

Topic 18F – Clean Coal and Carbon Management
Solar Energy Powered Materials-Based Conversion of CO₂ to Fuels
DE-SC0015855
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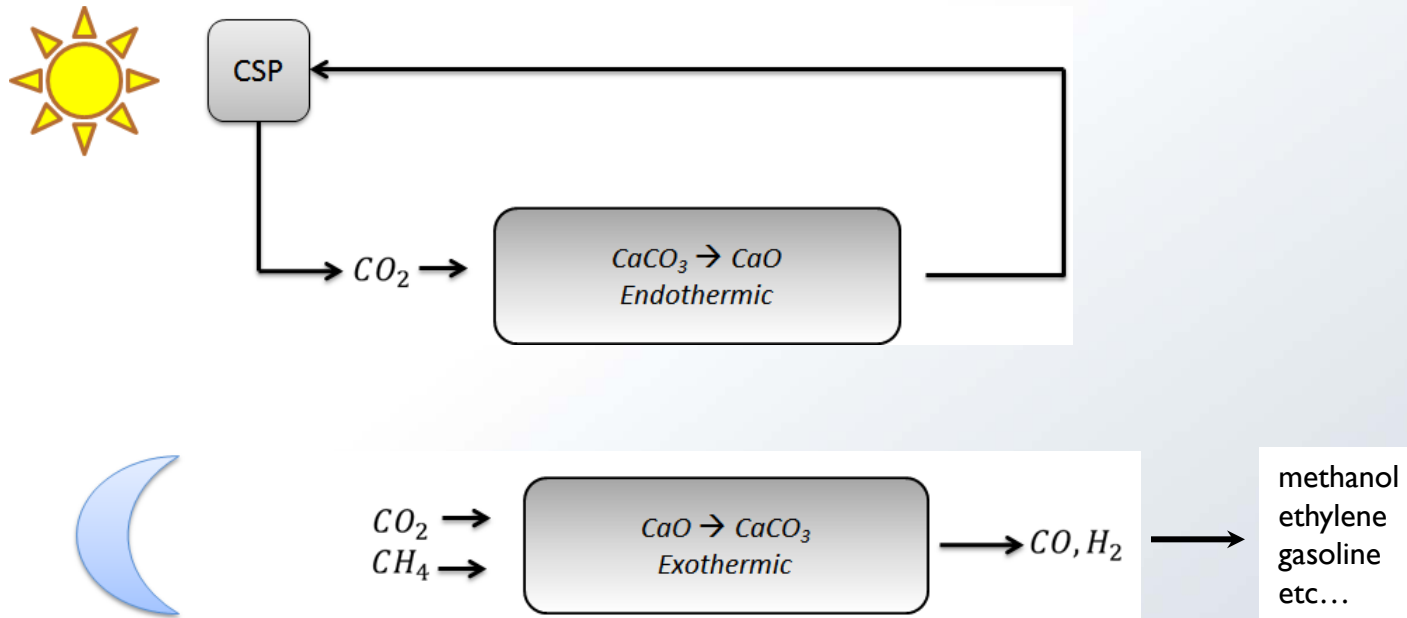
INTRODUCTION

Solar Energy Powered Materials-Based Conversion of CO₂ to Fuels

- Convert thermal energy to chemical energy
 - High grade thermal energy (750 – 900 °C)
 - from Concentrated Solar Power
 - Reactants
 - CO₂
 - CH₄
- Requirements
 - Ready sources of CO₂, natural gas, sunshine
 - CA, NM, TX – yes CT, PA, WV – not as likely
- Potential advantages of PCI approach
 - Compact, scalable, process intensification → improved efficiencies

