Overview of ARPA-E Methane Pyrolysis Program and Possible Future Directions

2023 Hydrogen Annual Merit Review

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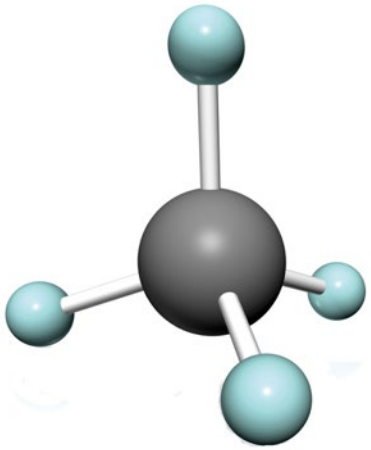
Methane Pyrolysis:
Lowest-cost Hydrogen Assuming Carbon Revenues



750 - 1200°C

Gaseous hydrogen

+

Solid carbon

¼ mass, ½ energy

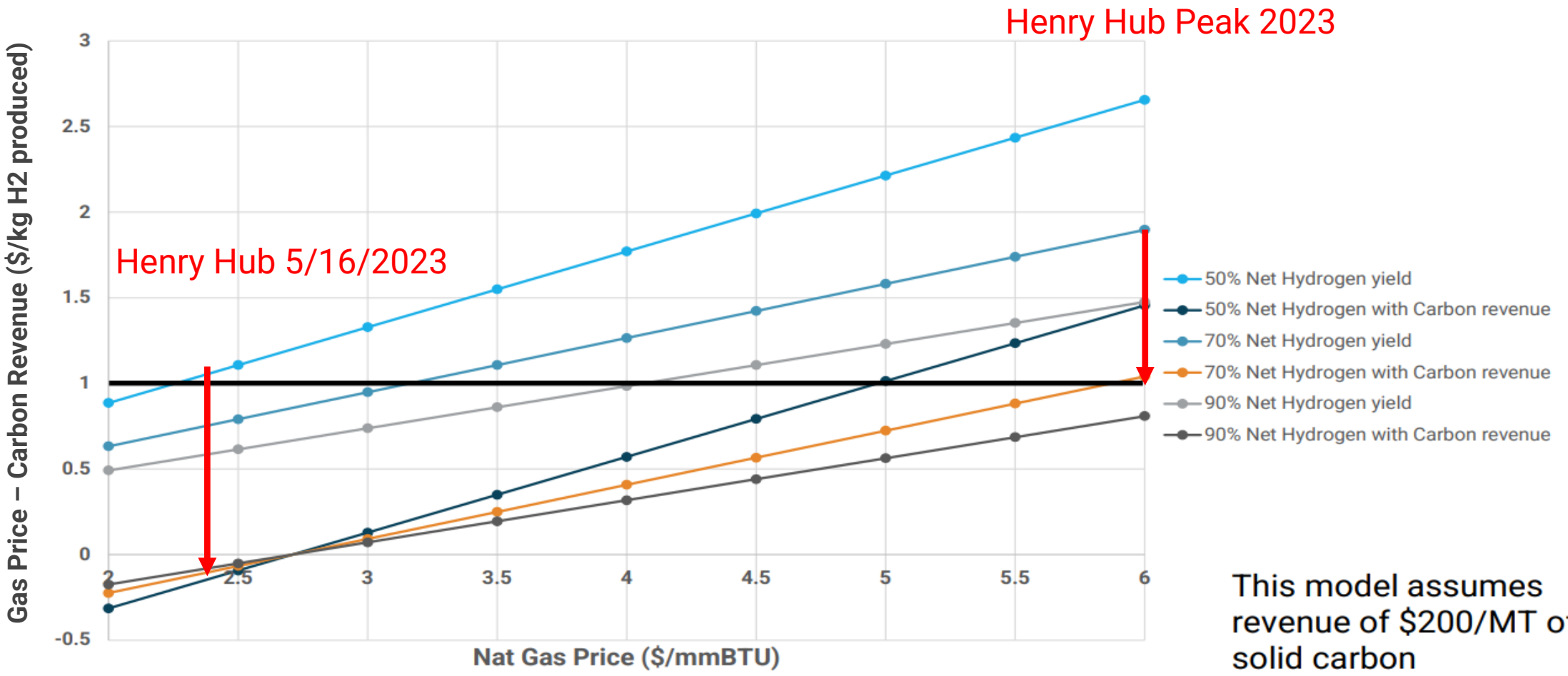
CH_4 ⟶ $2\ H_2$ + **C (s)**

1 Quad

32 MM ton*

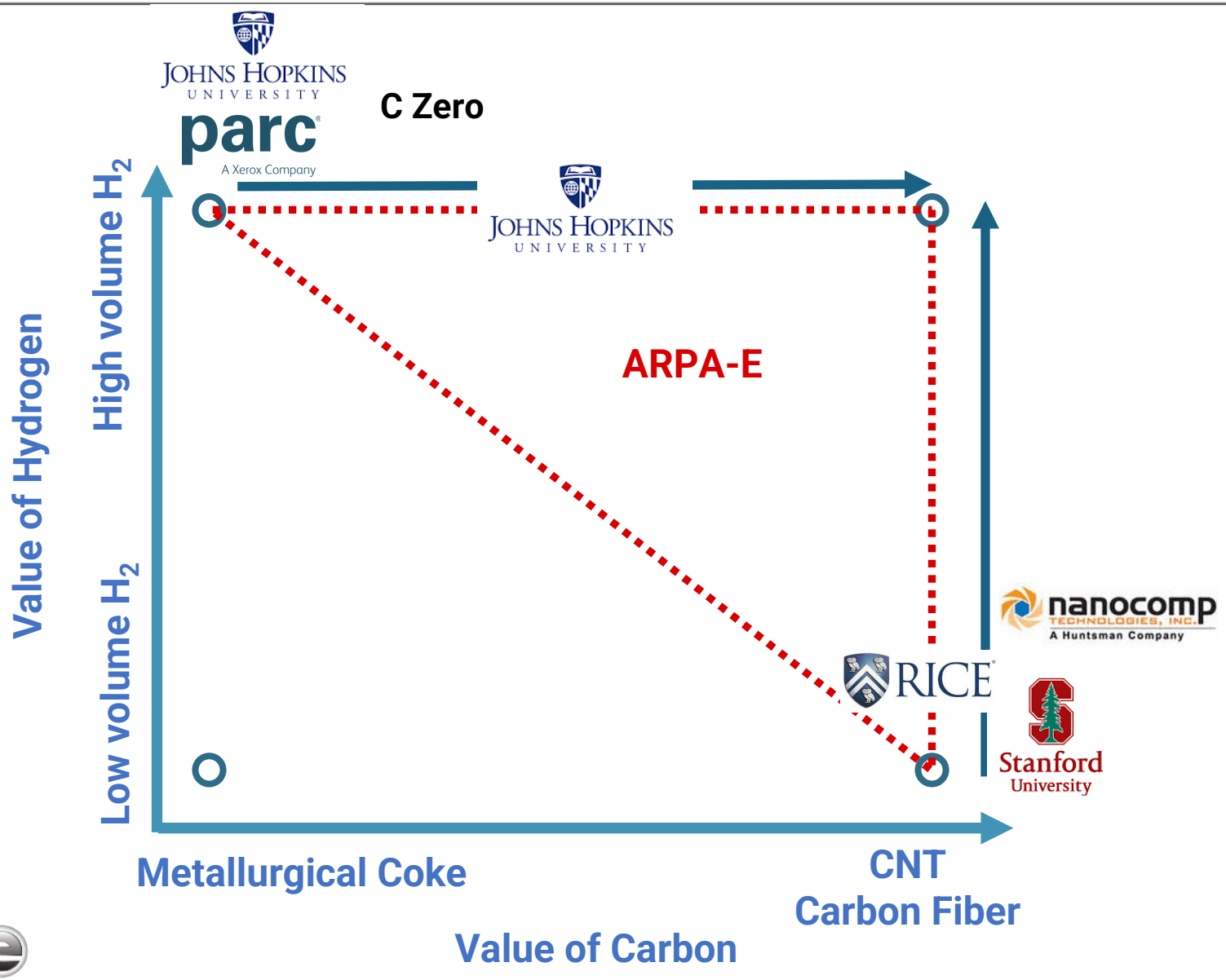
* 70% H_2 yield

