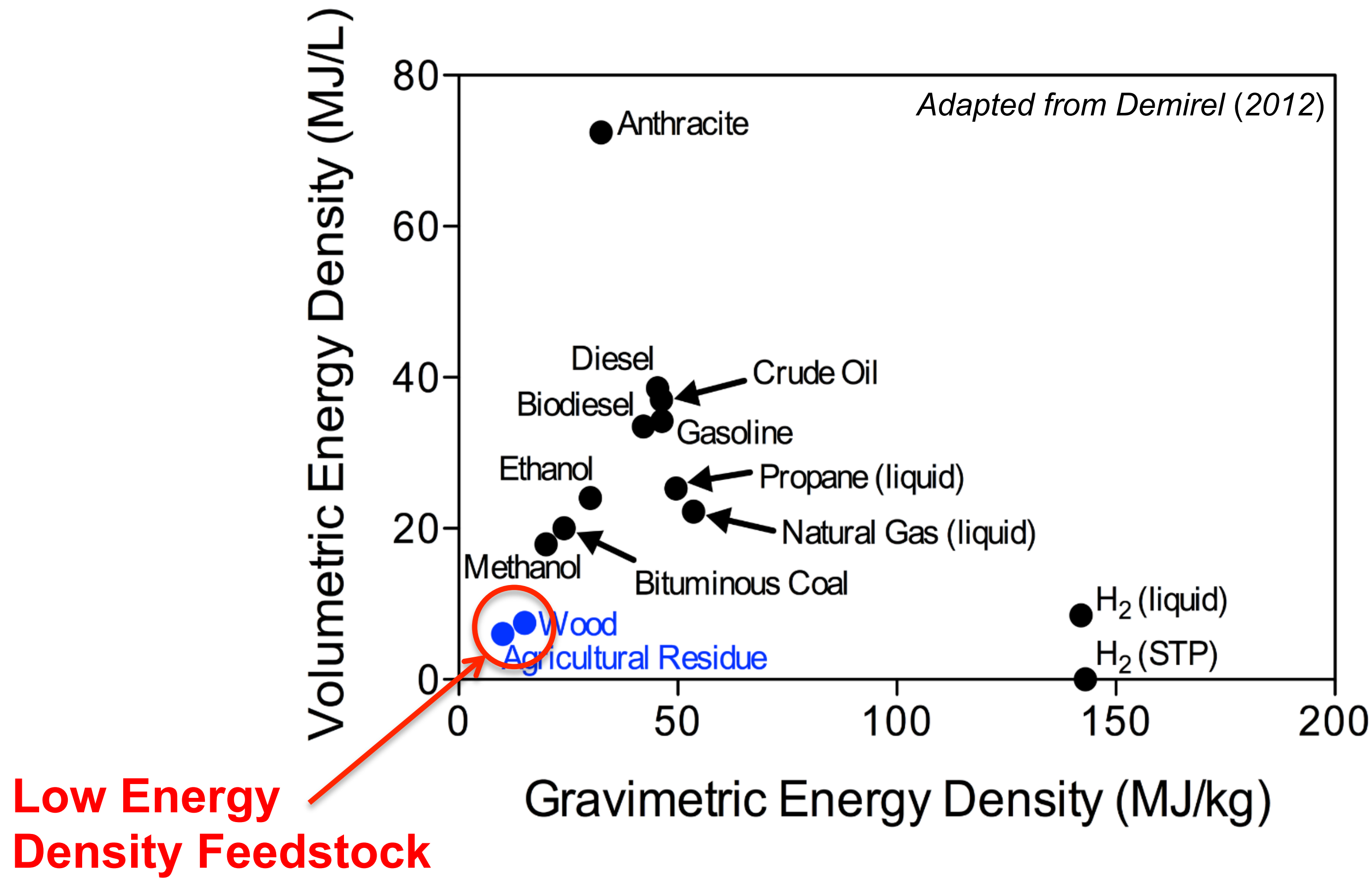
$Mg(COOH)_2$ (aq) formation
Is holding up CO conversion to $H_2$

Generally, slurry samples contained ~22x the concentration of COOH- as those with a water bulk phase

Elliott, D. C.; Sealock, L. J., Aqueous Catalyst Systems for the Water-Gas Shift Reaction. 1. Comparative Catalyst Studies. *Ind. Eng. Chem. Prod. Res. Dev.* **1983,** 22, 426-431.