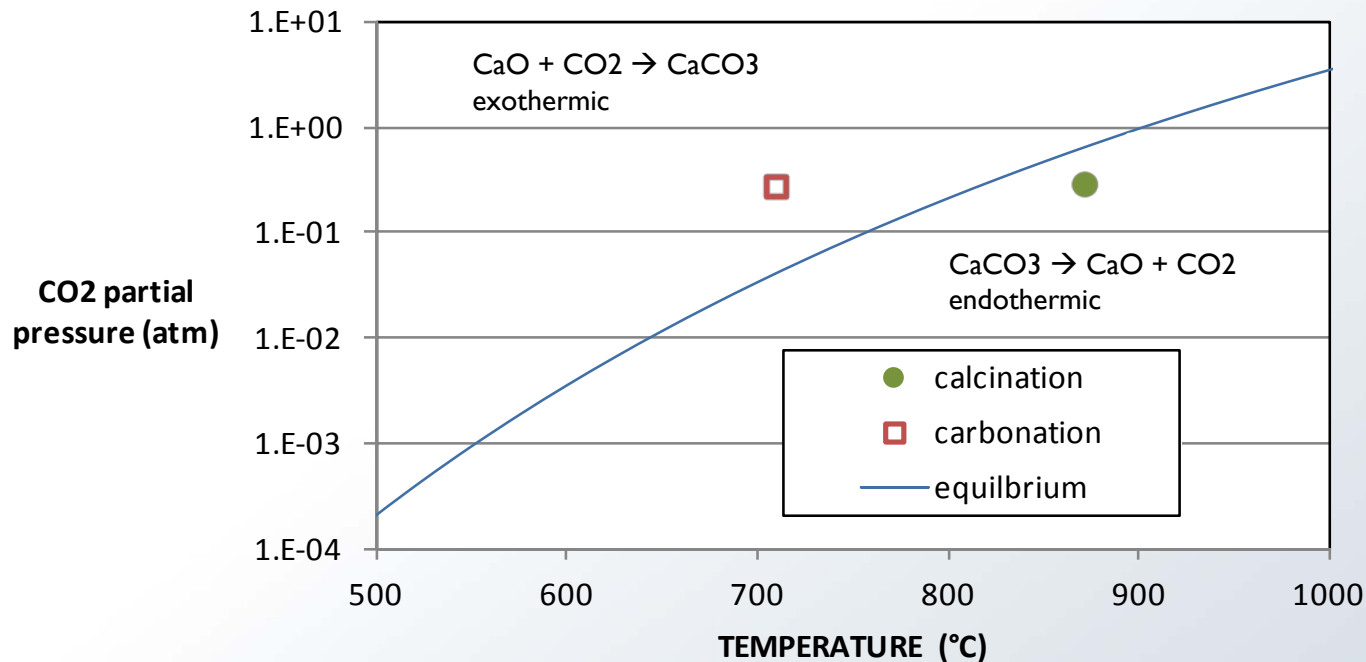
Process Overview - System

- Solar power driven conversion of CO_2 and CH_4 to fuels/chemicals via syngas intermediate
- Key aspects – energy storage/release and CO_2 conversion
- Concentrated solar power (CSP) – NREL technology
- CaCO_3 based energy storage – well known process
- CO_2 / CH_4 ‘dry reforming’ well known
- CO/H_2 upgrading – various processes available



Process Overview – Energy Storage and Release

- $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ equilibrium based energy storage
- CO_2 is used as:
 - Heat transfer fluid
 - Drives thermal energy storage reaction cycle
 - Reactant with CH_4



