Gas to Carbon Fiber Crystals

DE-FE0031868
SRI International
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U.S. Department of Energy
National Energy Technology Laboratory
Resource Sustainability Project Review Meeting
April 2-4, 2024

Background

Project Timeline & Funding

- **April 2020 to July 2022**: progress severely slowed/hampered due to COVID-19 (~20% spent to date)
- **July 2022 to March 2023**: wrapped Phase 1 with proof-of-concept reactor demonstration
- **March 2023 to Now**: Building scale-up demonstration reactor
- **December 2024**: Expected project wrap

	Federal ($MM)	Cost Share ($MM)
Phase 1	1.16	0.29
Phase 2	1.45	0.36
Total	2.61	0.65

Flare Gas in the US

Key Gaps

1. In the absence of a pre-existing pipeline, **no existing technology can monetize flared gas** at the required small scale
2. Flared gas **products must have high value** to justify transportation and a market size equivalent to the flared gas problem

Flared Gas Problem

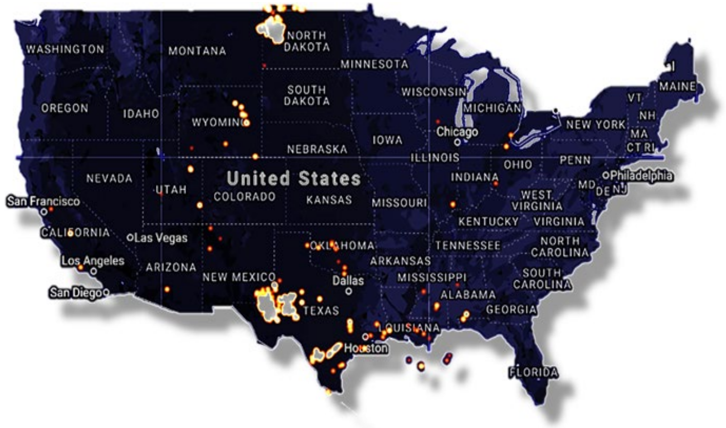
	Clustered Flares (sites)	Flared Volumes (MMcfd)	Ave Flare (Mcfd)
United States	70,749 (23%)	1,360 (10%)	8.1
N. America	96,968 (32%)	1,870 (13%)	8.1
Worldwide	303,590 (100%)	14,029 (100%)	19.3

- Ave flared site is small ~ 8 Mcf/d
- Nat gas price is low ~ 4.00 $/Mcf
- Ave value per site ~ $32 per day

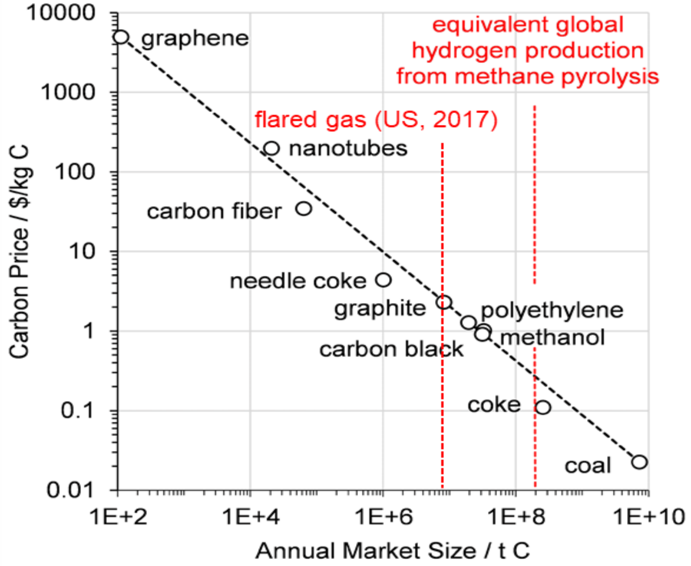
Market for Carbon Products

Product	Value	($/m³)	($/t-C)
Natural Gas	3.0 $/Mcf	0.11	105
LNG	6.5 $/Mcf	130	218
Methanol	380 $/t	300	142
Crude	50 $/bbl	310	289
Polyethylene	1.1 $/kg	1,034	942
Carbon Powder	2.0 $/kg	900	2,000
Carbon Fiber	30 $/kg	53,000	30,000

