DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

WBS: 3.7.3.005
Scaling Up Biocrude Derived Anode Material (BDAM)

April 4, 2023

Principal Investigators:
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Mark Nimlos, National Renewable Energy Laboratory

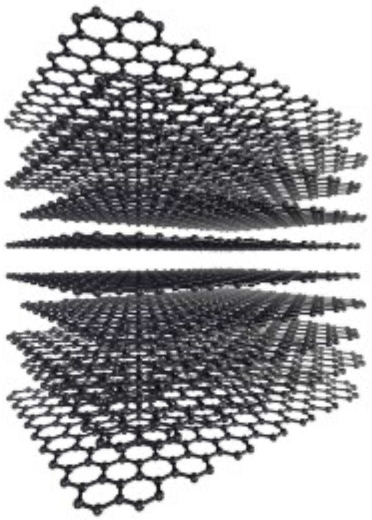
Project Overview

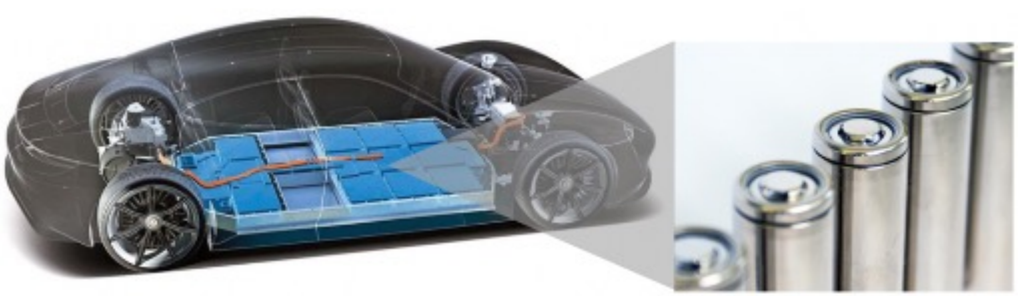
- The primary objective of this project is to **scale up the key process ("delayed coker") for converting biocrude pyrolysis oil into high-quality graphite** that is economically and environmentally preferred as anode materials in lithium-ion batteries.
- Multidisciplinary team involving academia, industries and national lab to facilitate the commercialization of biographite and thereby improve the economics of sustainable aviation fuel (SAF).
- Our project addresses BETO's goals
  - Process improvements to achieve $2.50/GGE with a maximum reduction in emissions relative to petroleum-derived fuels by 2030
  - Facilitate the commercialization of renewable products

Graphite: Definition and Applications

- Graphite is two dimensional, planar molecular structure of pure carbon
  - One of only two naturally occurring forms (diamond and graphite)
  - Occurs as flakes -- Multiple layers of graphene held together by weak bonds
  - Excellent conductor of heat and electricity
  - Highest natural strength and stiffness

- Graphite applications
  - Refractories (steel industry)
  - Structural materials (gasket, brake lining, etc.)
  - Lithium-ion batteries (phones, laptops, electric vehicles)