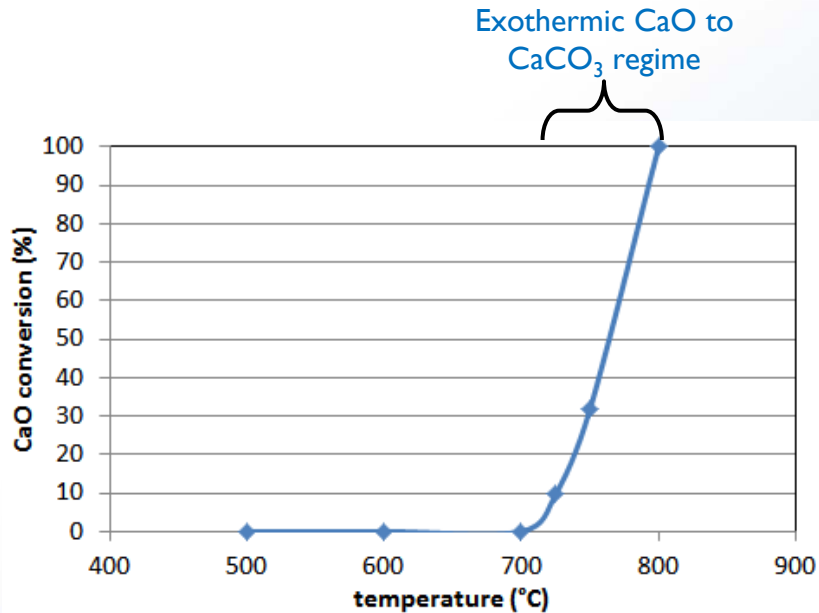


Process Overview - Chemistry

- Optimum performance of synthesis step 725-750 °C
 - Based on Gibb-free energy minimization to calculate equilibrium

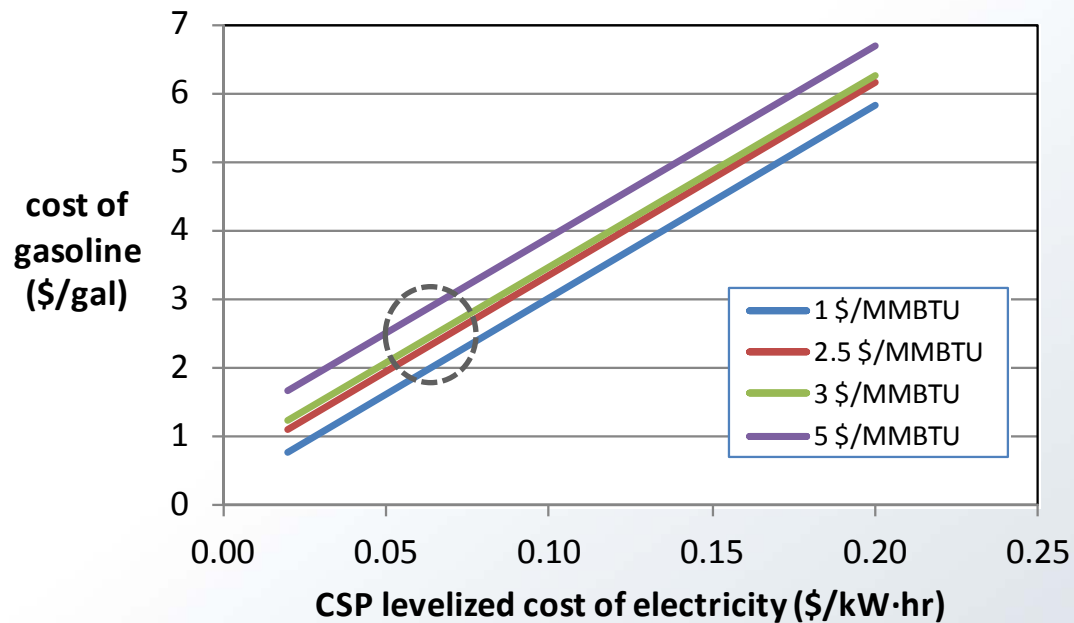
energy charging – endothermic calcination of CaCO_3 to CaO
 CO_2 acts as heat transfer fluid to carry CSP energy to reactor

energy release – exothermic heat release of reaction with CaO and CO_2
used to drive the endothermic reaction of CO_2 and CH_4 to CO and H_2



Process Overview - Economics

- Assuming overall process efficiency of 75 % (guestimate)
- 90% conversion of syngas to gasoline (based on MOG/MTG information)
- CSP levelized cost accounts for all cost factors
 - currently at 0.13 \$/kW-hr, DOE target is 0.06
- Need to factor in off-setting costs of CO₂ sequestration