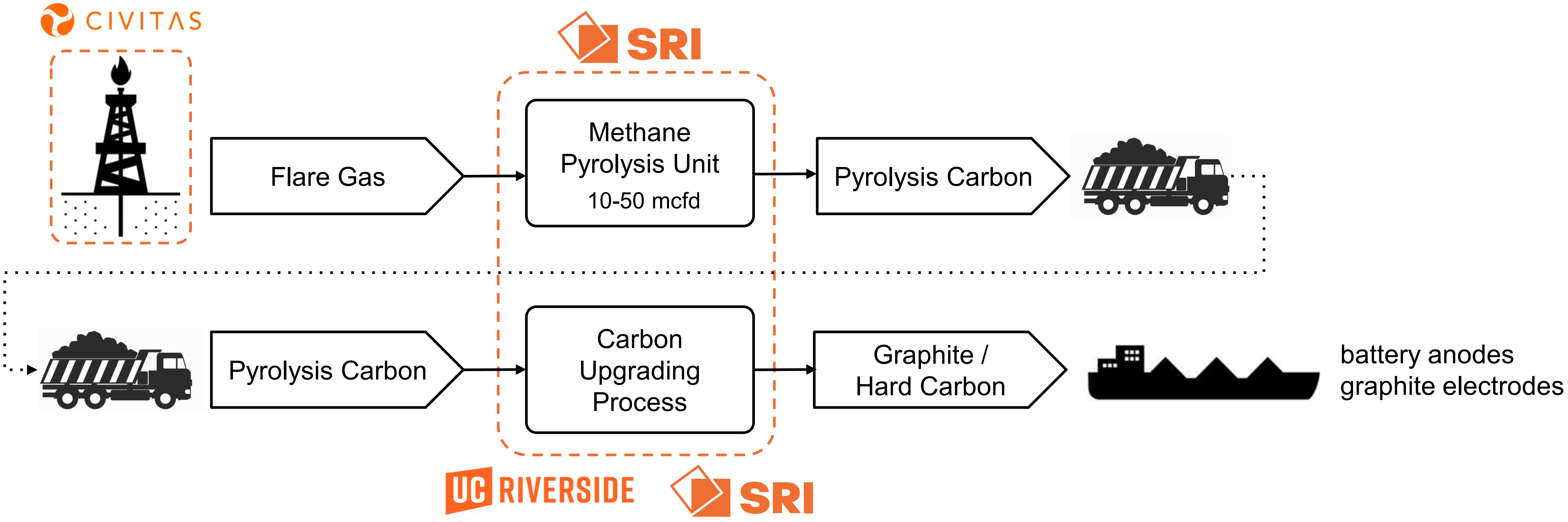
Flared Gas - United States, 2018



Carbon Price vs Market Size



Flared Natural Gas to Carbon Products

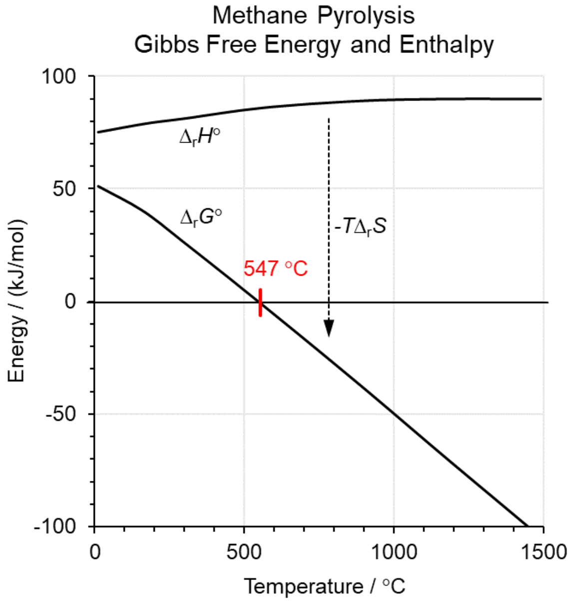


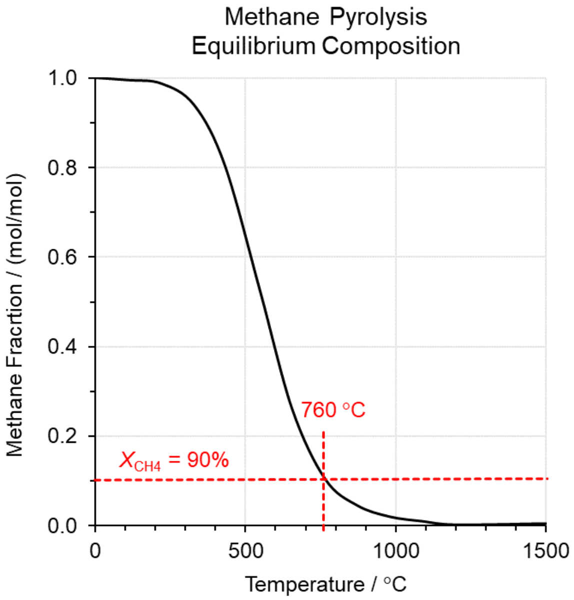
Flare gas will be mitigated by

(1) Pyrolyzing natural gas into solid carbon, and

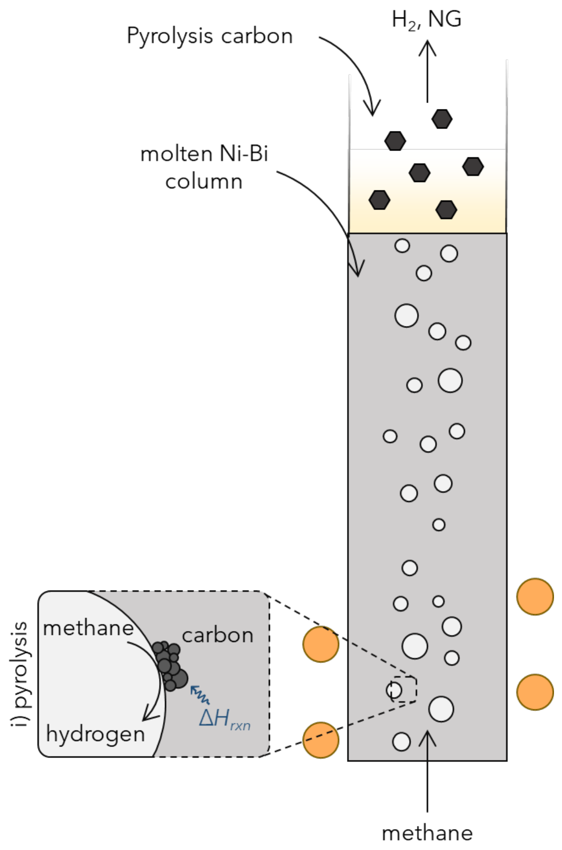
(2) Increasing value of solid carbon through a novel upgrading process to make graphite

Molten Metal Bubble Column Pyrolysis Reactor





Molten Ni-Bi converts natural gas to H_2 and solid carbon



$CH_4(g) = 2H_2(g) + C(s)$

Thermodynamics

- $\Delta_r H°_{298K}$ = +37.4 kJ/mol
- $\Delta_r G°_{298K}$ = +25.4 kJ/mol

Favorable reaction above 547°C

High conversion above 760°C

Civitas Flare Gas Site Composition

Site Considerations

- Source of current flare gas is vapors from oil tanks
- Potential for small amounts of H_2S (0-10 ppm)
- Ability to handle N_2 and CO_2
- Wide range of volumes available based on location (5,000 SCF/Day up to 100,000 SCF/Day)
- Equates to ~ 300 – 6,000 kg/day carbon produced
- Pilot-scale pyrolysis module would need to be able to shut down instantly if the facility has a safety shut down

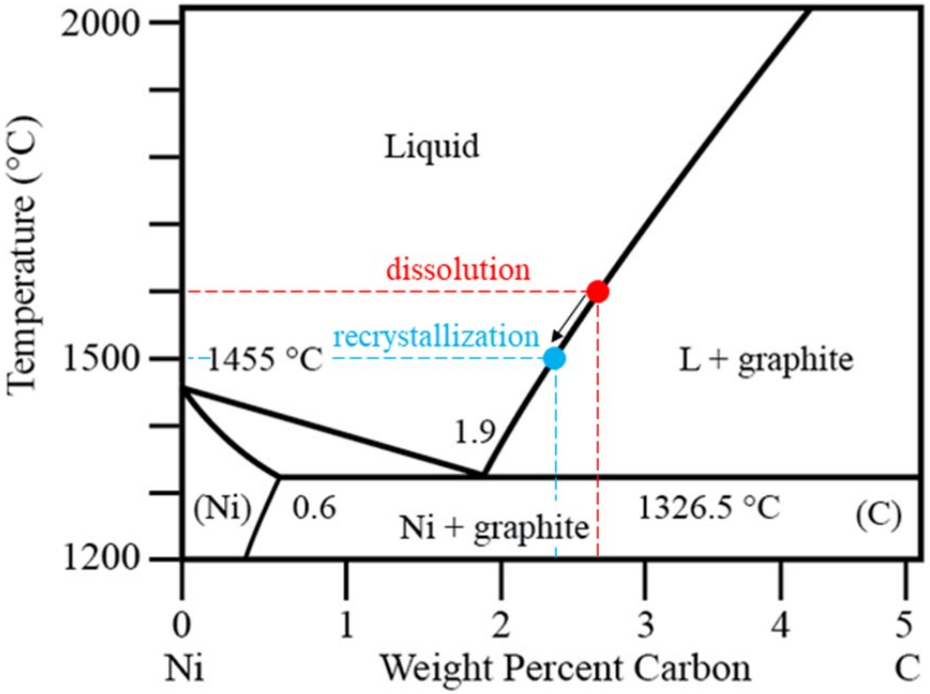
Flare Composition

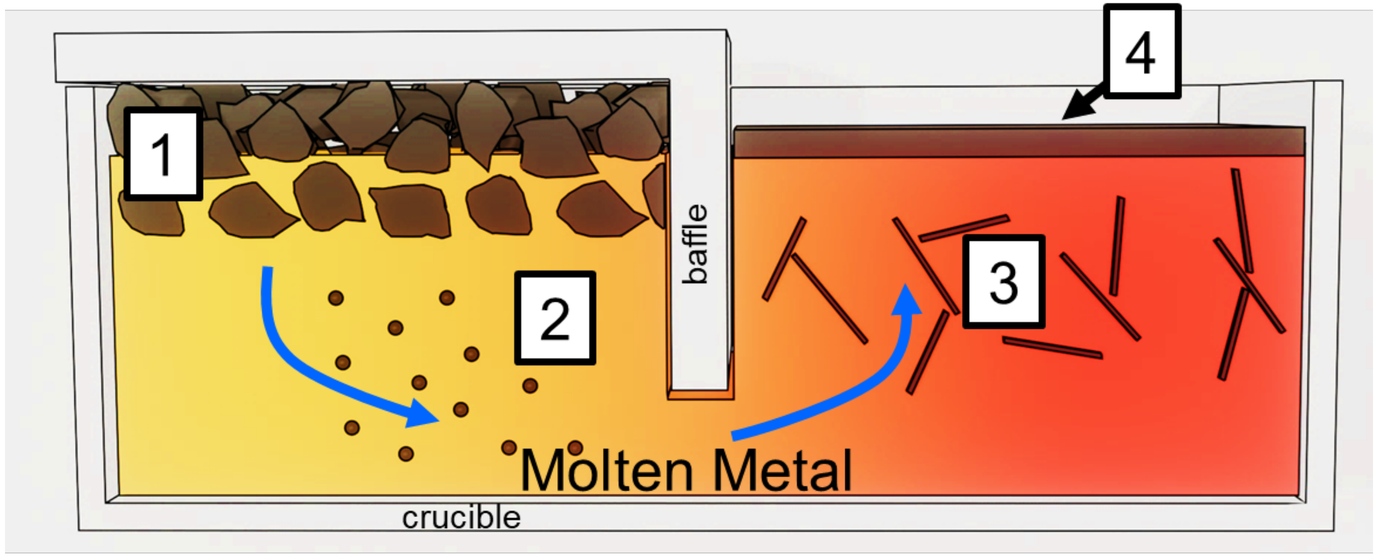
Component	Mol%
Nitrogen	5%
Carbon Dioxide	2%
Hydrocarbons	93%
Methane	29%
Ethane	19%
Propane	22%
C4+	23%

Certificate of analysis: 03/15/2022

Graphite Production Through Coke Dissolution & Precipitation

- Carbon feed is dissolved in molten metal at high temperature, transported through the melt, where it supersaturates and recrystallizes as highly pure and crystalline graphite.
- A temperature gradient along the long axis of the crucible promotes transfer and regrowth.
- The low density of graphite causes it to float to the surface to be collected.





- Carbon dissolution of 2.5 wt% at 1600°C.
- Carbon solubility decreases to 2.3 wt% at 1500°C.

1. Carbon Feed (amorphous, impure, or petcoke),
2. Dissolved carbon
3. Entrained graphite flakes
4. Purified graphite layer

Milestones & Success Criteria

Subtask	Milestone Title and Description	Anticipated Completion Date
4.2 Go/No-Go	Proof-of-concept demonstration of high-value carbon	03/31/2023
5.3	Batch production of high-value carbon	06/30/2023
1.3	Techno-economic model shows the feasibility of a process producing upgraded carbon which meets specs defined in Subtasks 2.1, 2.2, and 3.2	09/30/2023
6.3	Commission of bench-scale carbon upgrading prototype	06/31/2024

Phase 1

- Proof of concept (lab-scale) carbon upgrading process
- Preliminary TEA supporting economic process

Phase 2

- Integrated bench-scale carbon upgrading prototype
- Design for pilot-scale prototype

