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

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Background – Hydrogen

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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:

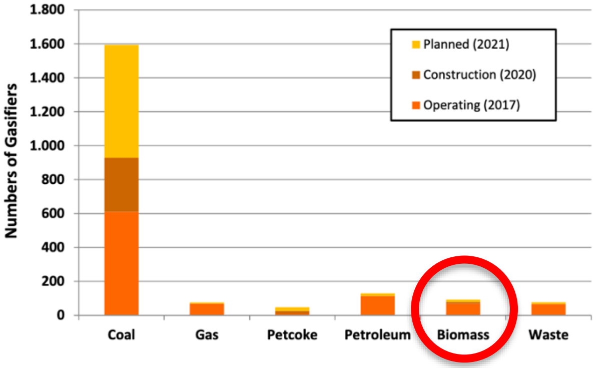
$C + H_2O \rightarrow H_2 + CO$ (requires heat)

$C + CO_2 \rightarrow 2\ CO$ (requires heat)

$C + O_2 \rightarrow CO_2$ (produces heat)

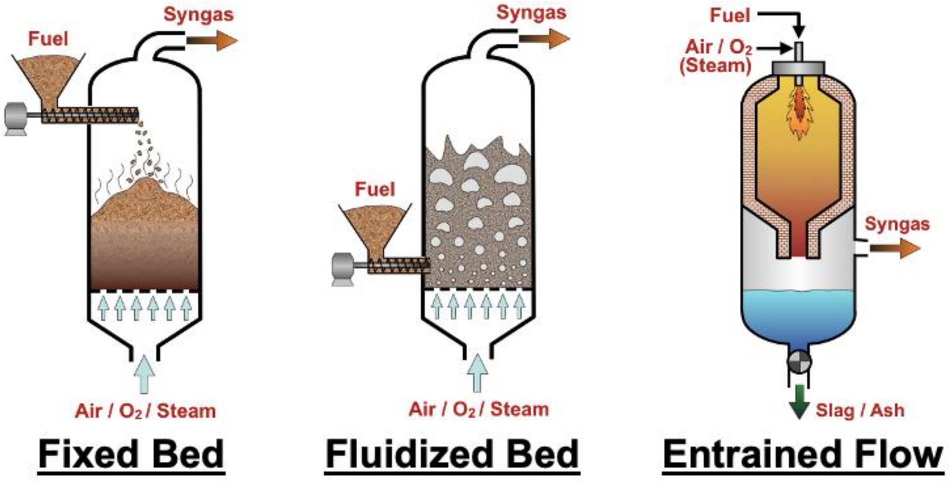
Güssing, Austria

GiBiGas, Sweden



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)

Municipal Solid Waste (RDF, SRF)

- Attractive due to potential for negative fuel cost
- Challenging due to
  - Heterogeneity of feedstock
    - requires sorting but will still contain small quantities of metal, glass, ceramic
    - day-to-day (hour-to-hour) variation
  - Physical properties (plastics, fluff, string) complicates feeding
  - Chemical impurities (chlorine, volatile metals)

Source: Grupo SPR

Source: srfpellets.com

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)