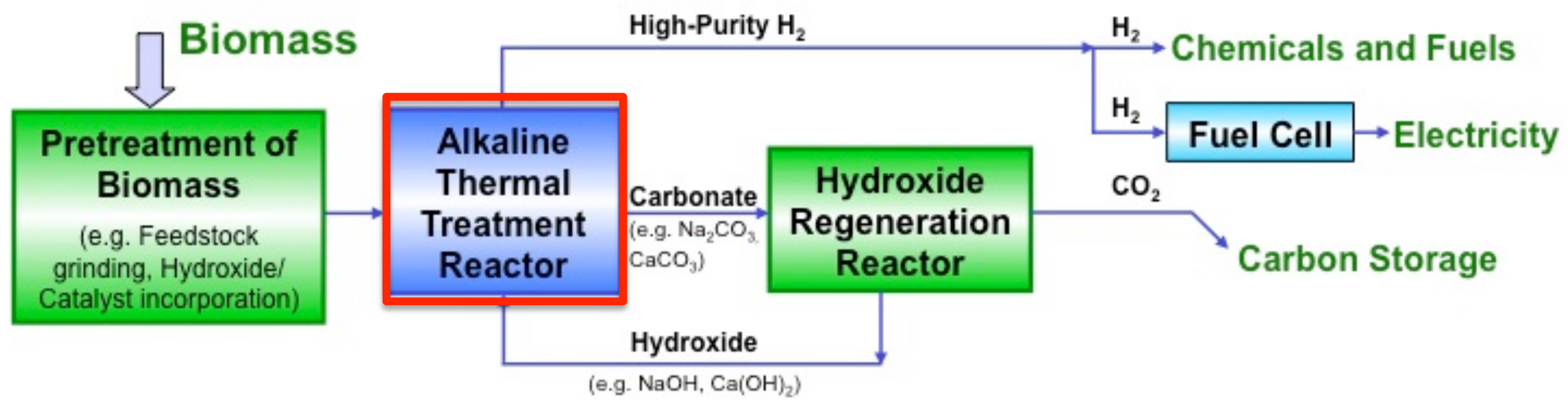
# Biogentic Wastes-to-Hydrogen with integrated CCS

# Biomass as an Energy Feedstock




**To sustainably utilize biomass as an energy source, energy densification or on-site generation schemes are necessary.**

# Alkaline Thermal Treatment (ATT) Fuel Pathway




- ATT Reaction for Cellulose

$$C_6H_{10}O_5 + 12NaOH + H_2O \rightarrow 6Na_2CO_3 + 12H_2$$

- Conditions
  - Low temperature (523 – 573 K)
  - Atmospheric pressure
  - Low to zero $CO_x$ emission

