Process Intensification of Hydrogen Production through Sorption-Enhanced Gasification of Biomass

DE-FE0032174

Salt Lake City, Utah

Idaho Falls, Idaho

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2024 FECM/NETL Spring R&D Project Review Meeting—Pittsburgh, PA

Tuesday, April 23, 2024

Background – Hydrogen

Production

- 120 million tons H_2 worldwide each year
- 540 GW equivalent

Sources

- 75% from natural gas reforming
- 25% from coal reforming

Usage

- 63% used for refining and ammonia production
- 37% for MeOH, iron ore processing, etc.

Potential

- Non-carbon energy production (energy carrier)
- Large-scale energy storage
- Hydrogen fuel cell EVs
- Industrial use

Source: ACES Delta

"ACES Delta will feature **220MW of electrolysers that will convert renewable energy, mainly solar and wind, into up to 100 metric tonnes of green hydrogen a day**. This will be stored in two huge salt caverns with a combined **storage capacity of 300GWh**."

Background – Biomass Gasification

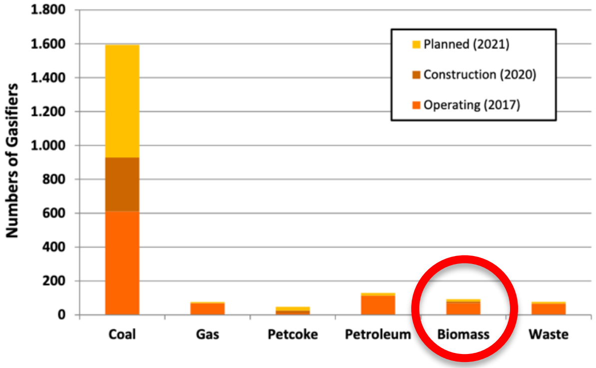
- Conversion of solid or liquid feedstock to *synthesis gas (syngas)*
  - Hydrogen (H_2)
  - Carbon monoxide (CO)
  - Carbon dioxide (CO_2)
  - Methane (CH_4)
  - Other hydrocarbons
- Gasification is common for coal, petroleum
- Main reactions:

$$C + H_2O \rightarrow H_2 + CO \quad \text{(requires heat)}$$
$$C + CO_2 \rightarrow 2\,CO \quad \text{(requires heat)}$$
$$C + O_2 \rightarrow CO_2 \quad \text{(produces heat)}$$

Biomass gasifiers

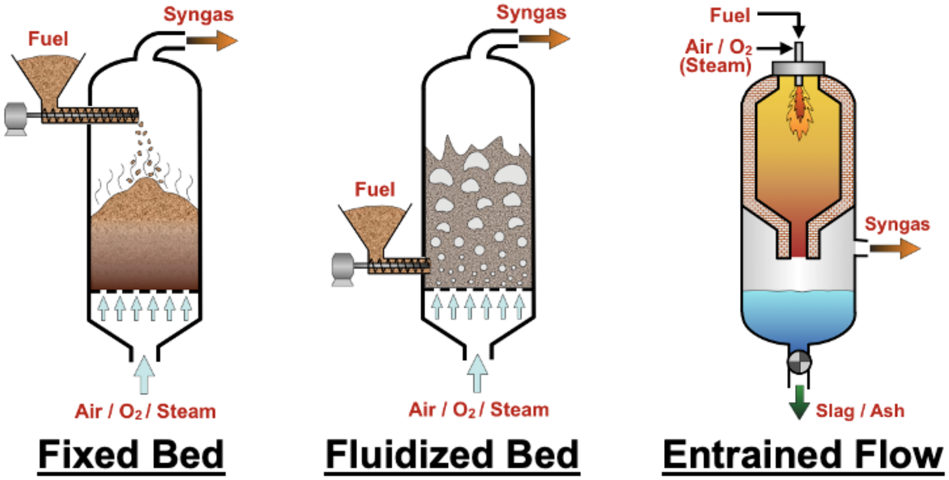
Güssing, Austria—heat and power production

GoBiGas, Sweden—Biomethane production



Higman, GSTC Conference, 2017

Background – Gasification Technologies



Property	Fixed Bed	Fluidized Bed	Entrained Flow
Required feedstock properties	Solid 0.5-2 inch	Solid or liquid	Liquid (slurry) or powder (dry)
Pressurizing/process integration	Difficult	Difficult	"Easy"
Conversion to syngas	80-95%	80-95%	>98%
Syngas quality	Very messy	Quite messy	Comparatively clean

Biomass Feedstocks

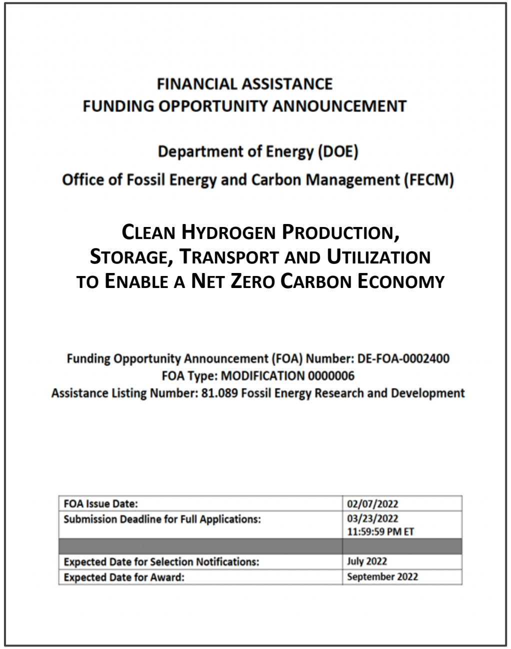
- Forest waste
  - Variety of trees, shrubs
  - Stumps, branches, twigs, needles/leaves
  - High-ash bark
  - Dirt, rocks, etc.
- Agricultural residues
  - Variety of plants
  - Stalks, leaves, roots, cobs
  - Soil, other contaminants
- Other biomass-based opportunity fuels
  - Manure
  - Poultry litter
  - Biosolids from wastewater treatment

Credit: Keith Robinson (phys.org)

Background – FOA Interest Area

- DE-FOA-0002400 mod 006 AOI 1:
  Clean Hydrogen Cost Reductions via Process Intensification & Modularization
  - "Seeks innovations that leverage process intensification"
  - "Combining multiple unit operations into a single subsystem that can accomplish multiple tasks simultaneously"

- Specific examples
  1. "Selective hydrogen extraction...that might have combinatorial benefits on reducing equipment size, advantageously shifting reaction equilibrium..."
  2. "CO_2 removal technologies integrated and combined with gasification system unit operations..."
  3. "Combining of multiple unit operations into a single unit operation..."