Carbon Sales Drive Down H_2 Costs



This model assumes revenue of $200/MT of solid carbon

ARPA-E Program: 8 Projects, Diverse Objectives



New Carbon Applications

Technical Challenges

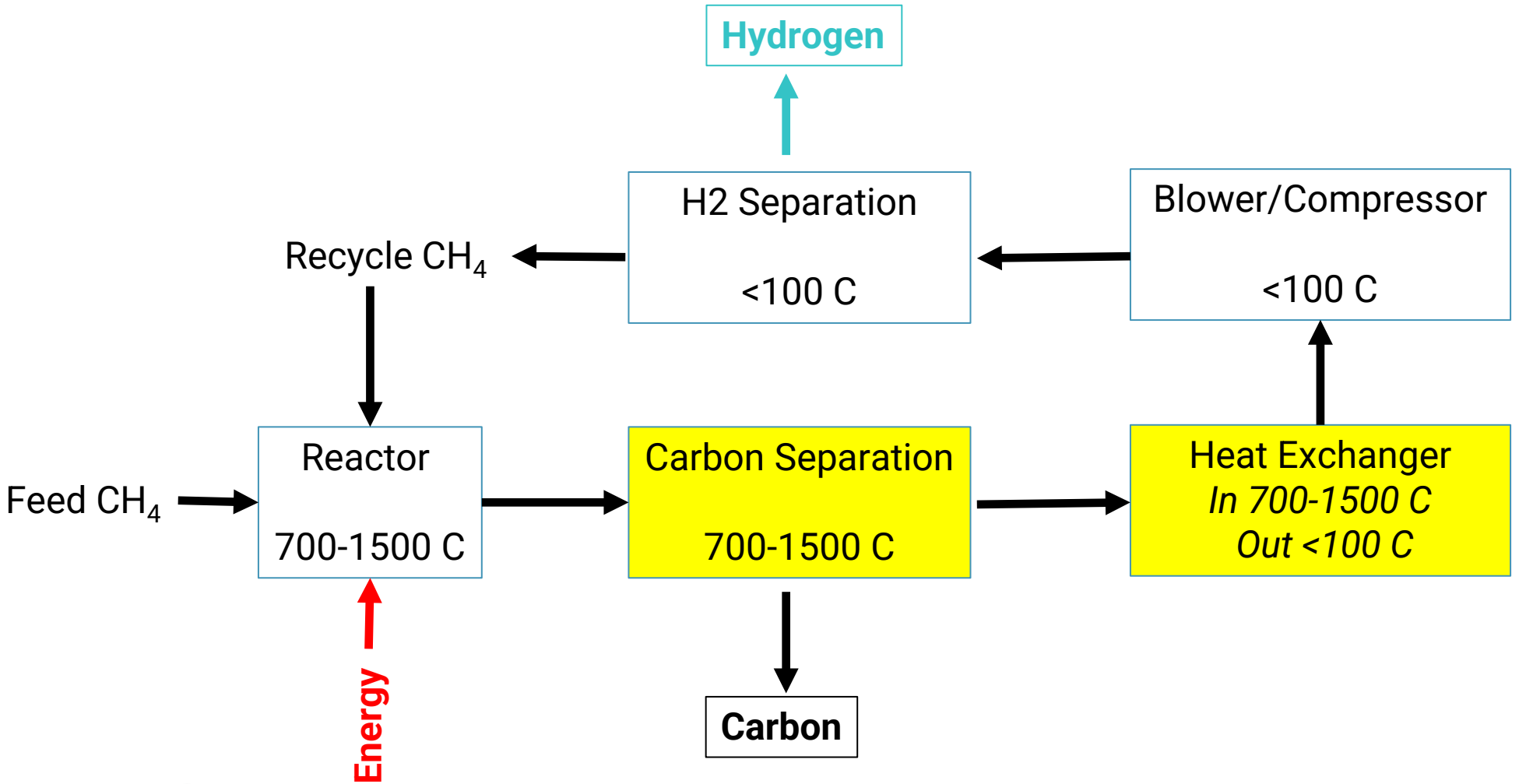
- Marc von Keitz review
  - Chemistry, kinetics, thermodynamics

  https://www.energy.gov/sites/default/files/2021-09/h2-shot-summit-panel2-methane-pyrolysis.pdf

- Process Flow Diagram
  - Unit Operations

- Materials of Construction

Generic Process Flow Diagram



Unit Operations

Unit	Requirements	Options	Challenges
Reactor	High per-pass CH_4 conversion Low acetylene production	High temperature Catalyst Non-thermal plasma	High energy demand Catalyst recovery/carbon contamination High energy demand
Reactor	Heat/energy transfer	Molten salts/metals Non-thermal plasma	Carbon contamination Scale
Carbon separation	Carbon/exit gas Carbon/molten media Carbon/catalyst	Candle filter ? Offline regeneration?	Carbon fouling Volatile metal/salt OPEX/CAPEX