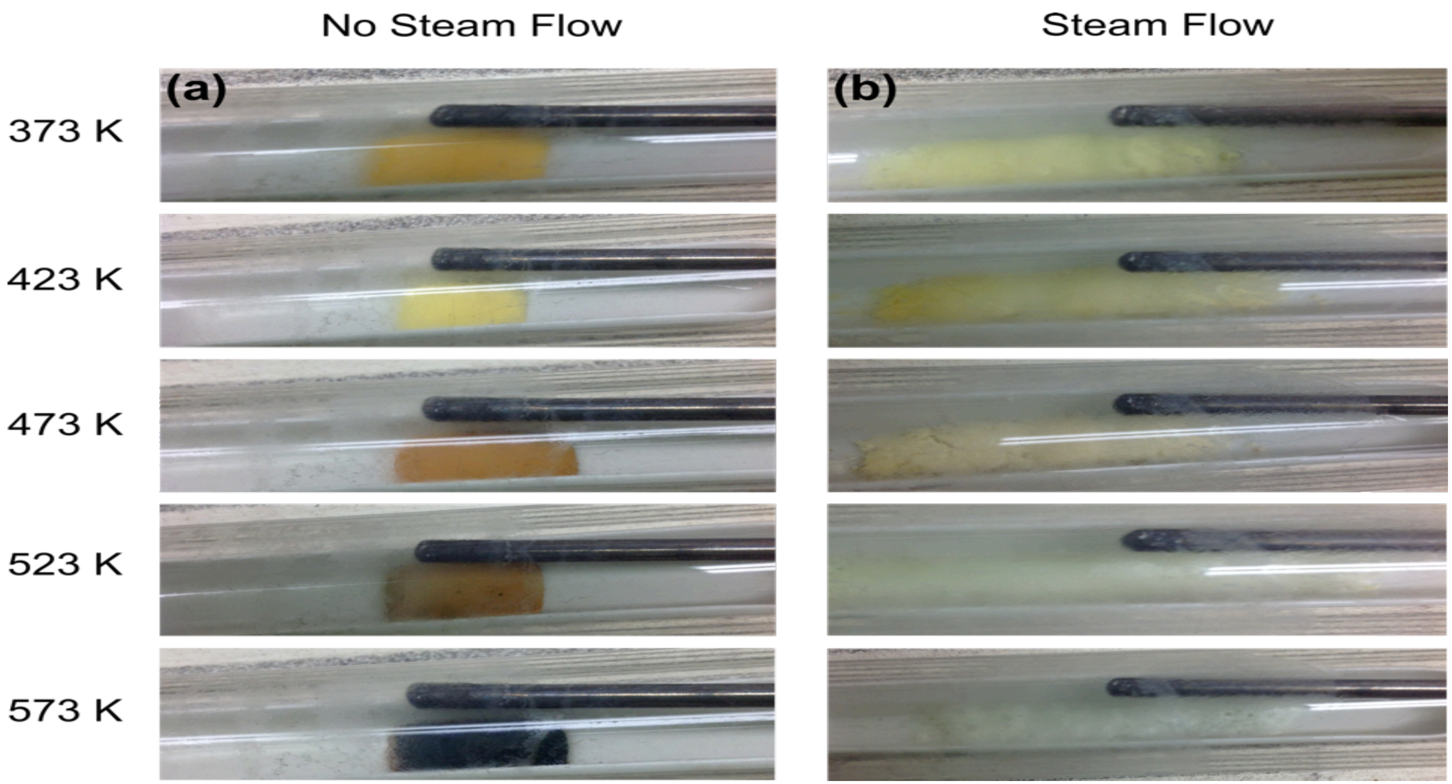
  Scalable reactor

  Unskilled operators

- Feedstocks
  - Sugars, lignocellulosic biomass
  - Wet and dry feedstocks

- Potential Applications
  - Energy generation
  - Fuel and chemical production
  - Well-suited for distributed applications