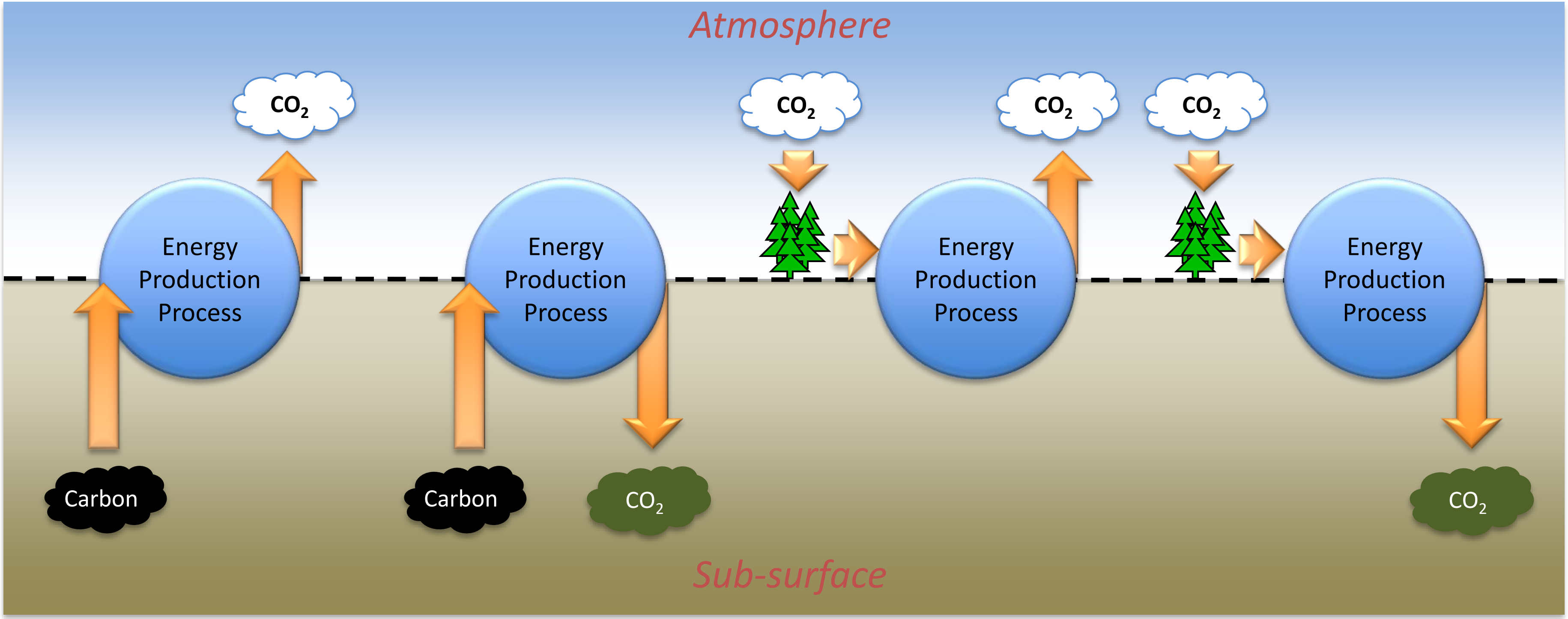
Office of Fossil Energy and Carbon Management (FECM)

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

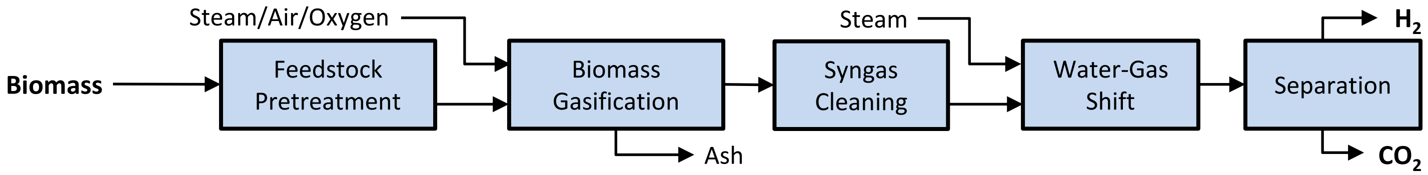
- Conventional conversion of biomass to H_2 is a multi-step process
  - Typically fluidized bed or fixed bed gasifiers
  - Needs feedstock preparation