FINANCIAL ASSISTANCE
FUNDING OPPORTUNITY ANNOUNCEMENT

Department of Energy (DOE)

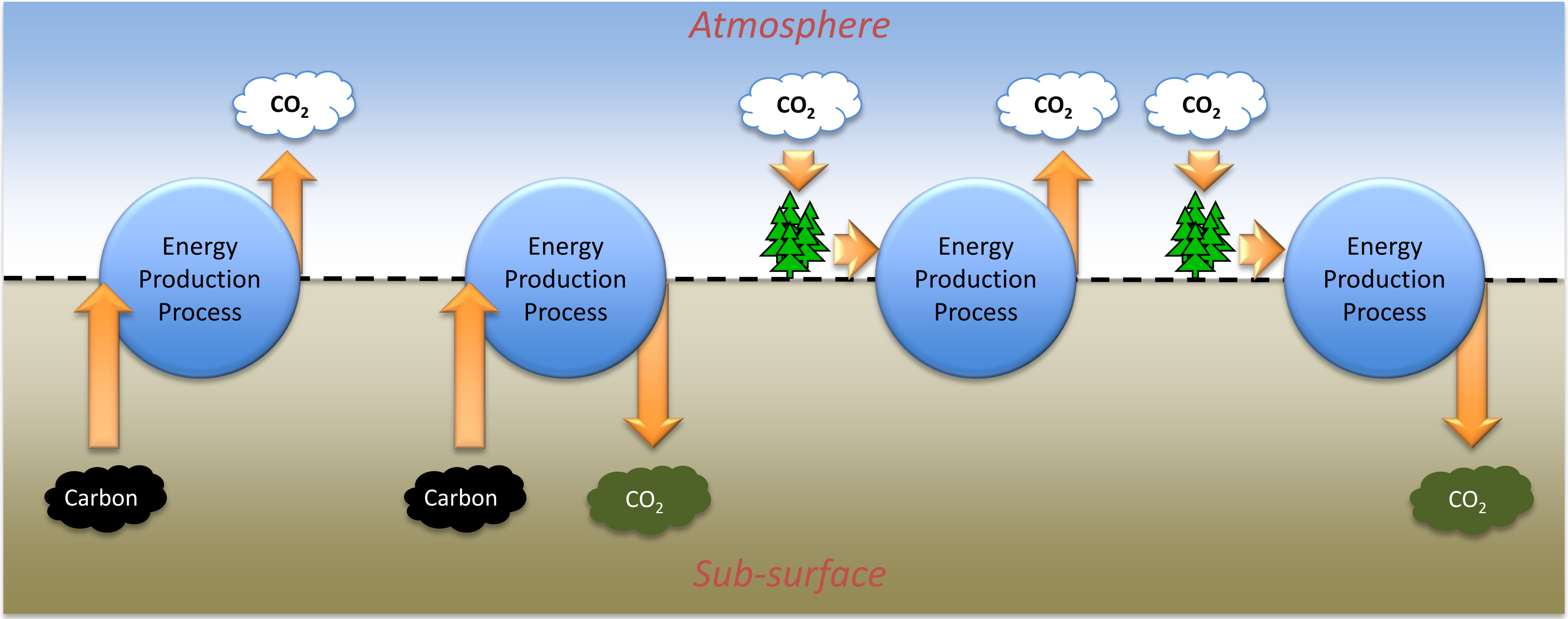
Office of Fossil Energy and Carbon Management (FECM)

CLEAN HYDROGEN PRODUCTION,
STORAGE, TRANSPORT AND UTILIZATION
TO ENABLE A NET ZERO CARBON ECONOMY

Funding Opportunity Announcement (FOA) Number: DE-FOA-0002400
FOA Type: MODIFICATION 0000006
Assistance Listing Number: 81.089 Fossil Energy Research and Development

FOA Issue Date:	02/07/2022
Submission Deadline for Full Applications:	03/23/2022 11:59:59 PM ET
Expected Date for Selection Notifications:	July 2022
Expected Date for Award:	September 2022

Bioenergy as an Enabler for Carbon Neutral and *Carbon Negative* Energy Production



Conventional fossil fuel combustion

Fossil fuel combustion with CCS

Biomass (and waste) combustion

Biomass combustion + CCS = *negative* CO_2

Technical Approach – Process Intensification

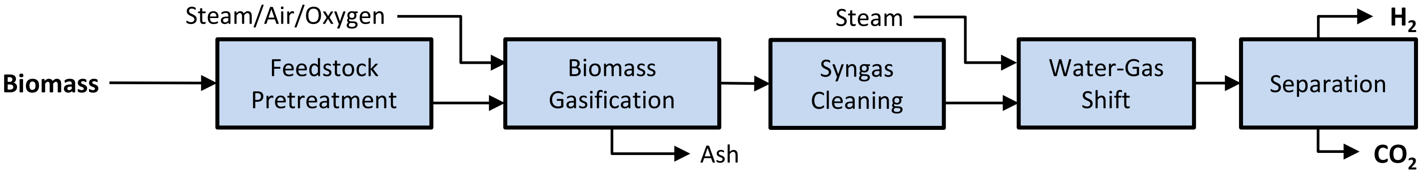
- Conventional conversion of biomass to H_2 is a multi-step process
  - Typically fluidized bed or fixed bed gasifiers
  - Needs feedstock preparation