Final Goal: Reactor demonstration which produces 1 kg/day of upgraded carbon

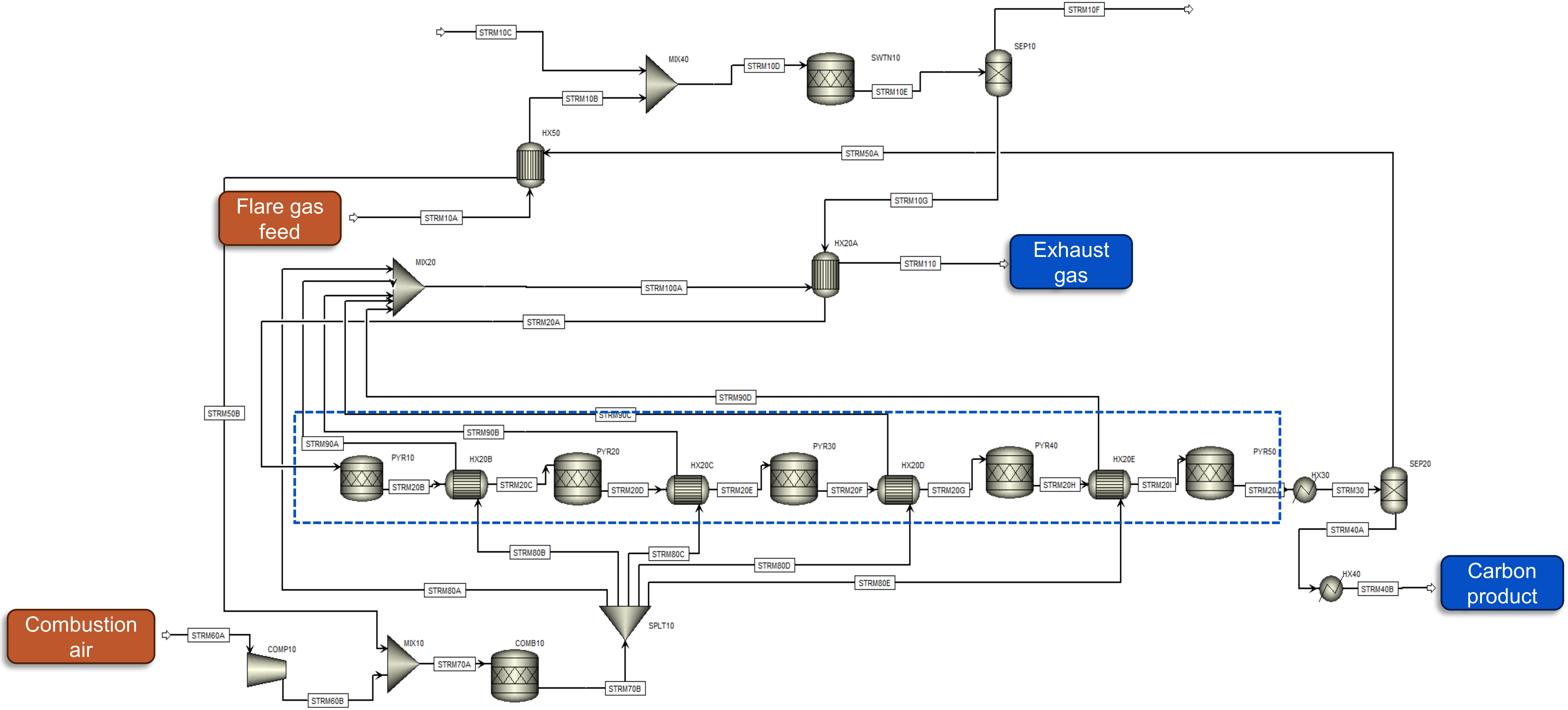
Risks & Mitigation

Risk	Potential Impact	Mitigation Strategy
Upgraded carbon quality insufficient to meet market spec	No offtake market for carbon product, unable to make business case	Expand market discovery options beyond graphite electrode and battery anodes
Laboratory activities delayed by COVID	Pace of laboratory work may be slow due limited laboratory access; parts procurement	Optimize the scheduling lab access to minimize our team's virus exposure; maintain larger materials/parts inventory
Pyrolysis reactor space time yield too low	Pyrolysis process becomes uneconomical	Evaluate other pyrolysis approaches. The project already includes exploring an upgrading method that is agnostic to type of carbon feedstock.
Flared gas contaminants could impact process performance	Process could become uneconomical	Evaluate pilot site gas compositions early in program
Equipment build delays due to supply chain issues	Due to the impact of COVID and other world events on supply chains, procurement of parts may be challenging and delay the timeline.	The team will identify components and parts needed early on and prioritize activities to minimize delays.
Environmental barriers for ultimate process	If carbon nano-particulates or NOx are produced during pyrolysis or carbon upgrading, public and environmental health concerns will arise.	Process equipment will be designed and operated to conform with OSHA standards. The cost of including ultra-low NOx H2-fired burners will be explored as a part of the process modeling task.
Availability of project team members	If team members are unable to spend the time required to achieve assigned tasks, the project progress may be delayed.	We will review the Gantt chart, progress against targets, and time needed to complete required tasks with the team at least once per month in order to ensure sufficient time to plan ahead and distribute resources accordingly to accomplish the tasks at hand.
Cost-share	If cost-share commitments are not upheld, the cost-share requirements and project budget could be impacted.	Over 90% of the cost-share is provided by PARC and will be completed as costs are incurred. As such, risk of cost-share loss is expected to be low.

Project Update

Aspen Plus Pyrolysis Process Model

Building process model to design pilot-scale system



Pyrolysis Site Process Model Results

Model Design Approach

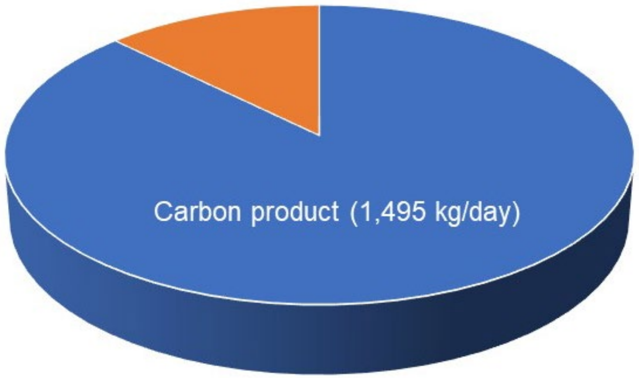
- 50 MCFD (or, 2,297 kg/day)
- 500 ppm H_2S removal
- Multi-stage molten metal reactor
- Byproduct H_2 and un-converted CH_4 as a fuel
- Minimum CAPEX
- Conservative reactor operation temperature (max 1,000°C)

Process Model Inputs

Process Design Elements	Value	Unit
Flare gas mass flow rate	2,297	kg/day
Carbon mass flow rate (in flare gas)	1,711	kg/day
Sweetening unit temperature	400	°C
C_4 pyrolysis temperature	900	°C
C_3 pyrolysis temperature	950	°C
C_2 pyrolysis temperature	1,000	°C
Combustor temperature	1,200	°C
Flare gas preheating temperature	1,100	°C
Cyclone temperature	800	°C

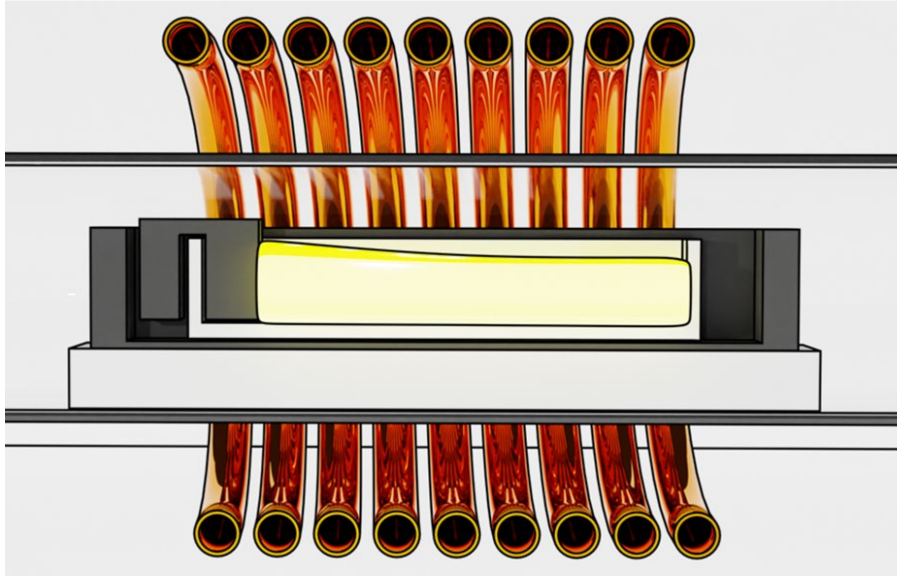
Process Model Outputs

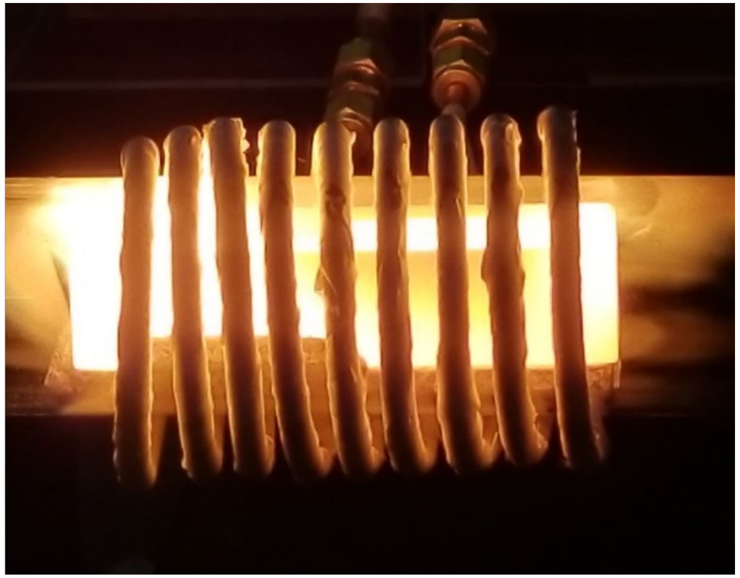
Process Design Elements	Value	Unit
Carbon production rate	1,495	kg/day
Exhaust gas temperature	962	°C
Exhaust gas mass flow rate	39,881	kg/day



Estimated ~90% reduction in CO_2 output from flare site

Carbon Upgrading Test Setup





- Carbon and metal are placed in a ceramic crucible. The raw material is inserted into the furnace at 1600°C (left).
- The sample after melting for 30 minutes and freezing (right).