    ...then gasification to make H_2 and CO

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

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

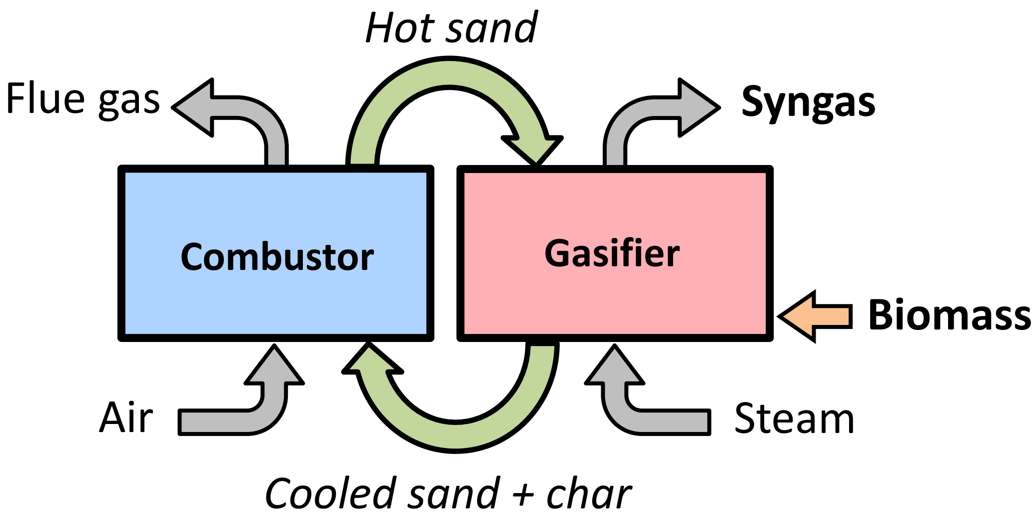
    ...then H_2/CO_2 separation by e.g. pressure swing absorption (PSA)
  - Overall, a complex, expensive process

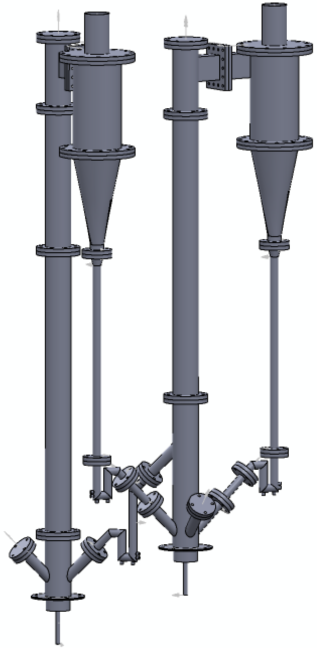


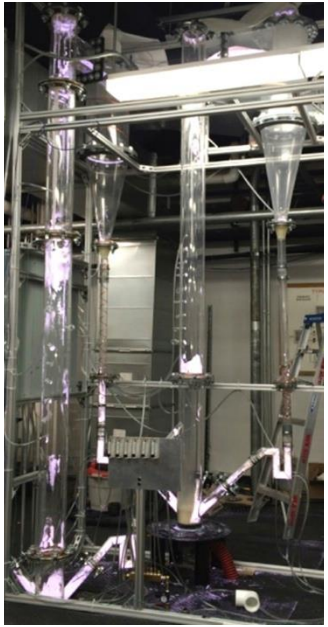
Conventional approach for hydrogen production from biomass

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

Dual Fluidized Bed (DFB) Gasification







Combustor:

$C + O_2 \rightarrow CO_2$

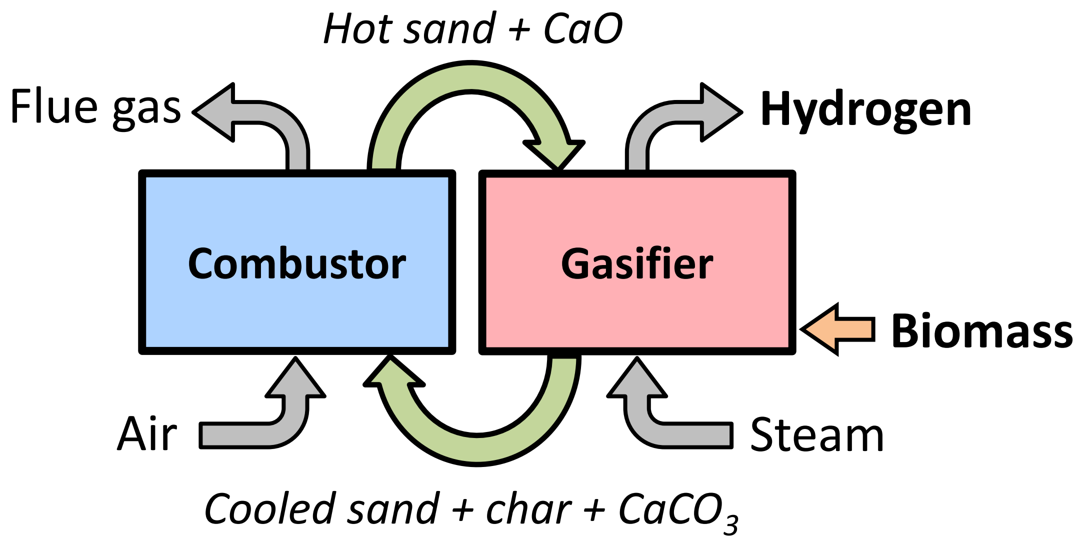
Gasifier:

$C + H_2O \rightarrow CO + H_2$

- 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

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

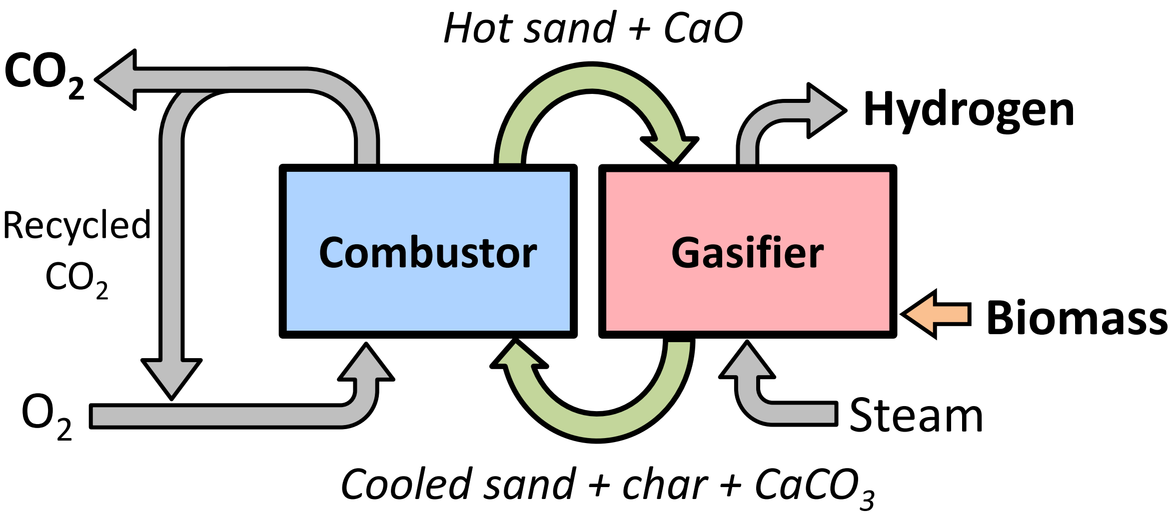


$$C + O_2 \rightarrow CO_2$$
$$CaCO_3 \rightarrow CaO + CO_2$$

$$C + H_2O \rightarrow CO + H_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$CaO + CO_2 \rightarrow CaCO_3$$

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

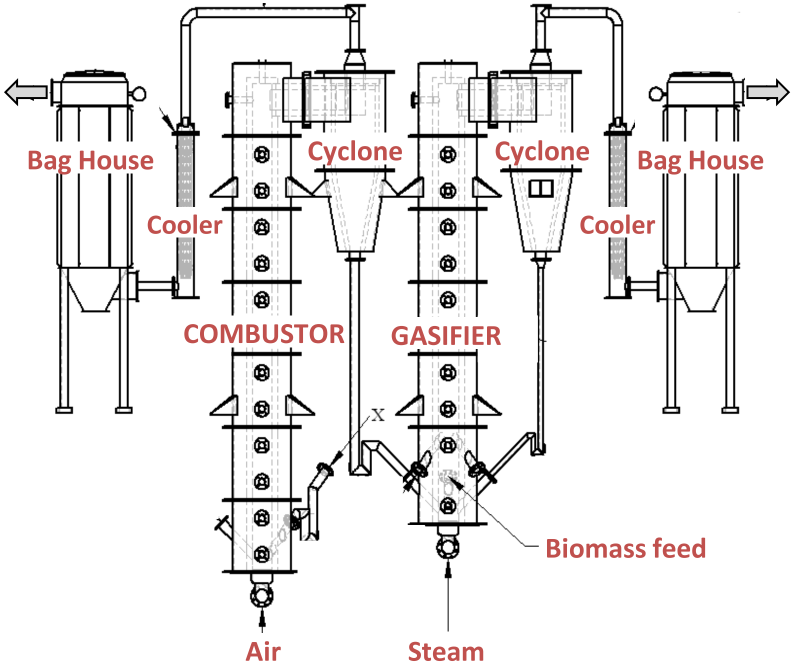
- **Overall objective:** Demonstrate the feasibility of sorption-enhanced biomass gasification for production of H_2-rich syngas in a dual fluidized bed reactor operating under industrially-relevant conditions. This will be achieved by pre-processing the biomass feedstock to ensure consistent composition 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