    ...then gasification to make H_2 and CO

    ...then syngas cleaning to remove tars and other contaminants

    ...then water-gas shift to maximize hydrogen ($H_2O + CO \rightarrow H_2 + CO_2$)

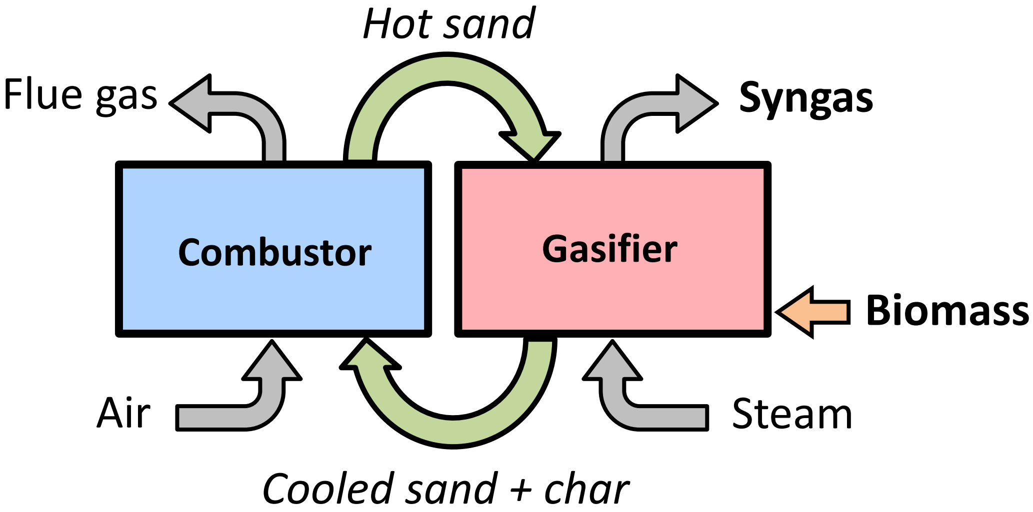
    ...then H_2/CO_2 separation by e.g. pressure swing absorption (PSA)
  - Overall, a complex, expensive process



Conventional approach for hydrogen production from biomass

- Need *process intensification* to reduce complexity and number of units
- Solution: *Sorption-Enhanced* Gasification

Dual Fluidized Bed (DFB) Gasification



Hot sand

Flue gas

Syngas

Combustor

Gasifier

Biomass

Air

Steam

Cooled sand + char

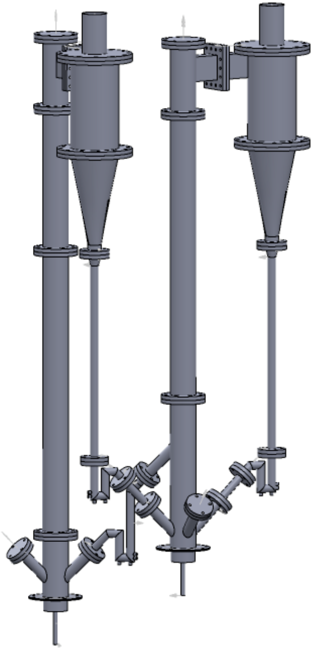
Combustor:

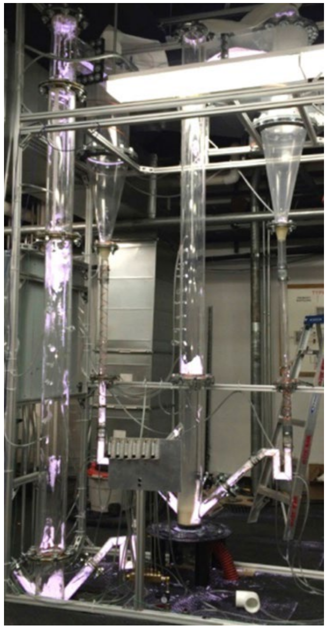
$C + O_2 \rightarrow CO_2$

Gasifier:

$C + H_2O \rightarrow CO + H_2$

- Sand (e.g. olivine) is heat carrier for gasifier
- 80-85% conversion of biomass in gasifier
- Unconverted char carried to combustor to heat sand