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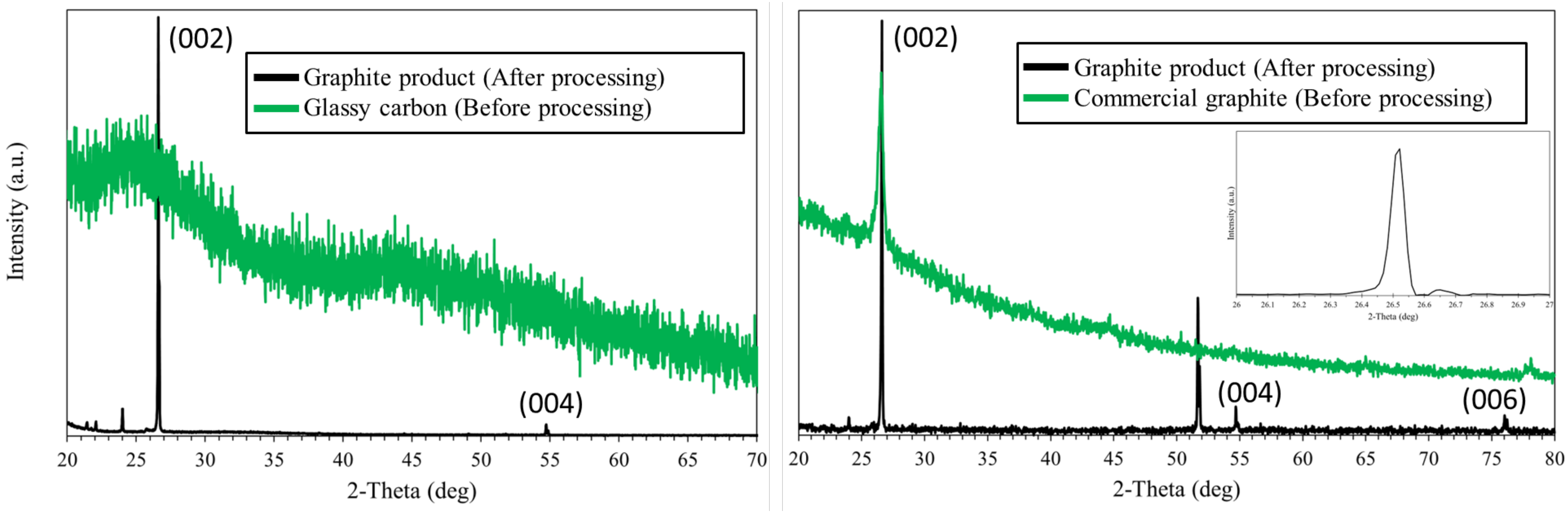
Producing Crystalline Graphite from Carbon Precursors

X-ray diffraction of amorphous carbon and commercial graphite before and after processing in molten metal at 1500°C



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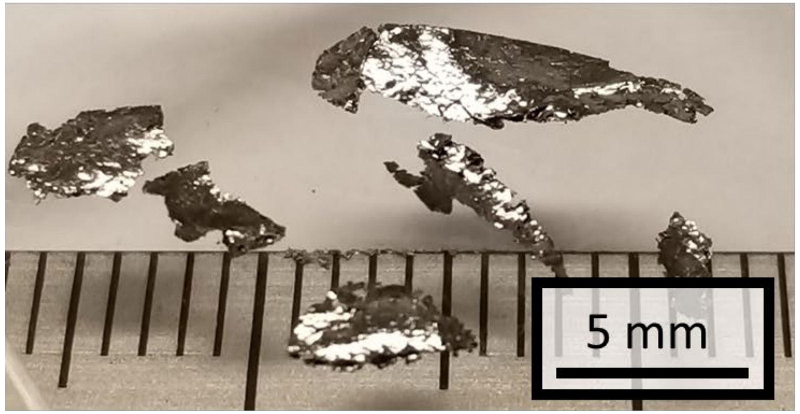
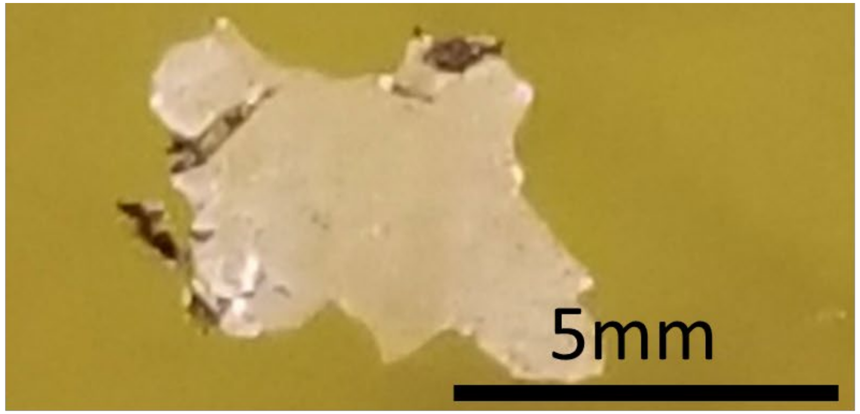
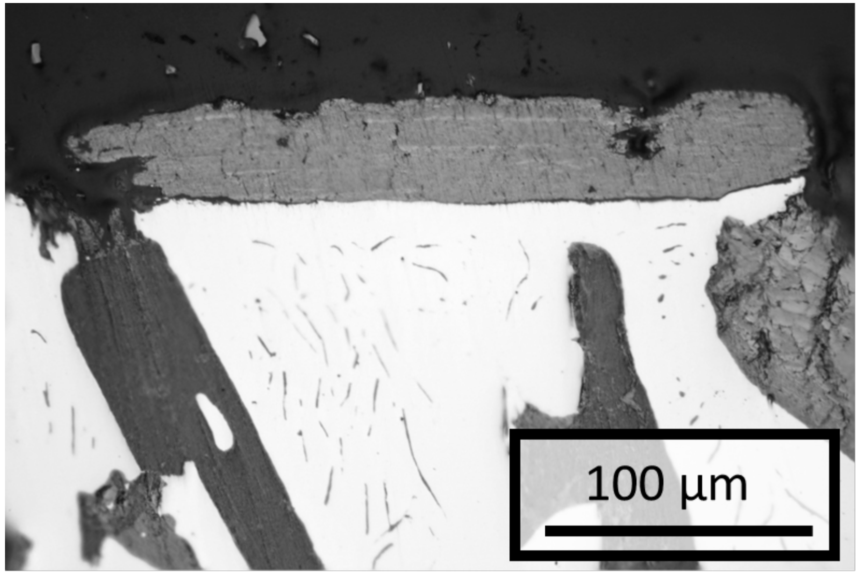
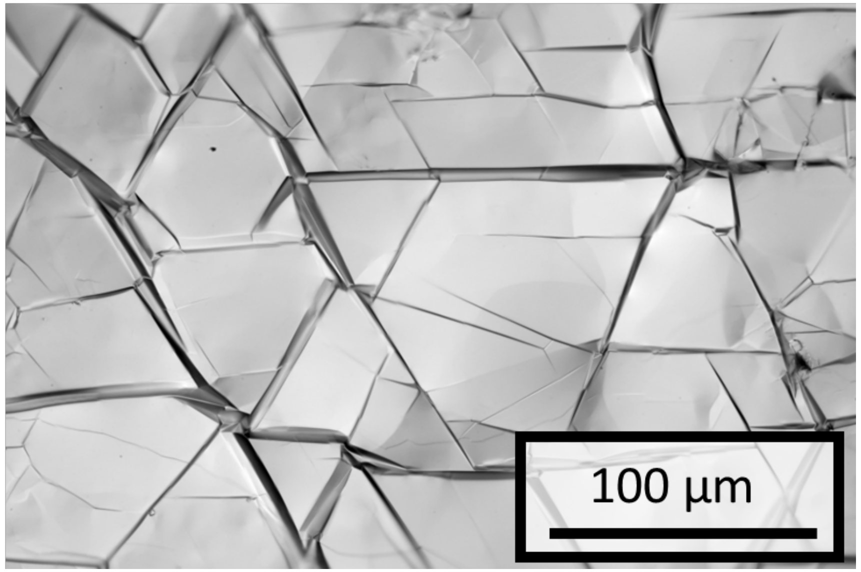
Typical Graphite Product