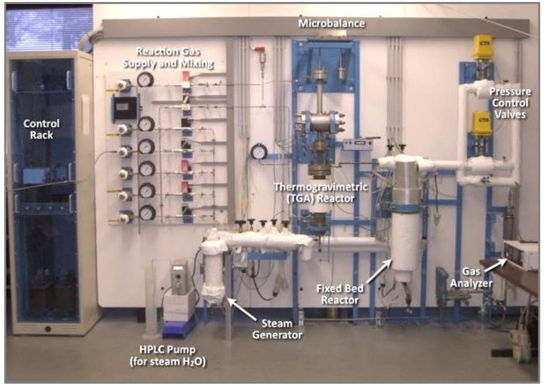
1. **Project management and planning**
2. **Biomass feedstock preparation**
   - 2.1 Procure and characterize biomass materials
   - 2.2 Prepare and pelletize biomass
   - 2.3 Prepare pellets of combined biomass and limestone
3. **Fundamental studies of sorption-enhanced gasification**
   - 3.1 Characterize 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

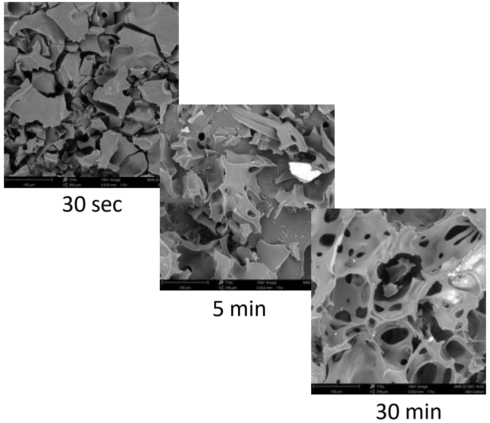


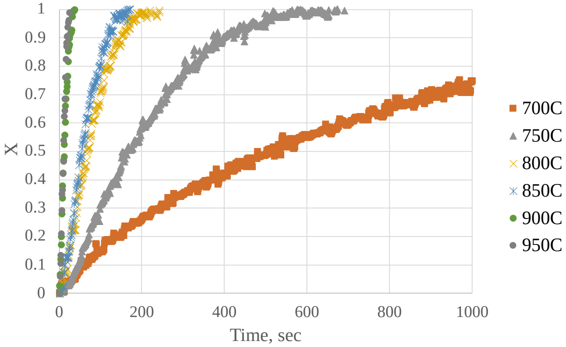
Biomass Conversion Studies

- 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

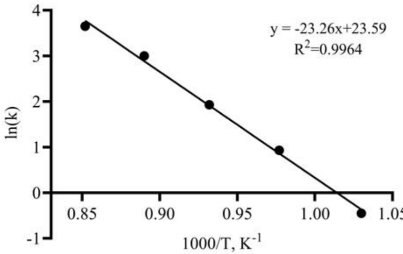


High pressure thermogravimetric analyzer





Influence of temperature on char gasification of loblolly pine