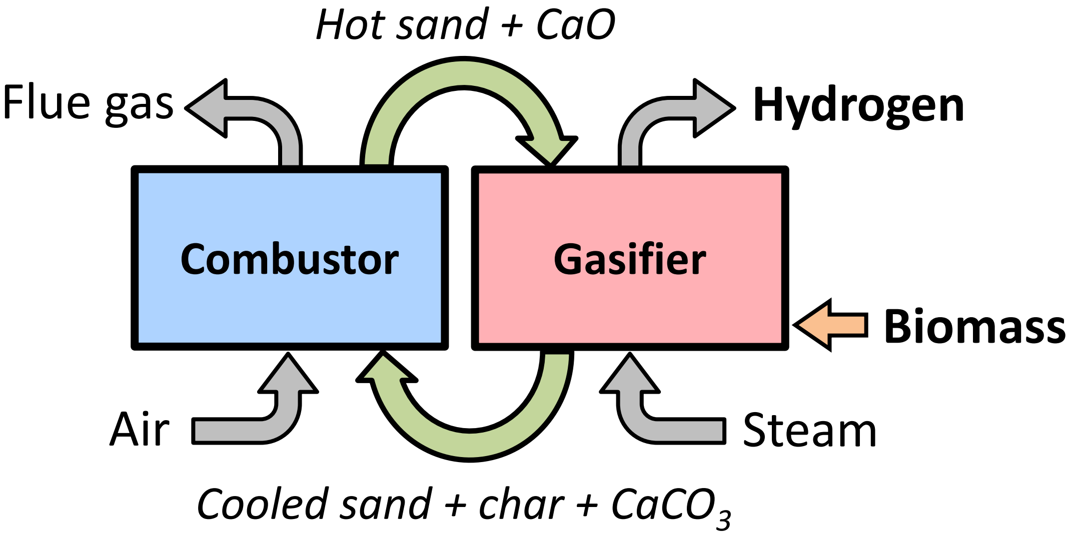




Sorption-Enhanced DFB Gasification

THE UNIVERSITY OF UTAH

- Add limestone to the dual fluidized bed gasification system to absorb CO_2



$C + O_2 \rightarrow CO_2$

$CaCO_3 \rightarrow CaO + CO_2$

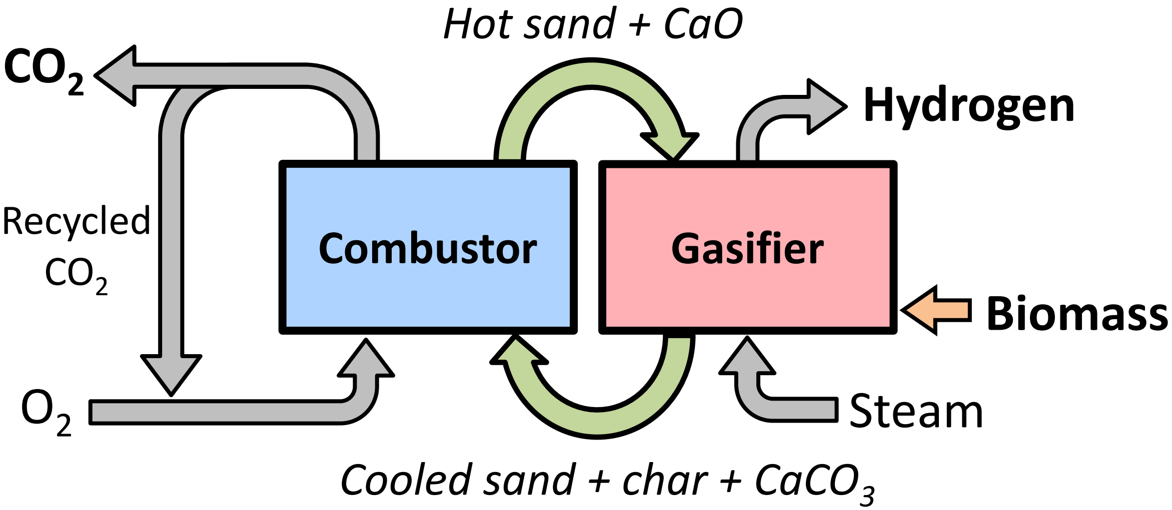
$C + H_2O \rightarrow CO + H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

$CaO + CO_2 \rightarrow CaCO_3$

Oxy-Sorption-Enhanced DFB Gasification

- Operate combustor as an oxy-fuel system with pure O_2 and recycled CO_2



$C + O_2 \rightarrow CO_2$

$CaCO_3 \rightarrow CaO + CO_2$

$C + H_2O \rightarrow CO + H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

$CaO + CO_2 \rightarrow CaCO_3$

Project Objectives

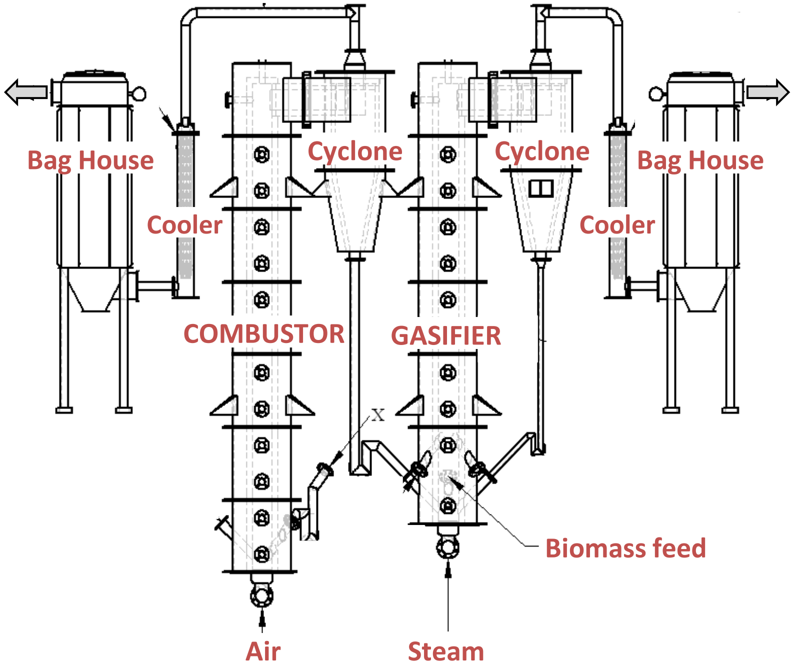
- **Overall objective:** Demonstrate the feasibility of sorption-enhanced biomass gasification for production of H_2-rich syngas in a dual fluidized bed reactor operating under industrially-relevant conditions. This will be achieved by pre-processing the biomass feedstock to ensure consistent composition and trouble-free feeding, combined with operation of an existing dual fluidized bed process development unit with addition of limestone to achieve in situ removal of CO_2 from the gasifier to create a clean, high-hydrogen syngas.