Graphite flakes collected from the melt surface for analysis









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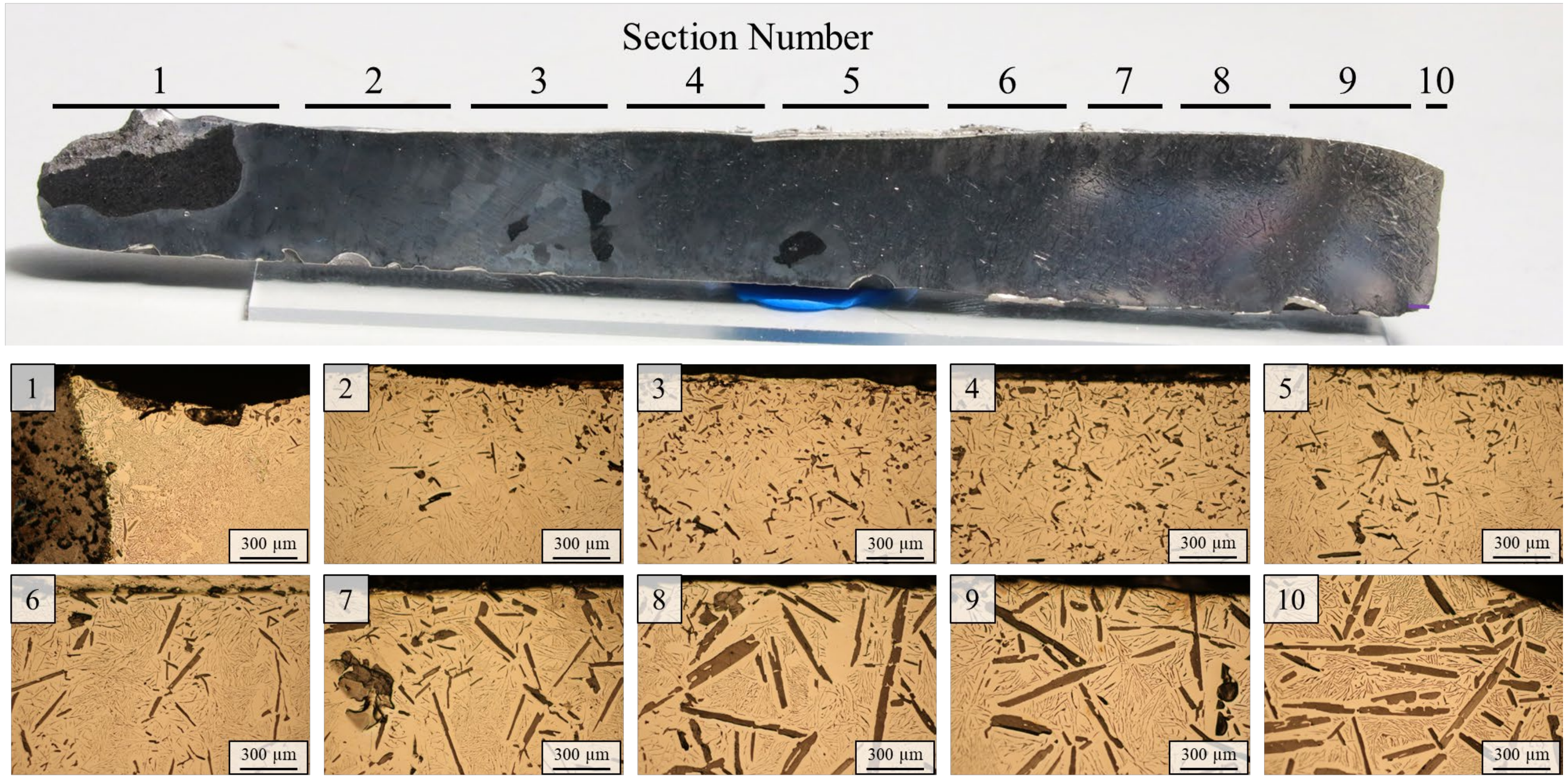
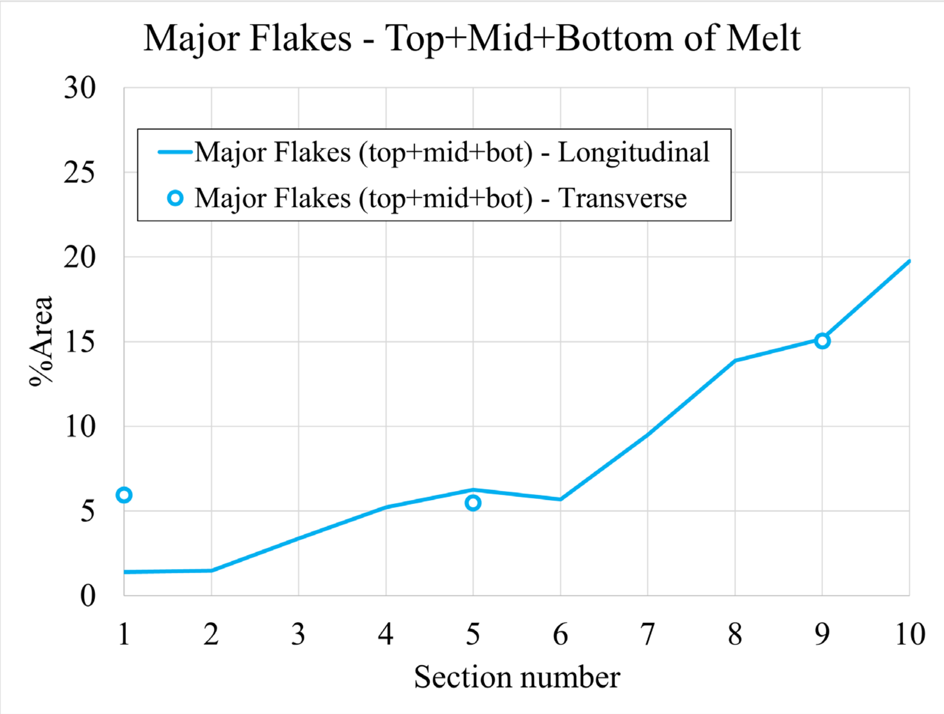
Graphite Distribution Along Temperature Gradient