# ATT of Cellulose with and without Steam Flow



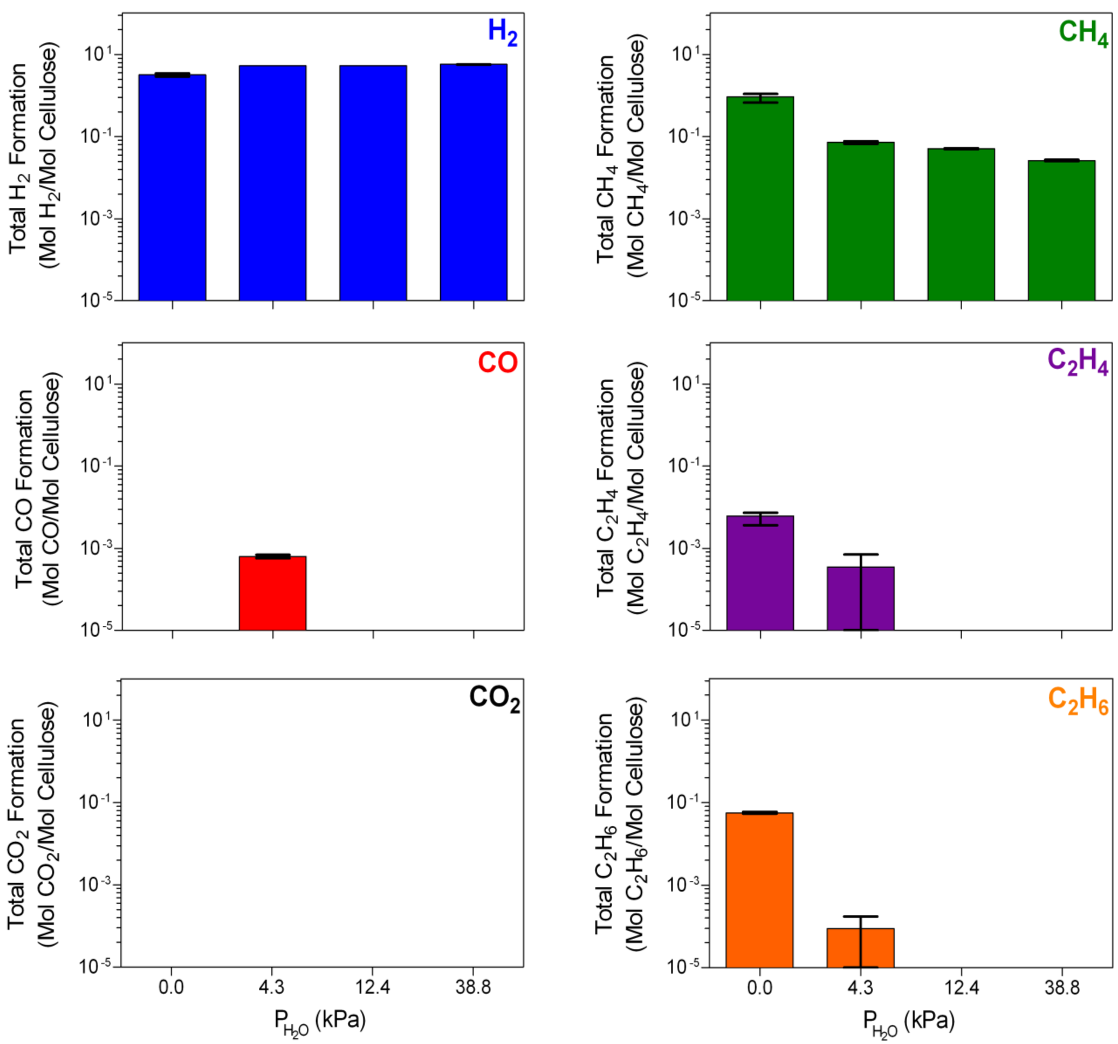

- Steam flow caused a melt to be formed around temperature of peak $H_2$ formation rate (518 K)
- Improved transfer with melt may be additional reason more $H_2$ formed under steam flow

Ferguson, T.E., Park, A.-H.A. Production of high-purity hydrogen from cellulose through a carboxylate intermediate pathway via alkaline thermal treatment, *In Review.*

Columbia University in the City of New York

# Effect of Steam on Cellulose ATT

**Stoichiometric, 12:1 NaOH:Cellulose**




- As $H_2$ increases, $CH_4$ and $C_2$ hydrocarbons decrease
- CO level right on the border of the instruments' detection limit, so quite low overall at 4.3 kPa, but perhaps indicates a minor role that steam plays in decarbonylating cellulose.
- $CH_4$ fell order of magnitude with addition of steam
- $C_2H_4$ and $C_2H_6$ fell ~17 times and ~600 times, respectively, with addition of steam, and were not detected beyond 4.3 kPa $H_2O$ partial pressure.