- **Specific objectives:**
  1. Demonstrate that waste biomass can be pre-processed to promote SEG
  2. Understand and model fundamental processes of SEG
  3. Evaluate SEG performance and syngas quality over a range of industrially-relevant conditions
  4. Demonstrate oxy-SEG to produce separate of H_2- and CO_2-rich streams

Project Structure – Tasks

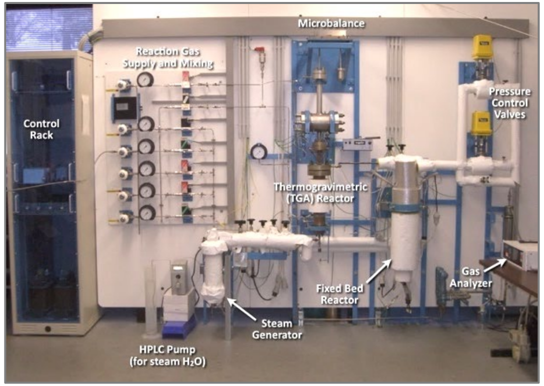
1. **Project management and planning**
2. **Biomass feedstock preparation (in collaboration with INL)**
    - 2.1 Procure and characterize biomass materials
    - 2.2 Prepare and pelletize biomass
    - 2.3 Prepare pellets of combined biomass and limestone
3. **Fundamental studies of sorption-enhanced gasification**
    - 3.1 Characterize gasification rates of prepared fuels
    - 3.2 Lab-scale sorption-enhanced gasification studies
    - 3.3 Evaluate methods to maximize hydrogen production
4. **PDU studies of sorption-enhanced gasification**
    - 4.1 Preparation of dual fluidized bed PDU for sorption-enhanced gasification
    - 4.2 Initial PDU testing and scoping trials
    - 4.3 Parametric testing of sorption-enhanced gasification
    - 4.4 Testing oxy-SEG for hydrogen production with CO_2 capture
5. **Modeling of sorption-enhanced gasification**
    - 5.1 Dual fluidized bed gasification reactor modeling
    - 5.2 Process modeling of sorption-enhanced gasification
    - 5.3 Economic modeling as a tool to reduce hydrogen cost

Dual Fluidized Bed Process Development Unit

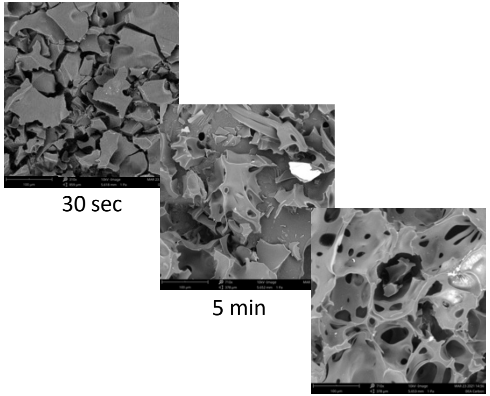


Biomass Conversion Studies

- **Chemical considerations**
  - Distribution into volatiles, char
  - Volatiles composition
  - Ash chemistry
- **Physical considerations**
  - Feedstock preparation
  - Char properties
  - Fluidizing characteristics
- **Gasification rates**
  - Influence of temperature
  - Influence of pressure
  - Influence of CO and H_2
  - Development of kinetic models



High pressure thermogravimetric analyzer



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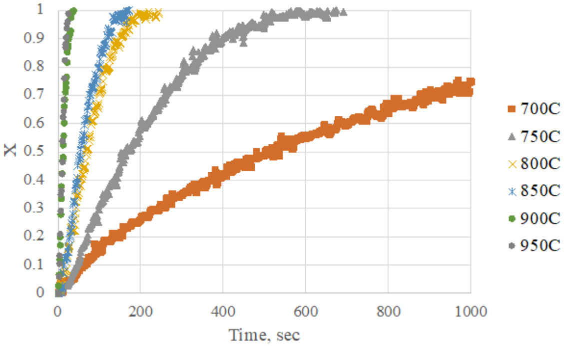
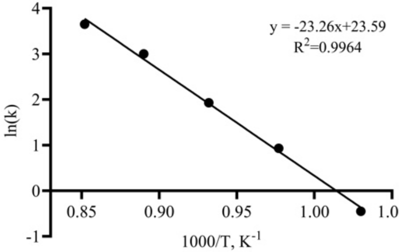


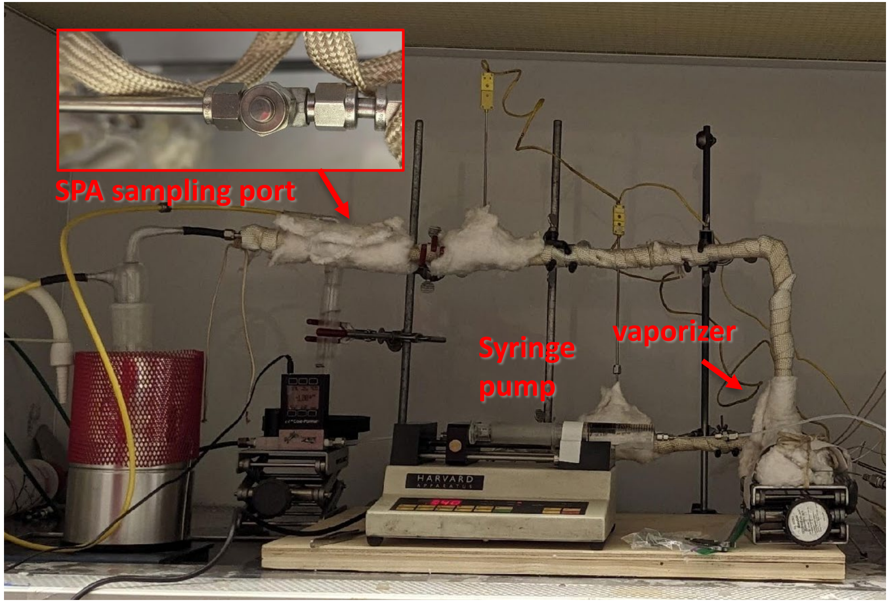
Influence of temperature on char gasification of loblolly pine