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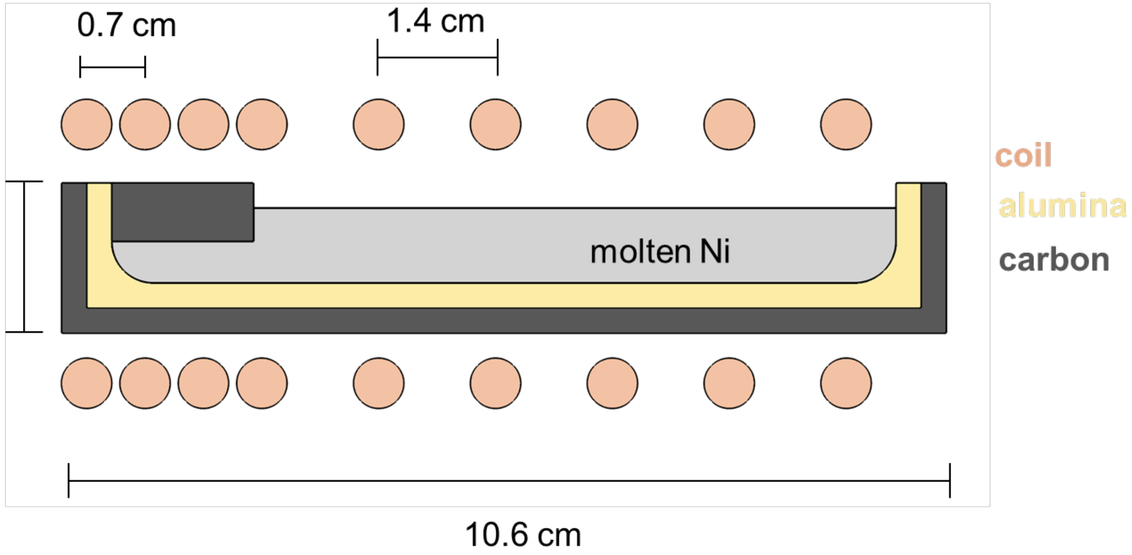
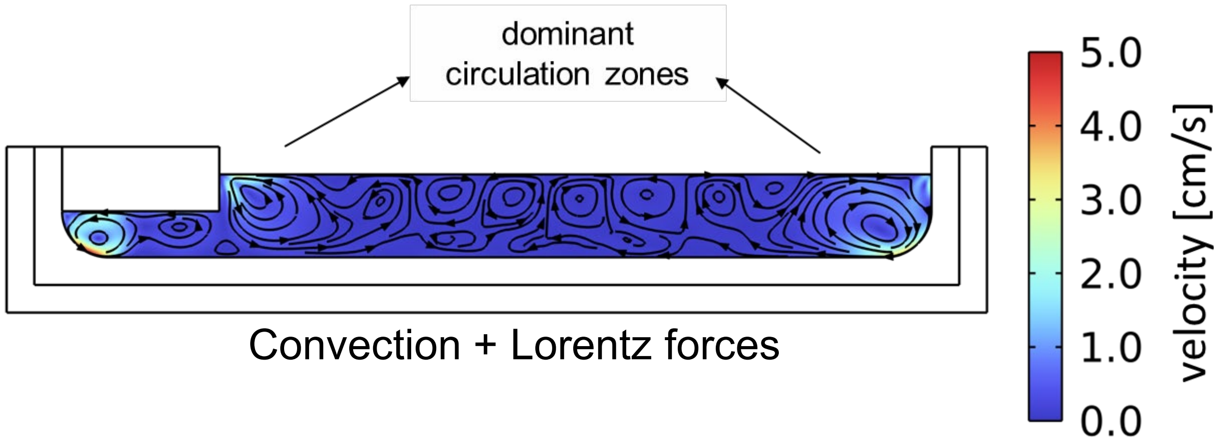
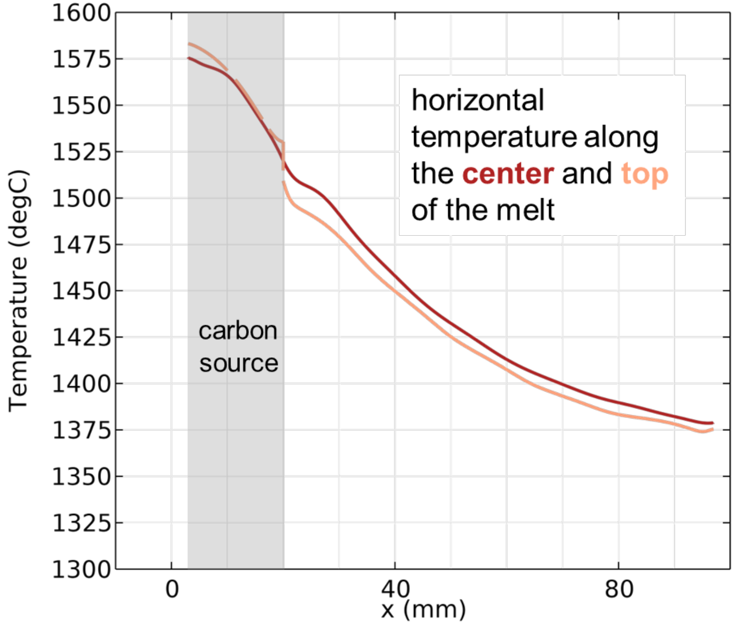
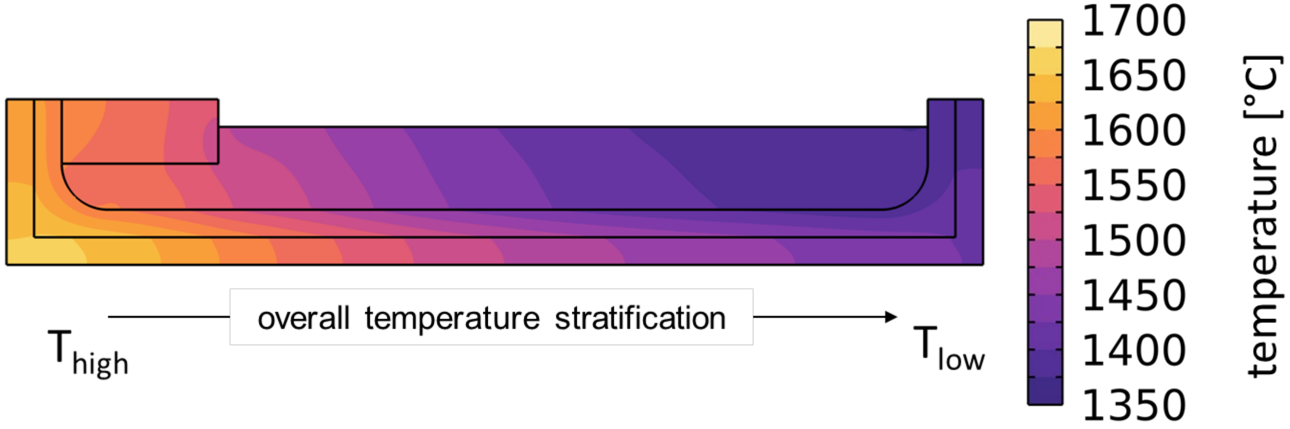
Modeling Reactor Conditions



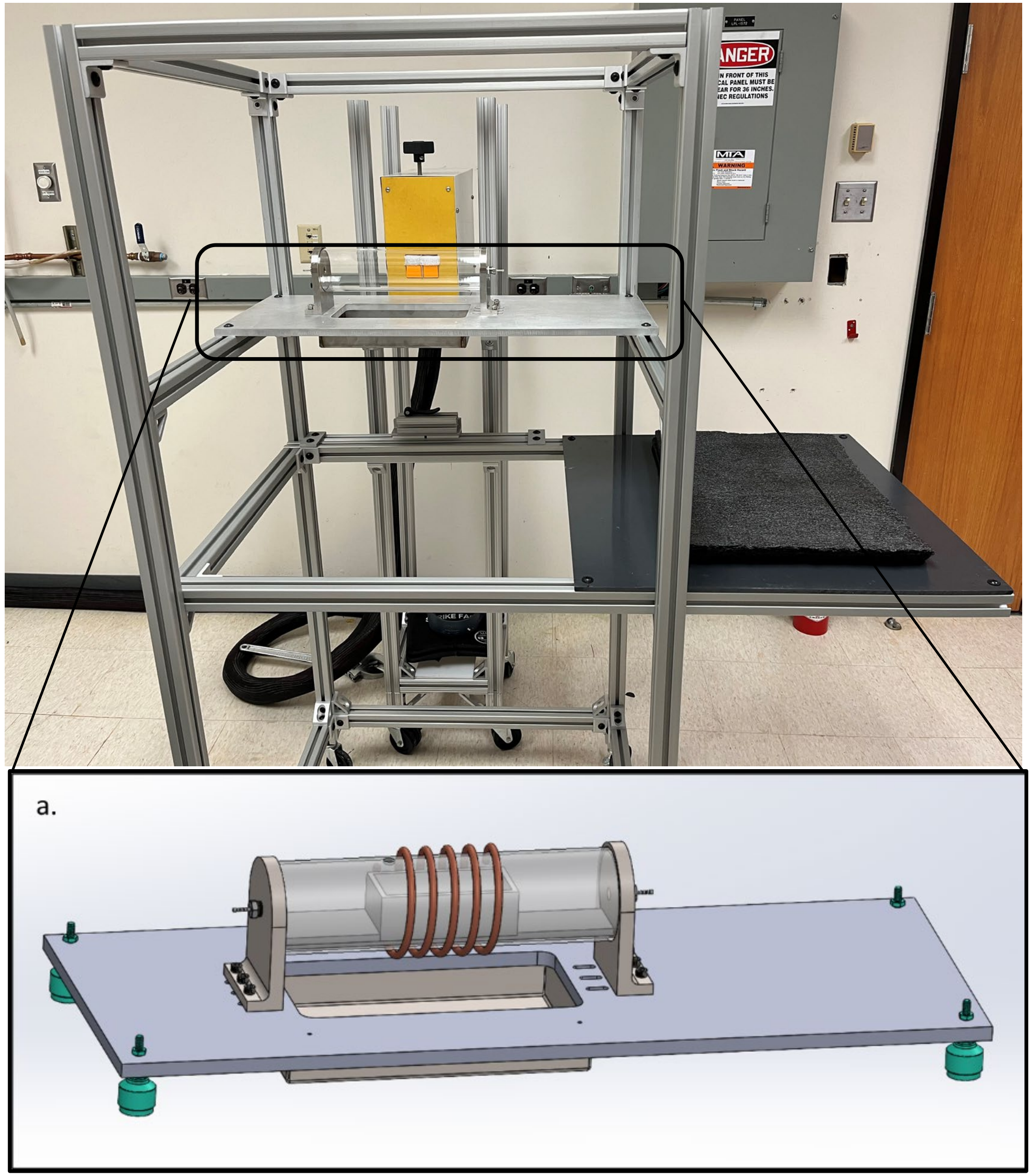






Scaled-up Reactor

- Expanding reactor size to accommodate 1 kg/day graphite production
- Installed new 25-kW induction heating system
- Reactor development in three pieces
  - Carbon feeding
  - Upgrading reactor
  - Carbon extraction
- Reactor setup built, full commission expected soon