Task Plan

- Task 1 – Qualify reactor with baseline materials
- Task 2 – Develop materials formulation and characterize
- Task 3 – Place materials onto support for testing
- Task 4 – Test materials for CO₂ cycling and CO₂/CH₄ reforming reactions
- Task 5 – Reactor test data analysis
- Task 6 – Process model and economic analysis
- Task 7 – Reporting



Task 1 – Qualify reactor with baseline materials

- Existing tubular reactor(s), ~1" OD
 - Three zone or one zone
 - Wide range of MFC's
 - Automated LabVIEW control
 - Micro GC on-line gas analysis
- Test Plan
 - Currently running baseline materials
 - Determine best space velocity, T, CO₂/CH₄ ratio for syngas conversion
- Outcome
 - Verify test stand performance, mass balance, and analytical capabilities
 - Pick set of standard operating conditions for performance and kinetics measurements



Task 2 – Develop materials formulation and characterize

- Prepare base materials as a powder
- Make use of existing small scale prep equipment
- Materials characterization
 - Particle size, surface area, pore volume, metal surface area
 - EDS/SEM
 - In-situ high temperature controlled atm. XRD
 - TEM if needed
- Outcome
 - Preliminary understanding of relationship between materials composition, materials properties and structure, and performance
 - Limited by number of samples in Phase I



Task 3 – Place materials onto support

- Apply base materials onto support
- Product tested for
 - Quality
 - EDS/SEM for chemical uniformity
- Outcome – quality sufficient for use in Task 4



Task 4 – Test materials for CO₂ cycling and CO₂/CH₄ reforming reactions

- Employ Separate Test Rigs
- CO₂/CH₄ reforming – use rig of Task 1
 - Initial operating conditions determined in Task 1
 - Measure kinetics as functions of SV, T, composition, CO₂/CH₄ ratio
- CO₂ cycling
 - Use existing test rig employed for materials development
 - ~20 g, calcine high temperature, carbonation at lower temperature
 - Measure mass change after each ½ cycle initially
 - Target – 50 cycles with less than 1% degradation
 - parallel to XRD measurements
- Outcome
 - Determine usefulness of materials for CO₂ reforming
 - Determine use of materials does not impact CaCO₃-CaO cycling performance



Task 5 – Reactor test data analysis

- Analysis of reaction products – mass balance
- Determine kinetics

- Outcome
 - Collect sufficient data to permit sizing of reactors for Task 6
 - Consider both energy storage and CO₂ conversion reactions

- Additional work if time allows
 - Sensitivity to potential CO₂ contaminants
 - We routinely test with H₂S, others?
 - Sensitivity to or need for air, water, etc...
 - Measure CO₂ sorption/desorption kinetics



Task 6 – Process model and economic analysis

- Data from Task 5 for preliminary reactor sizing and cycle time estimation
 - Relationship between flow rate, reactor sizes, conversion and product composition and cycle time, etc...
- Integration with CSP system
- Process modeling for unit operation mass and energy balances – ASPEN or similar
- Compare/contrast w/CO₂ sequestration and conversion schemes
- Outcome
 - Preliminary economic analysis on costs associated with a combined system
 - Demonstrate advantages of CSP to fuels/chemicals approach

Phase 1 Tasks and Schedule, as proposed

Task	Month								
	1	2	3	4	5	6	7	8	9
1 - Modify test stand, baseline testing	█	█	█	█					
2 - Synthesis and characterization	█	█	█	█	█	█	█		
3 – Add to support		█	MI	█	█	█	█		
4 - Testing – CO ₂ cycling and syngas gen				█	█	M2	█	M3	█
5 - Data analysis			█	█	█	█	█	█	█
6 - Preliminary economic analysis							█	█	█
7 - Reporting		█	█	█	█	█	█	█	█

Milestones:

1. Demonstrate applying materials on support
2. Demonstrate suitable CO₂-CH₄ conversion activity
3. Demonstrate stability of materials