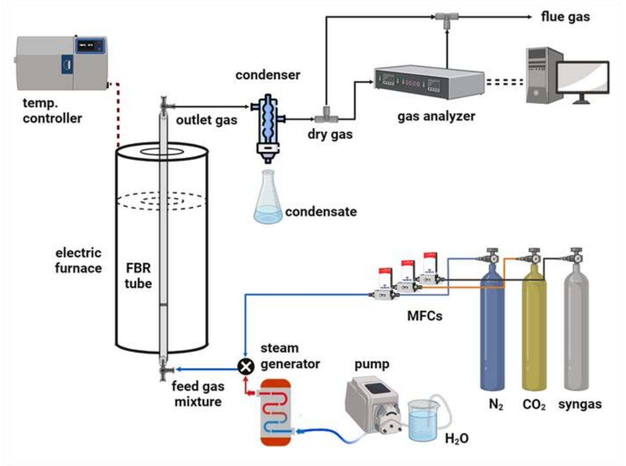


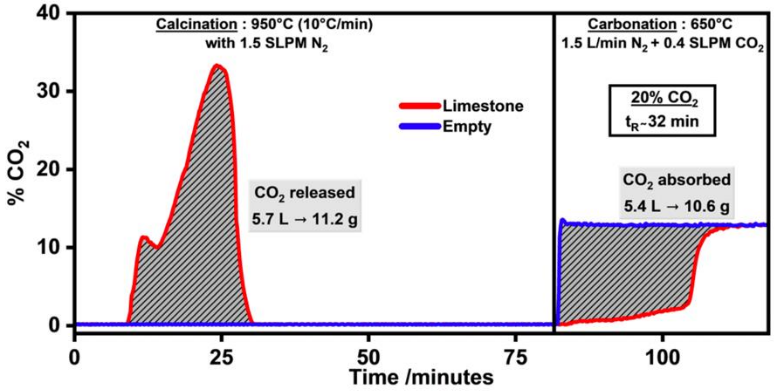
Activation energy 193 kJ/mol

Effectiveness of CO_2 Sorbents

$CaO + CO_2 \leftrightarrow CaCO_3$

- Sorption capacity
- Rates of reaction
- Suitable temperature regime
- Influence of H_2O, CO, H_2
- Different types of limestone and dolomite materials
- Influence of particle size

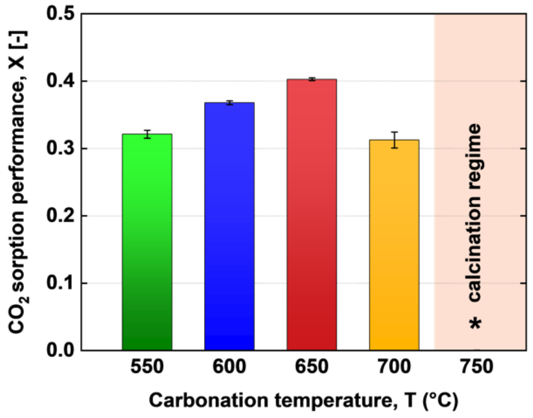


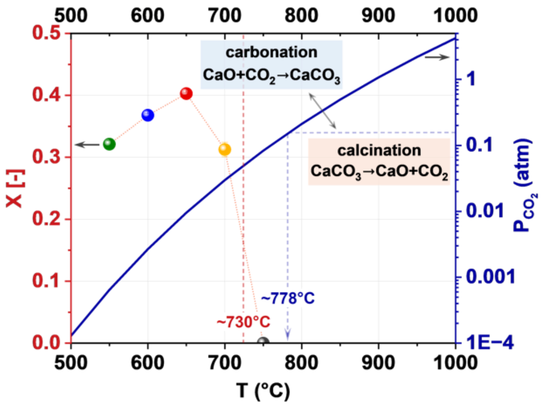


Temperature Effects on Carbonation

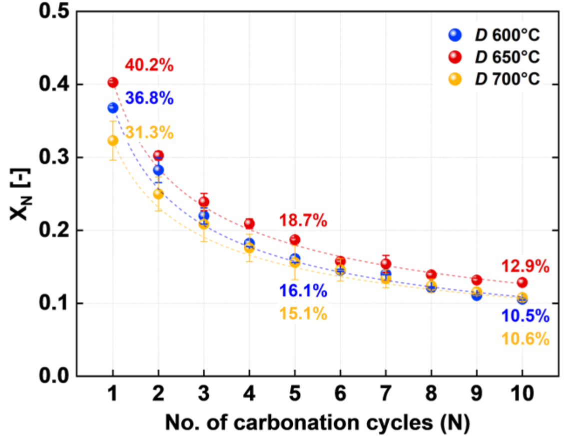
- **Increase in CO_2 sorption with increasing T**.
- Further increase of carbonation T would bring about thermodynamic limitations.
- At a given T, if $P_{CO2} > P_{eq}$ carbonation takes place.