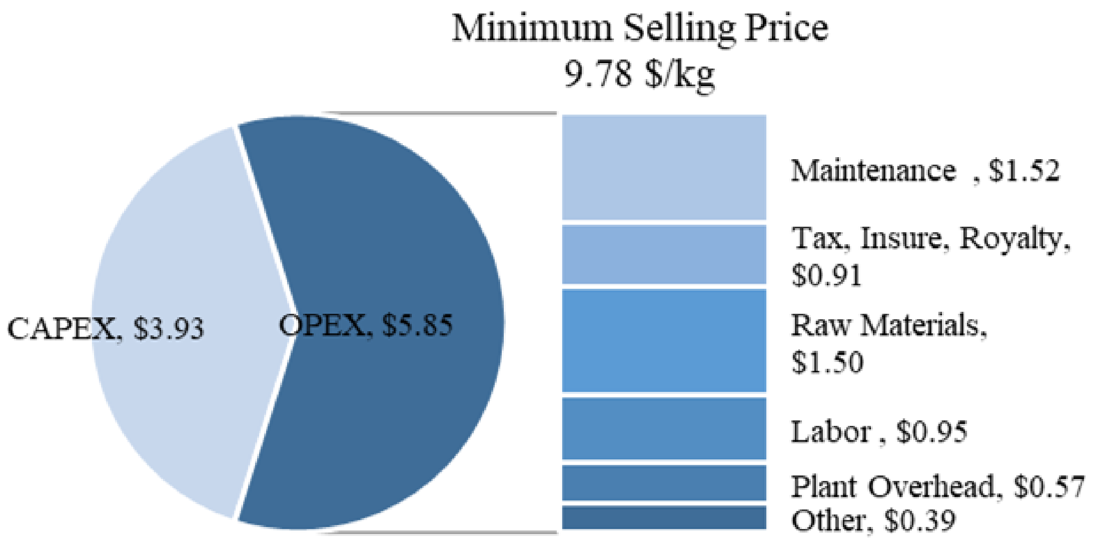


Graphite Production Techno-Economic Analysis

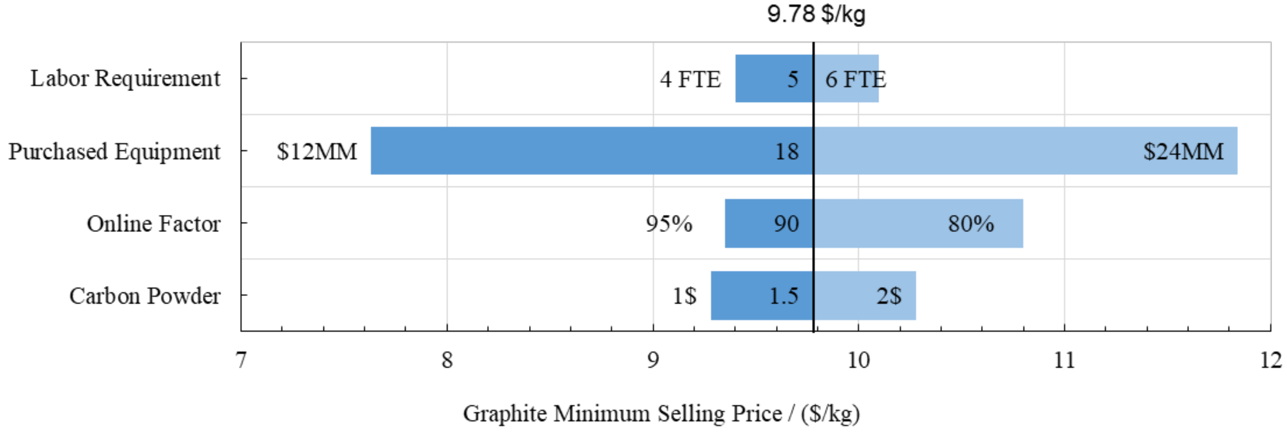
Process Summary

- Similar TEA for pyrolysis process yielded 1.07 $/kg to produce
- Graphite production plant capacity of 8,000 kg/day
- Total capital investment $88 million
- Breakeven price of 9.78 $/kg
- Rate of return of 19.3%

At 14 $/kg selling price, payback period for process is under 5 years

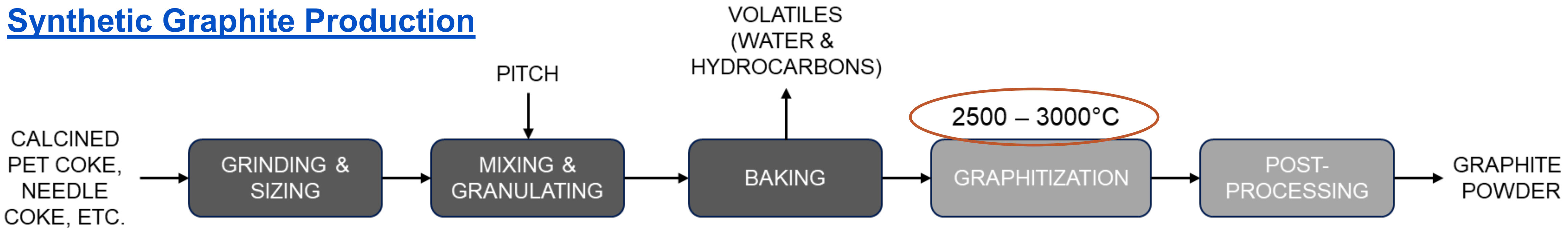


Sensitivity Analysis



Flake Graphite Production Energy Requirements

Synthetic Graphite Production



	Production Route	Energy Intensity (kWh/kg)
Natural graphite	Mining, beneficiation, purification	3.8 (Engel 2022)
Synthetic graphite	Calcination, baking, graphitization, purification	2.9-14.6 (Hupp 2003, Notter 2010, Majeau-Bettez 2011, Dunn 2015, Dai 2019, Daimer 2021, Surotseva 2022, various web sources[1-3])
G2CX graphite	Dissolution/precipitation via molten metal	**0.53***

*estimated theoretical low

Wrap Up

Outreach & Training

Training

Post-docs

- Aravindh Rajan
- Jessica Medrado
- Hooman Sabarou

Graduate Students

- Steven Herrera
- Ze He

Masters Students

- Daniel Wilbert
- Raquel Jaime

Outreach

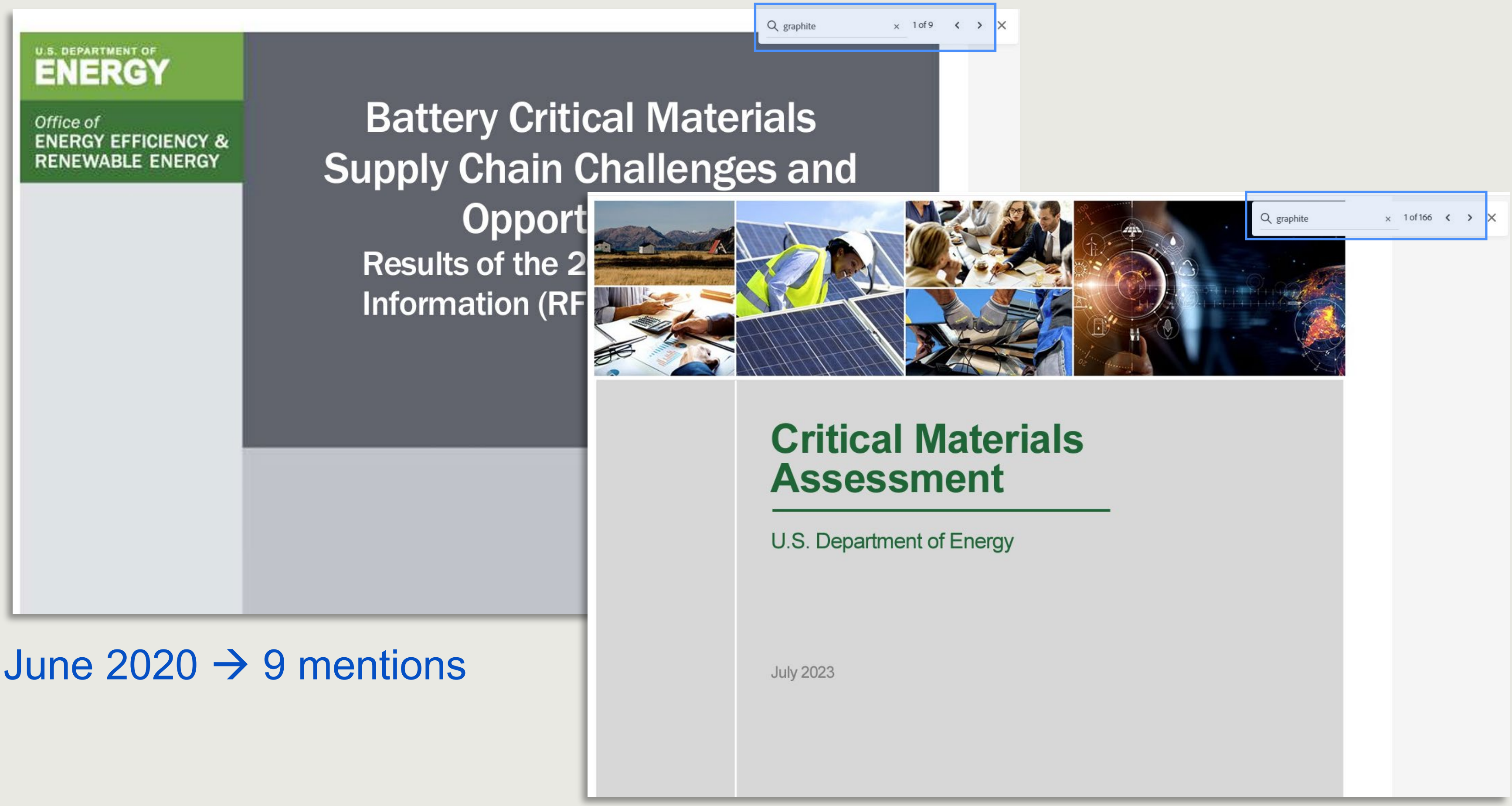
Maintaining public list of commercial pyrolysis efforts to track and highlight efforts in the area. These companies offer a path to sustainable, low-CO_2-emitting H_2.