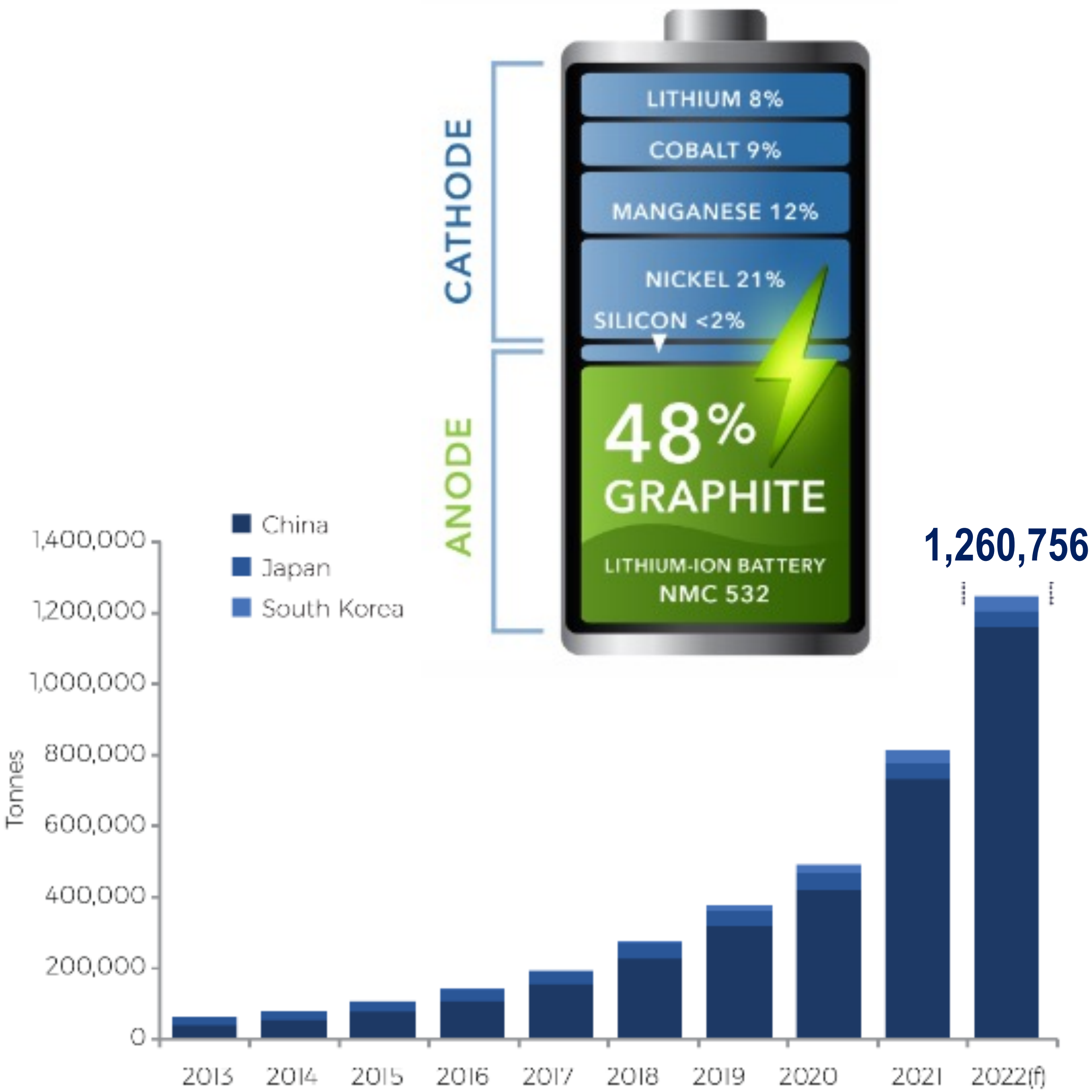


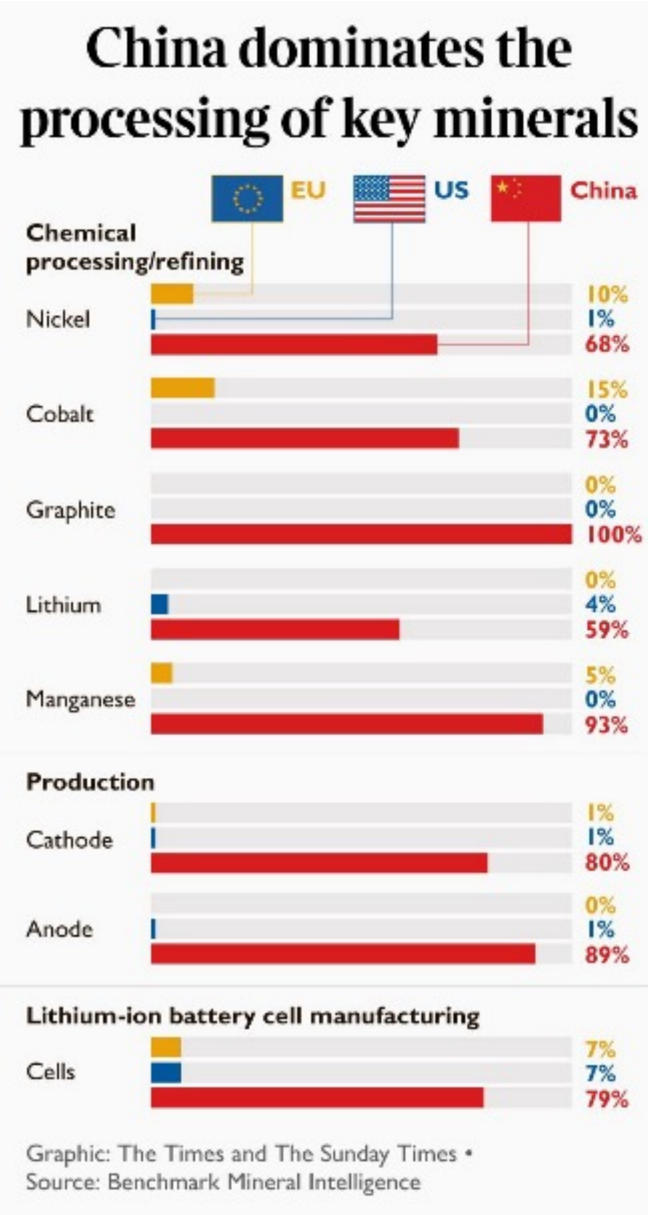


50~100 kg graphite per electric vehicle

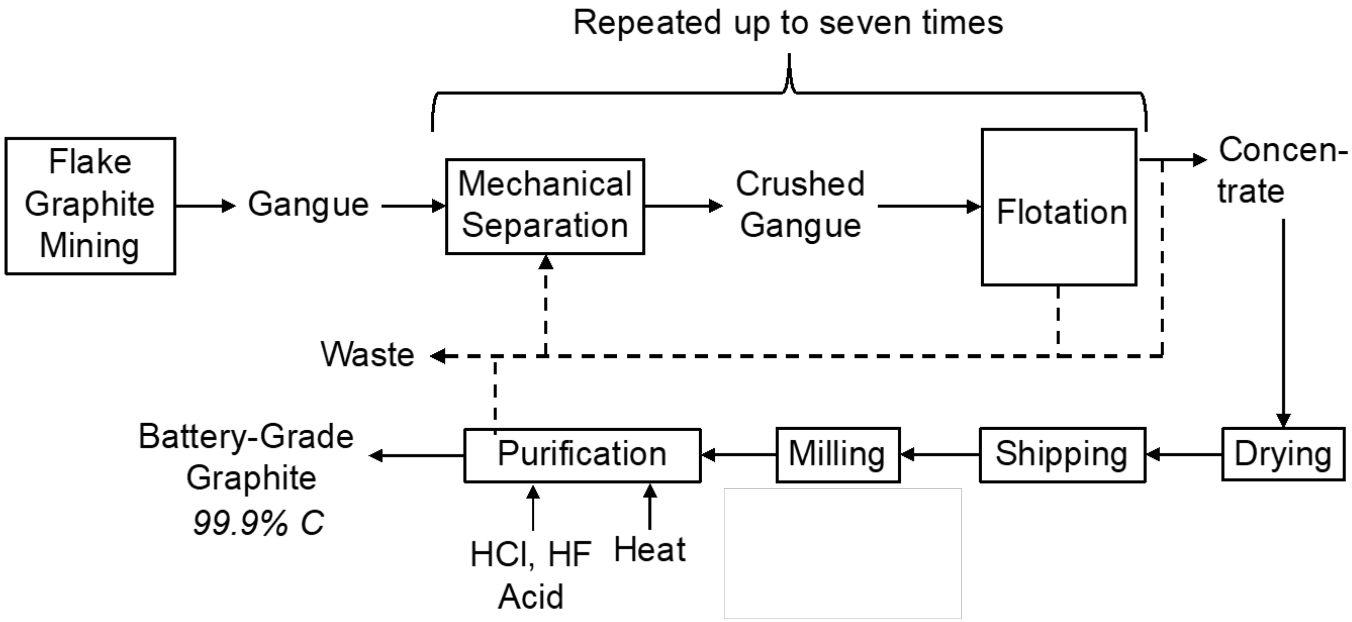
"Our cells should be called Nickel-**Graphite**, because the cathode is nickel and the anode is **graphite** with silicon oxide…[there's] a little bit of lithium in there, but it's like the salt on the salad" – Elon Musk