Ferguson, T.E., Park, A.-H.A. Non-catalytic conversion of cellulose to high-purity hydrogen at mild reaction conditions via alkaline thermal treatment, *In Review*.

# Summary and Future Direction

- Use of municipal solid wastes and industrial wastes (e.g., stainless steel slags, scrap metals), Urban mining → **energy, water and atom efficiencies**
- Development of multifunctional smart $CO_2$ capture media → Combined $CO_2$ capture and conversion
- Integrated systems (e.g., chemical looping, enhanced WGS using mineral carbonation) for **process intensification and flexibility** (production of heat, electricity, chemicals and fuels in any combination)
- Carbon Capture, **Utilization** and Storage
- Integration of renewable energy into various CCUS schemes
- Need for international and trans-disciplinary collaborations

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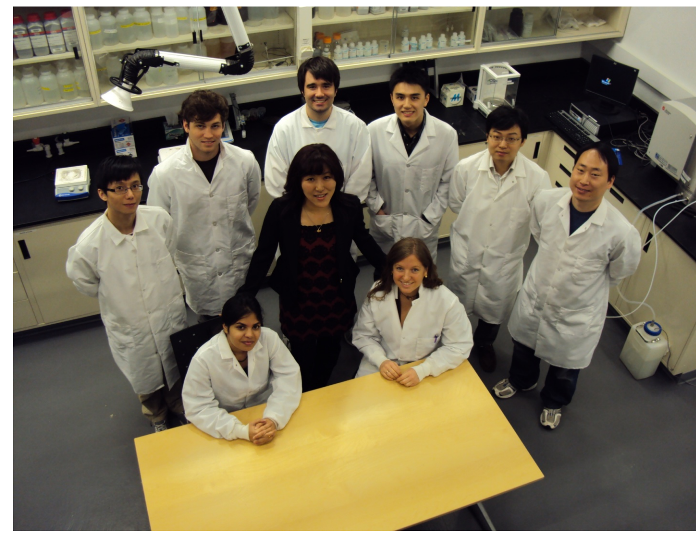
IN THE CITY OF NEW YORK

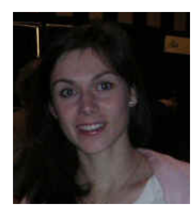
EARTH & ENVIRONMENTAL ENGINEERING
HENRY KRUMB SCHOOL OF MINES

CHEMICAL ENGINEERING

## SUSTAINABLE ENERGY, ENVIRONMENT & PARTICLE TECHNOLOGY LAB

### INTEGRATED CARBON CAPTURE, USE AND STORAGE (CCUS) RESEARCH





Park Group

# Acknowledgements


## Collaborators

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## Sponsors (Current & Past)

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- King Abdullah University of Science and Technology (KAUST-Cornell Center)
- **ORICA Mining Services Ltd.**
- **POSCO (Fluidization, Biomass-to-$H_2$)**
- **KIGAM**
- **CLIMAX GLOBAL ENERGY**
- New York State Energy Research and Development Authority (NYSERDA)
- New York State Foundation for Science, Technology and Innovation (NYSTAR)
- **Columbia University (Diversity Initiative, Earth and Engineering Center)**
- **U.S. Environmental Protection Agency STAR fellowship**

# NSF RCN-SEES: Multidisciplinary Approaches to Carbon Capture, Utilization and Storage (CCUS)

**PI: Ah-Hyung Alissa Park**

(09/2012 – 08/2016, NSF Program Director: Bruce Hamilton)