Activation energy 193 kJ/mol

Tar cracking studies

- Tars will be formed as a result of biomass gasification
- *How can tars be cracked to form smaller molecules?*
- Solid acids with metal dopants as catalyst to crack tars
- Naphthalene as a representative for tars



Effectiveness of CO_2 Sorbents

$CaO + CO_2 \longleftrightarrow CaCO_3$

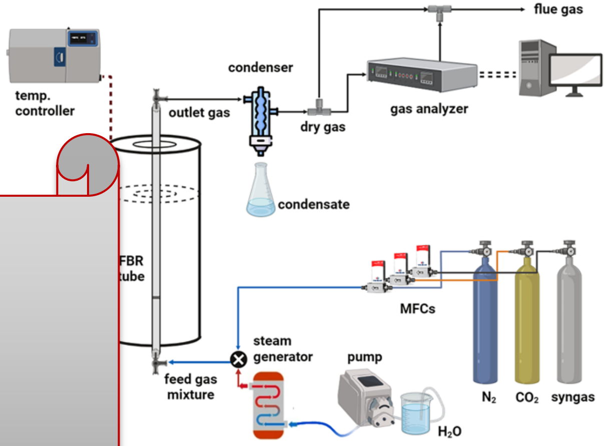
- Sorption capacity
- Rates of reaction
- Suitable temperatu
- Influence of H_2O, C
- Different types of l estone and dolomite materials
- Influence of particle size

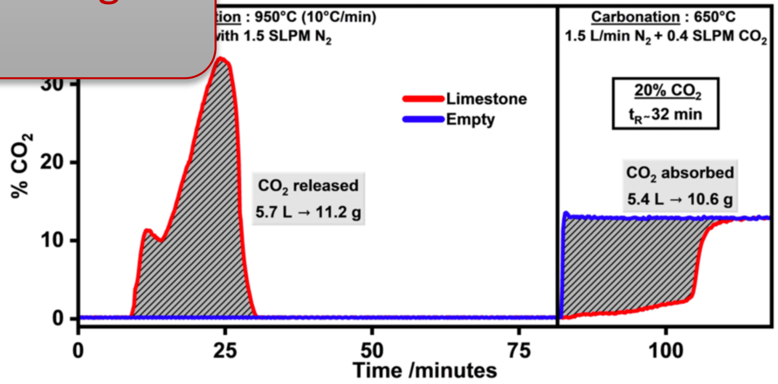
For more details:

Poster presentation:

S.A. Sufyan

on Wednesday evening.

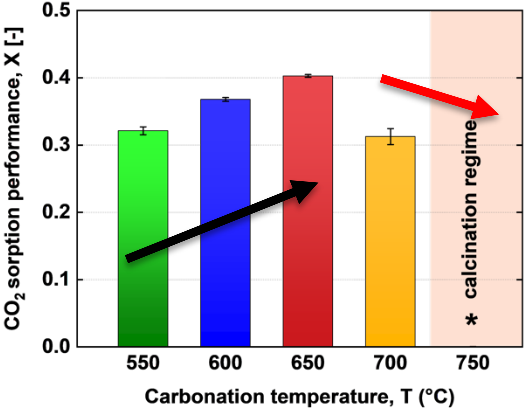




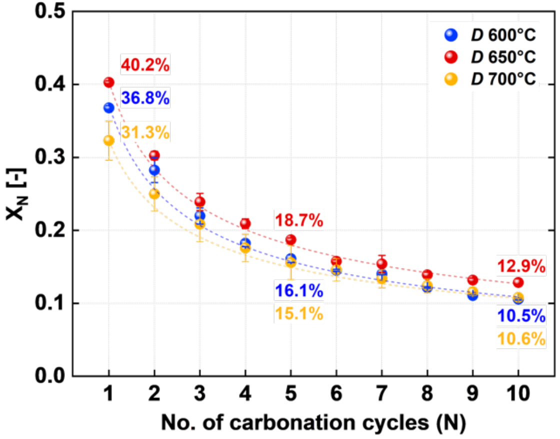
Temperature Effects on Carbonation

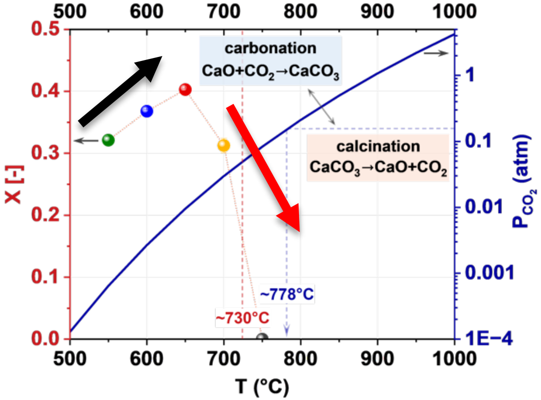
- **Increase in CO_2 sorption with increasing T**.
- Further increase of carbonation T would bring about thermodynamic limitations.
- At a given T, if $P_{CO2} > P_{eq}$ carbonation takes place.