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

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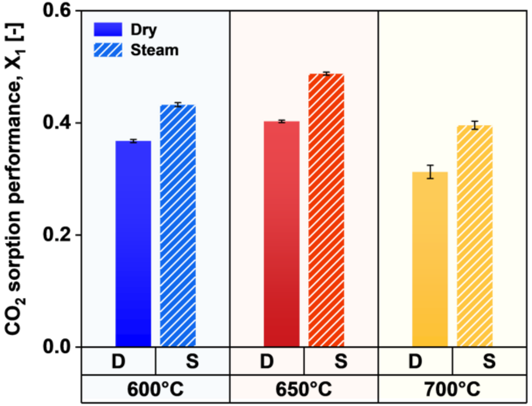
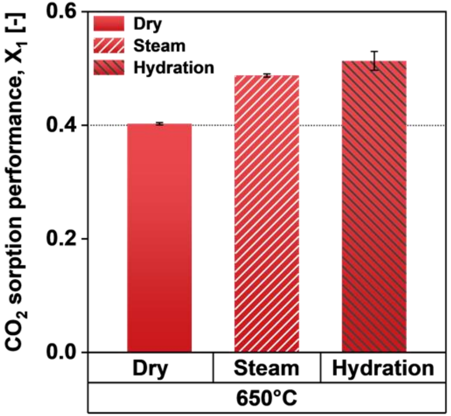
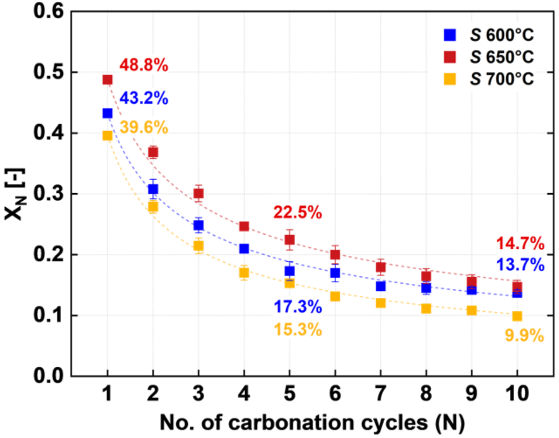
- **Increase in CO_2 sorption with steam** across carbonation T°C.
- **Increased pore volume** and **formation of cracks** (large increase of the reaction surface) enhance the **solid-state diffusion through the carbonate layer**.
- **CaO hydration** to obtain $Ca(OH)_2$ can be used to increase carbonation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

Sorption capacity is enhanced with steam, holds true over multi-cycle



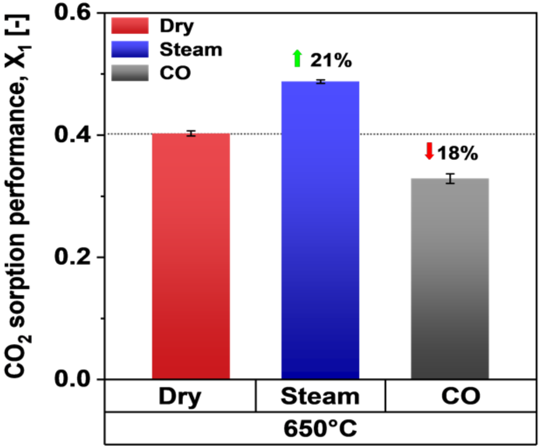
Carbonation @600-700°C
(20% CO_2+ 50% steam, balance N_2)