## Project Management
**LCSE - Columbia University**

PI: **A.-H. Alissa Park**

Columbia PMs: **Taylor** and **Lall** & AIChE team: **Schuster**

## Steering Committee
Thrust POC: **Park**

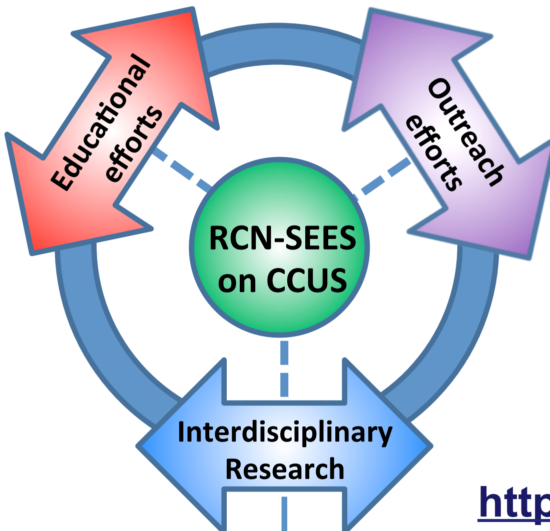
Members: Park, Lackner, Schlosser, Kelemen & Mutter (Columbia), Fan (OSU), Fritt & Socolow (Princeton), Jones (Georgia Tech), Keairns (AIChE), Mazzotti (ETH-Zurich), Rubin (CMU), Sageman (Northwestern), Smit (Berkeley), Snurr (Northwestern) and Song (PennState)

## Educational Thrust
Thrust POC: **Schuster & Pfirman**

- K-12: K-12 teachers (Buck and Miller)
- Young Professional (TBA)
- MCM at Columbia (Lackner)
- Research Experience in C Sequestration (Tomski)
- Women in Science and Engineering (Gadikota)
- Council of Environmental Deans and Directors (CEDD, TBA)

*** Columbia participants unless noted**

*** International participants are in blue**




## PE Society Thrust
Thrust POC: **Keairns & Nguyen** (AIChE)

AIChE (TBA), AIME (TBA), ASCE (TBA), ASME (TBA), IEEE (TBA), Fox (IMECHE)

## Industrial Thrust
Thrust POC: **Gupta (RTI) & Chan** (AIChE)

B&W (Vargas), GE (Perry), RTI (Gupta), SK Energy (Park), ARAMCO (Katikaneni), ORICA Ltd. (Brent), POSCO (Jung), and others to be invited and confirmed

http://www.aiche.org/ccus-network

Academic

## $CO_2$ Capture & Conversion Thrust
Thrust leader: **Petit & West**

Aines (LLNL), Panagiotopoulos & Bocarsly (Princeton), Chen, Coppens (UCL), Lee (SKU), Farrauto, Liu & Heldebrant (PNNL), Li (NCSU), Wang (Zhejiang), Park, Reimer (Berkeley), Snurr (Northwestern), Song (PSU), Wilcox (Stanford), Yegulalp, Zhang & Zhang (CAS-IPE), etc

## $CO_2$ Transportation, Storage & EOR Thrust
Thrust leader: **Matter (USH) & Brady (SNL)**

Baciocchi (UR-TV), Bonneville (PNNL), Blunt (Imperial), Bryant (UT Austin), Dipple (UBC), Dlugogorski (UNewcastle), Goldberg, Lee (KAIST), Park, Peters & Fritt (Princeton), Sageman & Husson (Northwestern), Wang (Yale), Zhu (Indiana), etc

## $CO_2$ MVA & Risk Analysis Thrust
Thrust leader: **Stute & Venkat**

Bonneville (PNNL), Goldberg, Lackner, Meinrenken, Park, Peters (Princeton), Romanak (BEG Texas), Zhu (Indiana), etc

## Policy, Business & Law Thrust
Thrust leader: **Barrett & Gerrard**

Coppens (UCL), Fox (IMECHE), Lackner, Marcotullio, Shindell, Urpelainen, van Ryzin, Weber, Welton, van der Zwaan (ECN), etc