Commercial Methane Pyrolysis Efforts

Start	Logo	Organization Name	Location	Key People	
2010	HazerGroup	Hazer Group	Nedlands (AUS)	Geoff Ward (CEO) Andrew Cornejo (CTO, fdr)	$116, Publi
2012	MONOLITH	Monolith Materials	Lincoln NE (USA)	Pete Johnson (fdr), Robert Hanson (CEO, fdr)	$64,3
2012	BASF The Chemical Company	BASF	Ludwigshafen (DEU)	Andreas Bode (lead) Dieter Flick	public
2013	KIT Karlsruher Institut für Technologie	KIT (Karlsruhe Institute of Technology)	Karlsruhe (DEU)	Tobias Geißler Alberto Abánades	grant
2016	ETCH	Etch, Inc.	Baltimore MD (USA)	John Fini (fdr, CEO) Jonah Erlebacher (fdr)	$3,69
2016	NU:IONIC TECHNOLOGIES	NU:Ionic (Nuionic Technologies LP)	Portland ME (USA) New Brunswick (CAN)	Gregory Caswell (CEO, fdr) Jim Tranquilla (CTO, fdr)	Comp Valen Techn
2016	Shell	Royal Dutch Shell	Rotterdam (NLD)	Carl Mesters (Chief Scientist) Hans Geerlings (Pr Scientist) Leonardo Spanu (Sr Research)	intern
2017	EKONA	Ekona Power Inc.	Vancouver (CAN)	Chris Reid (CEO, fdr) Ken Kratschmar (CTO, fdr)	$2,80 BDC
2017 2020		Standing Wave Reformers LLC New Wave Hydrogen, Inc.	Gainsville FL (USA) Calgary AB (CAN)	Robert Kielb (founder, CTO), Kathleen O'Neil (founder, CEO)	$3,00 ERA
2018		Maat Energy Company	Cambridge MA (USA)	Kim-Chinh Tran (CEO, fdr)	$1,35 NSF
2018	ExxonMobil	ExxonMobil (Imperial College)	Annandale NJ (USA)	Brett Parkinson, Sumathy Raman David Dankworth	intern
2019	HiiROC	HiiROC Ltd.	Hull (GBR)	Ate Wiekamp (CTO)	$2,10 Winte

Document Info | Commercial Methane Pyrolysis Efforts

Graphite is a Highly Critical Mineral for Energy Applications



June 2020 → 9 mentions

July 2023 → 166 mentions

- Graphite identified as highest level of criticality (along with REE)
- Highly important to growing lithium-ion battery market
- Demand expected to grow
- Largest sources of battery graphite from outside US

Future Plans

Within the project

- Demonstrate 1 kg/day continuous carbon upgrading reactor
- Develop design package for pilot-scale carbon upgrading plant

After the project

- Explore opportunities to further develop the reactor (scale TRL)
- Explore other feedstocks (carbon recycling/upcycling)

Summary

- We are developing a scalable process to monetize flare gas by converting it into valuable graphite
- Process proof-of-concept and TEA done to support feasibility
- Process makes highly crystalline graphite good for Li-ion battery applications
- While being potentially cost-competitive, process also lower energy to produce graphite compared to current processes
- Final goal of scaled-up graphite production underway

THANK YOU

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Dr. Reza Abbaschian
Dr. Steven Herrera

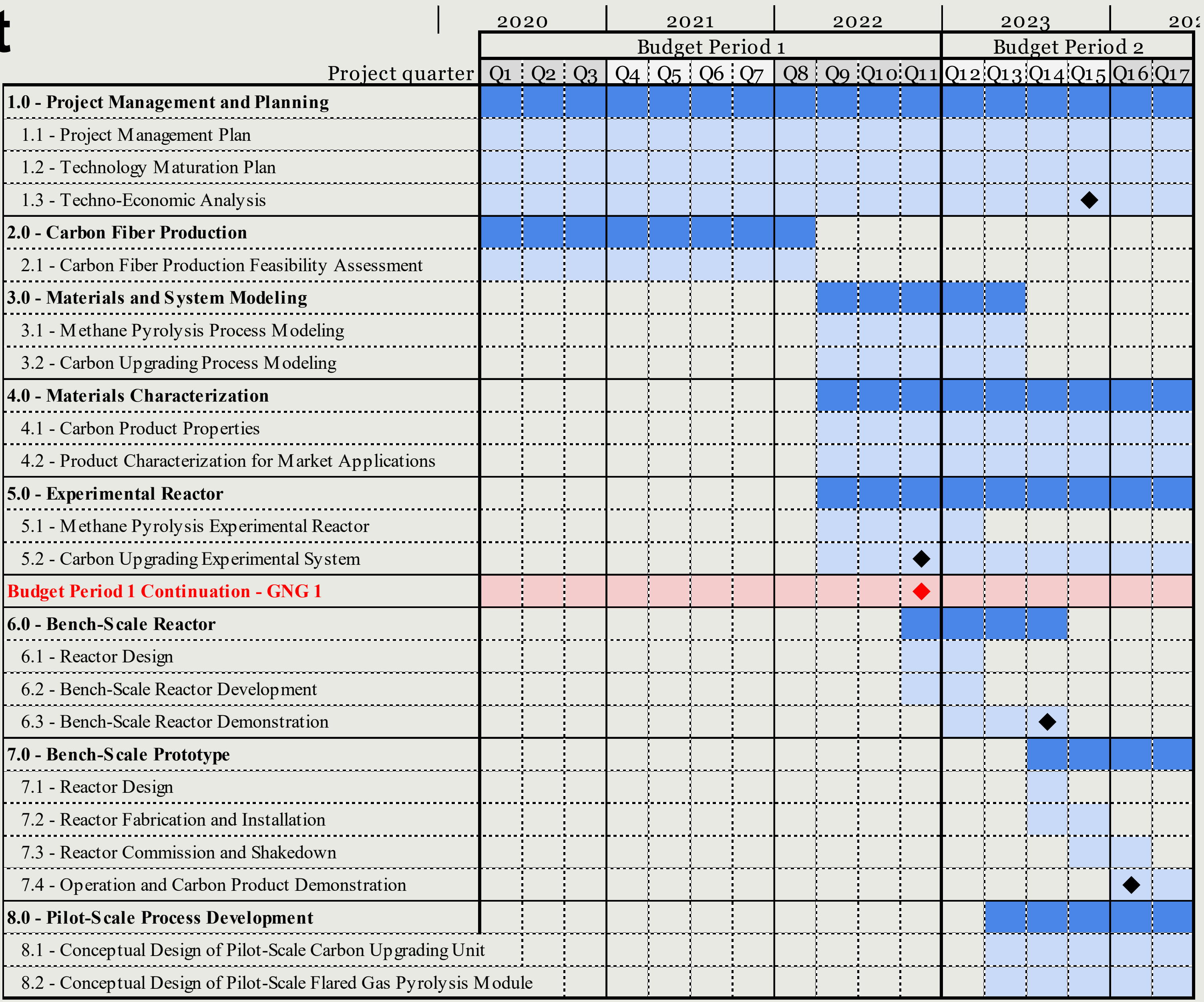
Dr. Mary Louie

Appendix

Organization Chart

Organization	Contributors	Roles & Responsibilities	
SRI	Dr. Brad Rupp (PI) Dr. Jin Ki Hong Dr. Jessica Medrado Dr. Austin Wei Dr. Rahul Pandey	▪ Project Management ▪ Pyrolysis Process Development	▪ Pyrolysis Carbon Production ▪ Bench-Scale Pyrolysis Process
CIVITAS	Mr. Sheldon Mullet, PE	▪ Flared Gas Site Host (Future) ▪ OSBL Site Evaluation	▪ Business Case Development ▪ Commercialization Partner
UC RIVERSIDE	Prof. Reza Abbaschian Dr. Steven Herrera	▪ Graphitization Proof-of-Concept ▪ Carbon Characterization	▪ Bench-Scale Graphitization
	Dr. Mary Louie	▪ Carbon Product Characterization	▪ Graphitization Process Design

Gantt Chart



2020
2021
2022
2023
Budget Period 1
Budget Period 2
Project quarter
Q1 Q2 Q3 Q4 Q5 Q6 Q7 Q8 Q9 Q10 Q11 Q12 Q13 Q14 Q15 Q16 Q17
1.0 - Project Management and Planning
1.1 - Project Management Plan
1.2 - Technology Maturation Plan
1.3 - Techno-Economic Analysis
2.0 - Carbon Fiber Production
2.1 - Carbon Fiber Production Feasibility Assessment
3.0 - Materials and System Modeling
3.1 - Methane Pyrolysis Process Modeling
3.2 - Carbon Upgrading Process Modeling
4.0 - Materials Characterization
4.1 - Carbon Product Properties
4.2 - Product Characterization for Market Applications
5.0 - Experimental Reactor
5.1 - Methane Pyrolysis Experimental Reactor
5.2 - Carbon Upgrading Experimental System
Budget Period 1 Continuation - GNG 1
6.0 - Bench-Scale Reactor
6.1 - Reactor Design
6.2 - Bench-Scale Reactor Development
6.3 - Bench-Scale Reactor Demonstration
7.0 - Bench-Scale Prototype
7.1 - Reactor Design
7.2 - Reactor Fabrication and Installation
7.3 - Reactor Commission and Shakedown
7.4 - Operation and Carbon Product Demonstration
8.0 - Pilot-Scale Process Development
8.1 - Conceptual Design of Pilot-Scale Carbon Upgrading Unit
8.2 - Conceptual Design of Pilot-Scale Flared Gas Pyrolysis Module