Due to the chemical equilibrium of the capture reaction, gasification temperature is limited to T < 720°C



Carbonation @550-750°C ($20\%\ CO_2$, balance N_2)



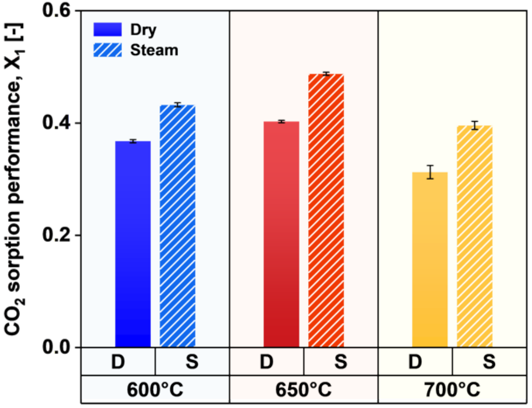


Baker, *J. Chem. Soc.* **1962**

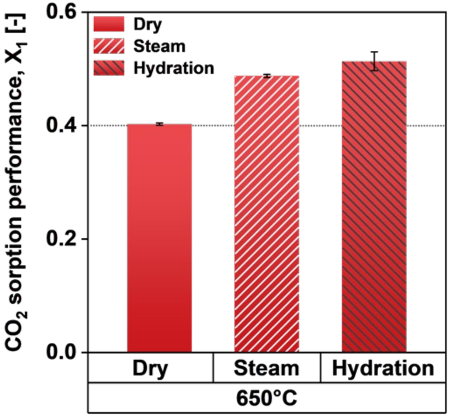
Effect of Steam Addition during Carbonation

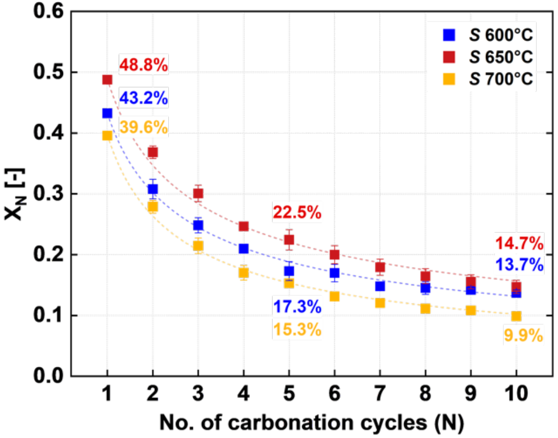
- **Increase in CO_2 sorption with steam** across carbonation T.
- **Increased pore volume** and **formation of cracks** (large increase of the reaction surface) enhance the **solid-state diffusion through the carbonate layer**.
- **CaO hydration** to obtain $Ca(OH)_2$ can be used to increase carbonation extent.

Sorption capacity is enhanced with steam, holds true over multiple cycles



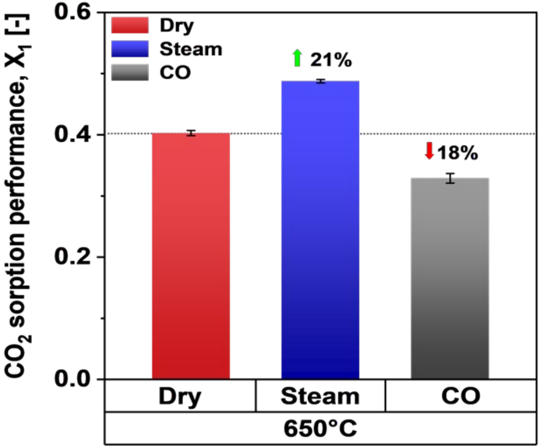
Carbonation @600-700°C
(20% CO_2 + 50% steam, balance N_2)



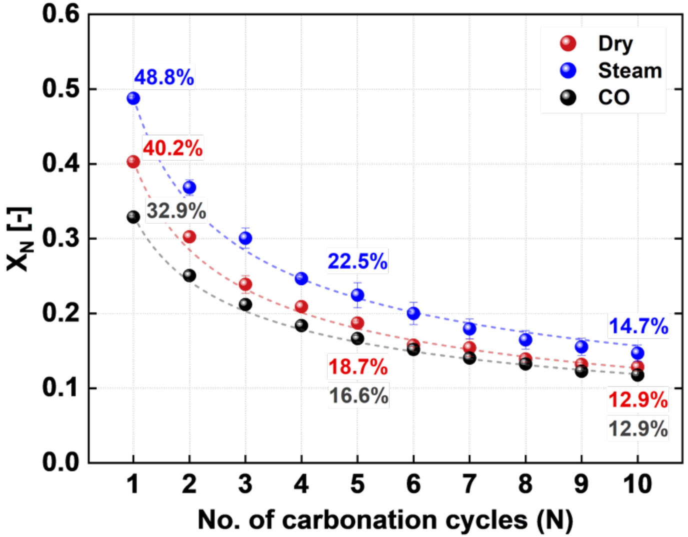


Effect of CO Addition during Carbonation

- **Decrease in CO_2 sorption** is observed when CO is introduced, even with as little as **2 *vol.%* CO**
- Competitive adsorption of CO and CO_2 for CaO*
- **Boudouard reaction**: $2CO \rightarrow CO_2 + \mathbf{C}$



Carbonation @650°C
(20% CO_2 + 10% CO)



CO_2 sorption performance is limited by CO addition; C – deposition, sorbent deactivation

Effect of H_2 Addition during Carbonation

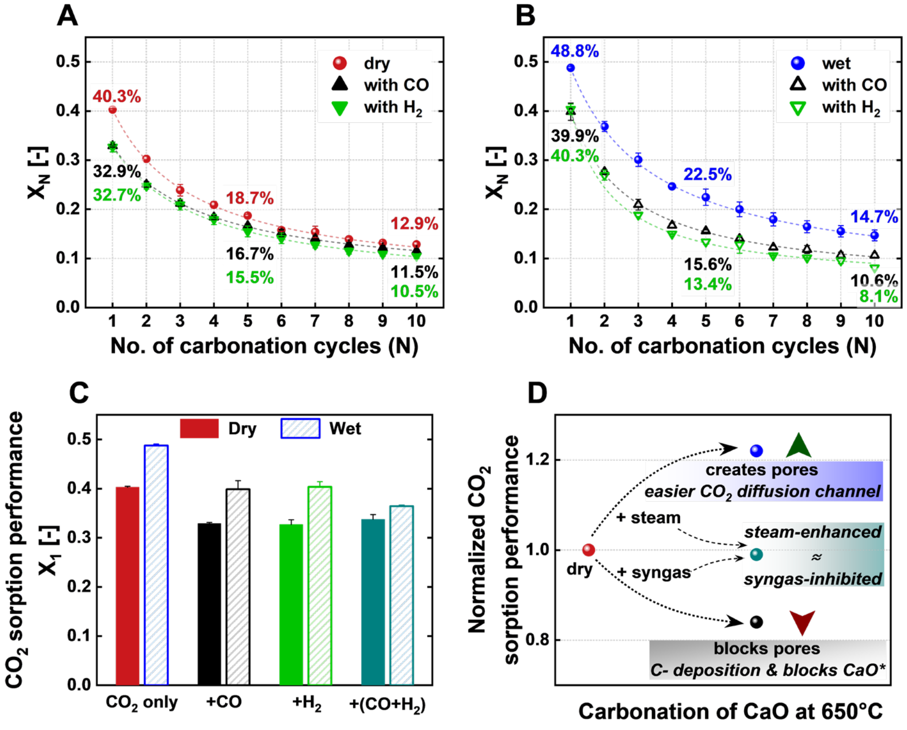
- **Decrease in CO_2 sorption** is observed when H_2 is introduced, similar to that of CO addition
- Competitive adsorption of H_2 and CO_2 for CaO*
- Instance of **RWGS:**