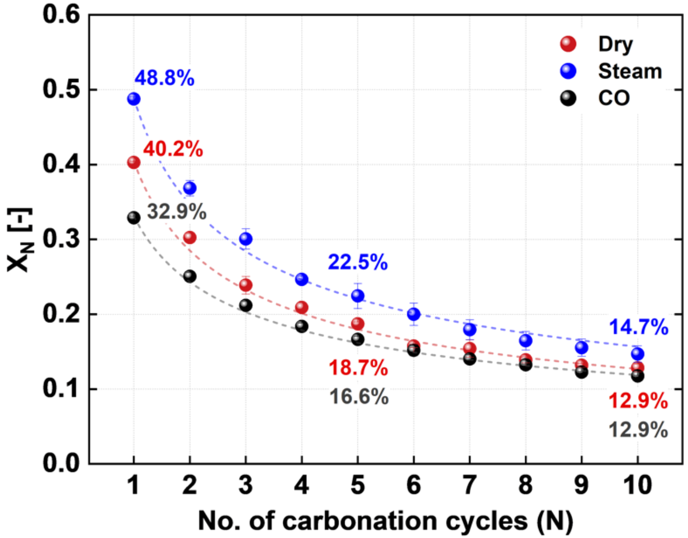


Effect of CO Addition during Carbonation

- **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**: $2CO \leftrightarrow CO_2 + \mathbf{C}$

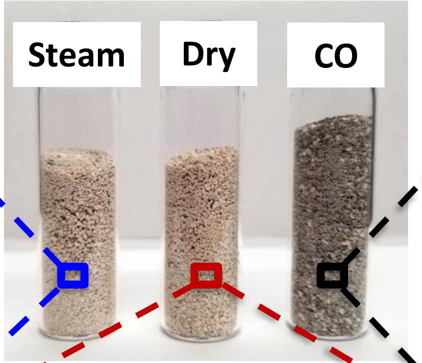


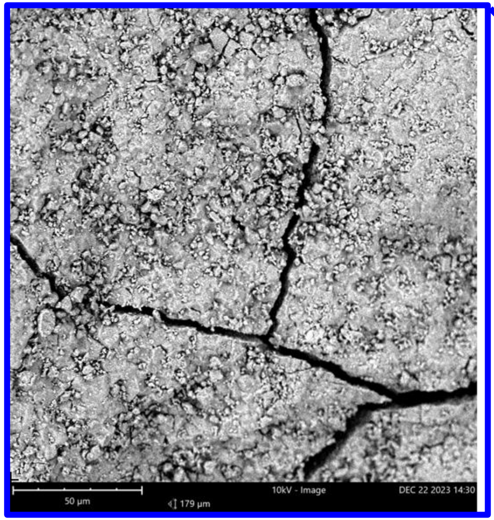
Carbonation @650°C
(20% CO_2 + 10% CO, balance N_2)



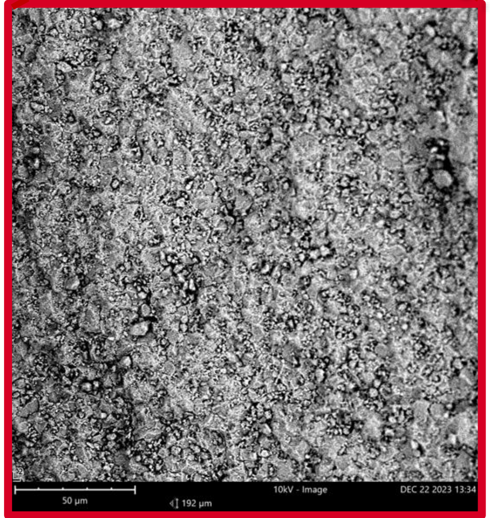
CO_2 sorption performance is limited by CO addition; C – deposition, sorbent deactivation

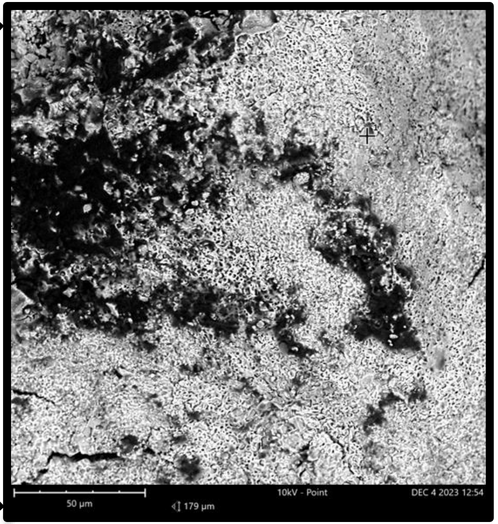
SEM Characterization of Spent Sorbents





Formation of cracks and increased pore volumes, creating easier diffusion channel for CO_2 towards unreacted CaO core





Visible carbon deposits on CaO, blocking CaO* and pores, otherwise available for CO_2

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