Unit Operations

Unit	Requirements	Options	Challenges
Heat exchanger	Cool gas Energy recovery	Fluid – gas, steam, etc Quench	High temperature Fouling Low energy recovery
Hydrogen separation	High H_2 recovery/purity	PSA, membrane	Feed compression Need high CH_4 conversion to avoid low H_2 recovery
Instruments	High temperature “Carbon sensor” Control valves	Thermocouples? Pressure drop?	Life Speed Materials

Materials of Construction Challenges

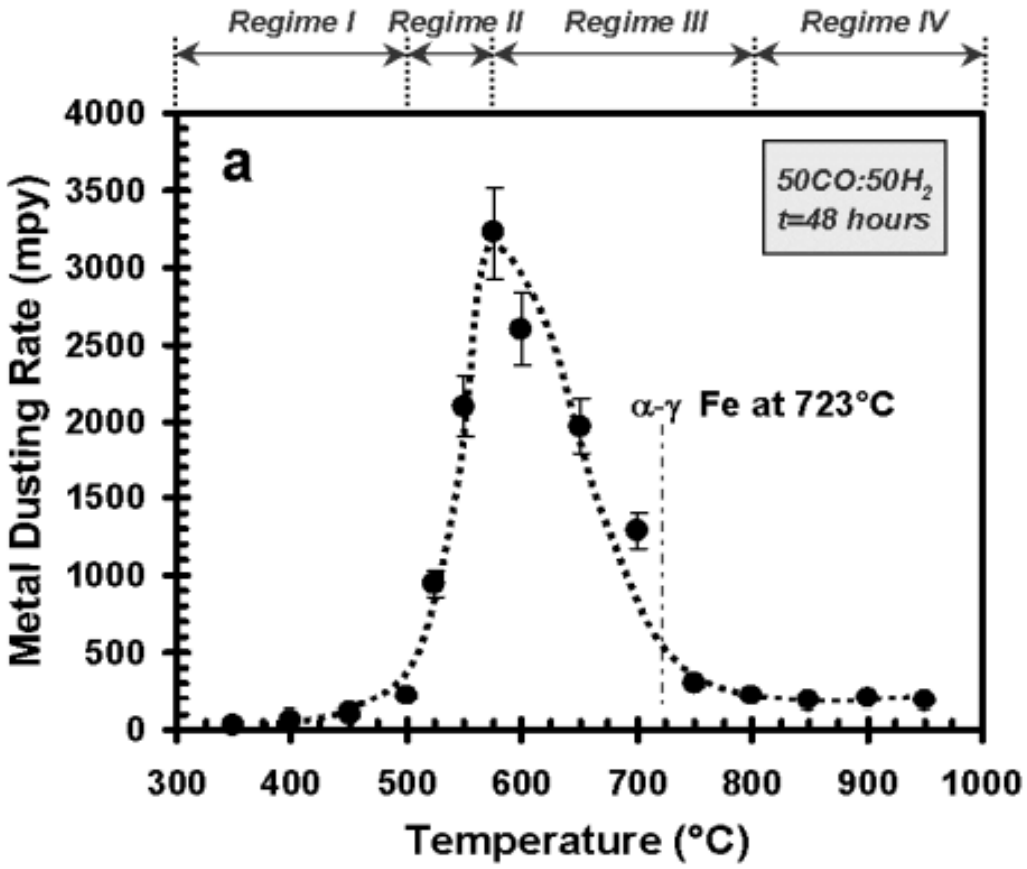
- Extensive DOE history – gasification, concentrated solar power, etc.

- High temperature/reducing environment
  - Exceed allowable temperatures for carbon steel (420 C)
  - Refractory lining
  - High-grade materials (stainless, etc)

- Molten salts/molten metals
  - High corrosion rates

- Fewer options for instruments, control valves, heat exchangers, etc

Metal Dusting – High temperature/reducing conditions



https://www.electrochem.org/dl/ma/201/pdfs/1111.pdf

Figure 3. Photograph of commercial Ni-base Alloy 600 and ANL-developed alloy after 5,700-h exposure to the same metal dusting environment at 593°C.

https://www1.eere.energy.gov/manufacturing/industries_technologies/imf/pdfs/metaldusting.pdf

Conclusions

- DOE has to collective capabilities to advance methane pyrolysis
- Economically attractive option, esp if carbon markets can scale
  - IDEO/AMMTO: replace materials with higher LCA?
- “Historical” focus on reactor needs to expand to other unit operations
  - Starting points - FECM prior work on gasification, candle filters, heat exchange
- Leverage DOE’s prior work on materials of construction
  - Starting points – FECM prior work on gasification, EERE work on CSP

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CHANGING WHAT'S POSSIBLE