$$CO_2 + H_2 \rightarrow \mathbf{CO} + H_2O$$

- Addition /*in situ* formation of **CO** limits CO_2 sorption performance of CaO, even with steam-added carbonation

Steam-enhanced and syngas-inhibitory effects balance out in presence of both.

Carbonation @650°C
(20% CO_2 + 10% H_2)



Multicyclic performance of CaO

$$X_N = Xr + \frac{X_1}{k(N-1) + \left(1 - \frac{X_r}{X_1}\right)^{-1}}$$

X_1 initial conversion; ***k*** decay constant, ***X_r*** is residual conversion

- Decrease in surface area due to sintering is proportional to a power of available surface area
- Conversion is proportional to the surface area available

Conditions	**X_1**	**k**	**X_r**	**% decay 1-5**	**% decay 1-10**
Dry-650	0.403	0.463	0.047	53.5%	68.1%
Dry-CO	0.329	0.427	0.05	49.4%	65.0%
Dry-H_2	0.327 ↓	0.395 ↓	0.033 ↓	52.5% ↓	68.0% ↓
Wet-650	0.489	0.446	0.051	54.0%	69.9%
Wet-CO	0.4	0.613	0.045	60.9%	73.3%
Wet-H_2	0.403	0.633	0.046	66.8%	79.9%

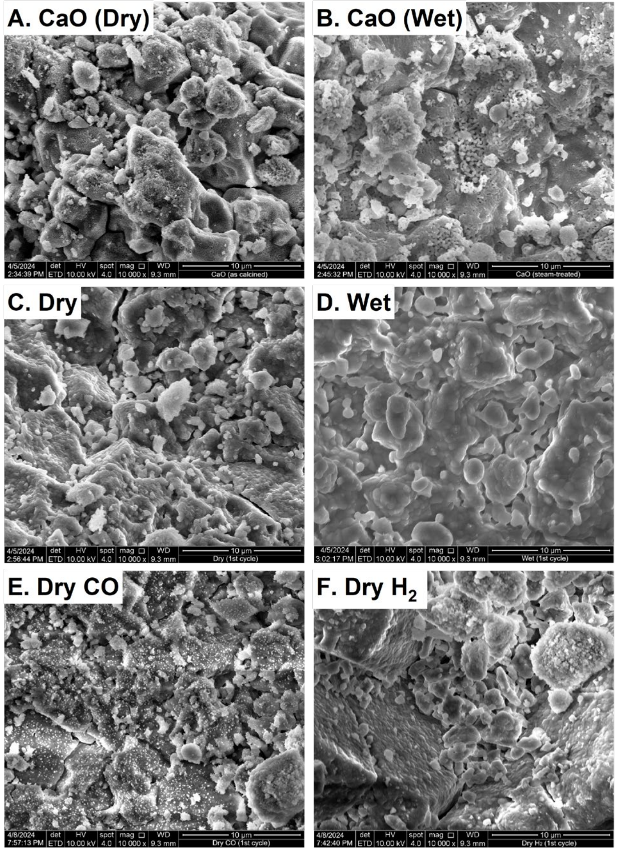
↓ indicates direction of increase

- **Steam increases** initial & residual activity
- Sorbent decay **increases** with **steam** addition
- Steam **increases** elutriated fines/ fragmentation
- Sorbent **loses** activity with syngas introduction
- Decay with syngas is **more pronounced** in steam

Characterization of Spent Sorbent(s)

- **More open microstructures** & **increased pore volume** of CaO with <u>steam treatment</u>, less resistance to CO_2 diffusion to CaO core.
- **Grain sizes are noticeably larger** with <u>steam carbonation</u>, due to **sintering** enhanced with steam.
- Particles formed **aggregates** with CO/H_2 addition, resulting in a **loss of surface area** & **pore volume for CO_2 sorption**.

Sample	**BET surface area, m^2/g**	**BJH pore volume, cm^3/g (x 10^{-3})**
CaO (dry)	8.76	83.81
CaO (wet)	**9.54**	**132.65**
Spent sorbent after 1st carbonation at 650°C		
Dry	0.25	7.52
Wet	**0.38**	**9.12**
Dry CO	**0.22**	**4.55**
Dry H_2	**0.24**	**4.18**



Acknowledgements

- This material is based upon work supported by the U.S. Department of Energy under award number DE-FE0032174 (PM: Sarah Pfeiffer)
- Idaho National Laboratory (INL)
  - Jordan Klinger
  - Nepu Saha
- University of Utah Gasification Research Group
  - Kevin Whitty
  - **Sayed A Sufyan**
  - Jieun Kim
  - Rashmi Charde
  - David Wagner
  - Daniel Varga
  - Hayden West