Anode Production and Key Minerals



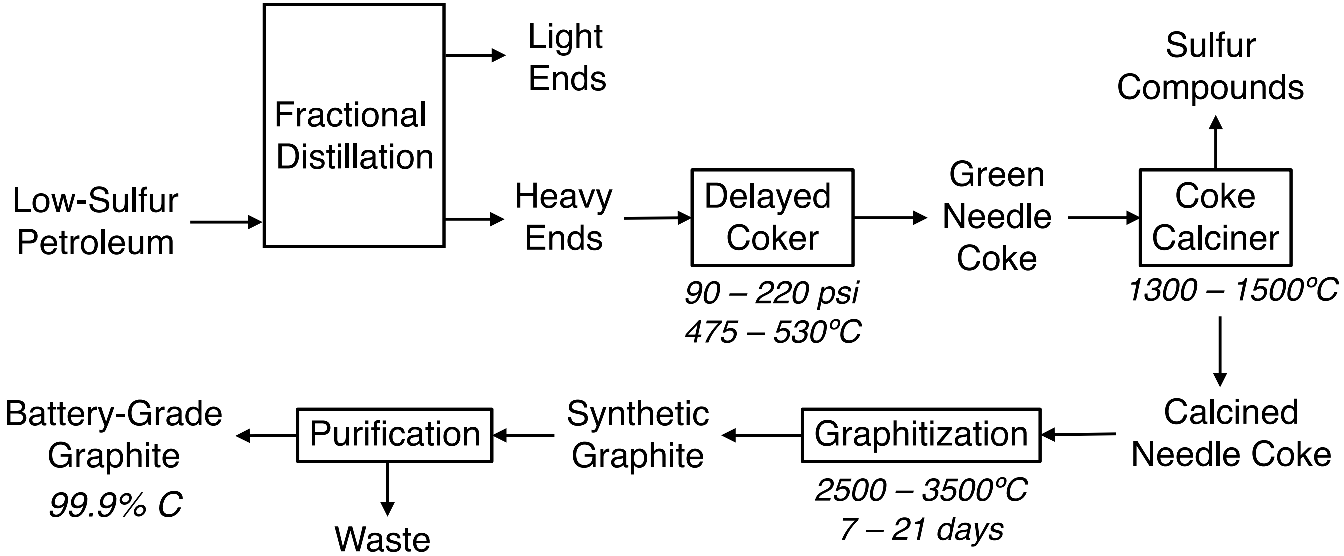


Commercial Graphite Production



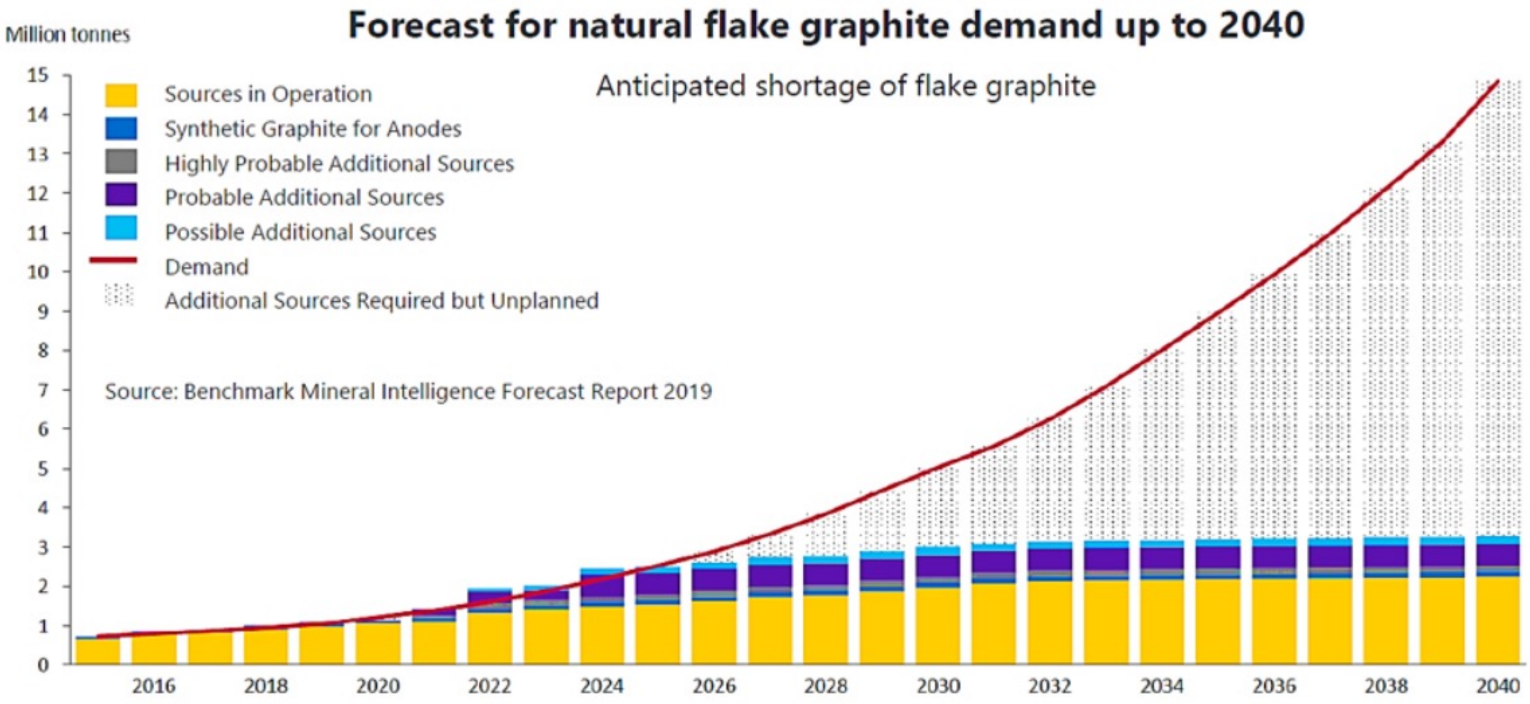
Natural graphite mining

Synthetic graphite from petroleum



Graphite Supply vs. Demand

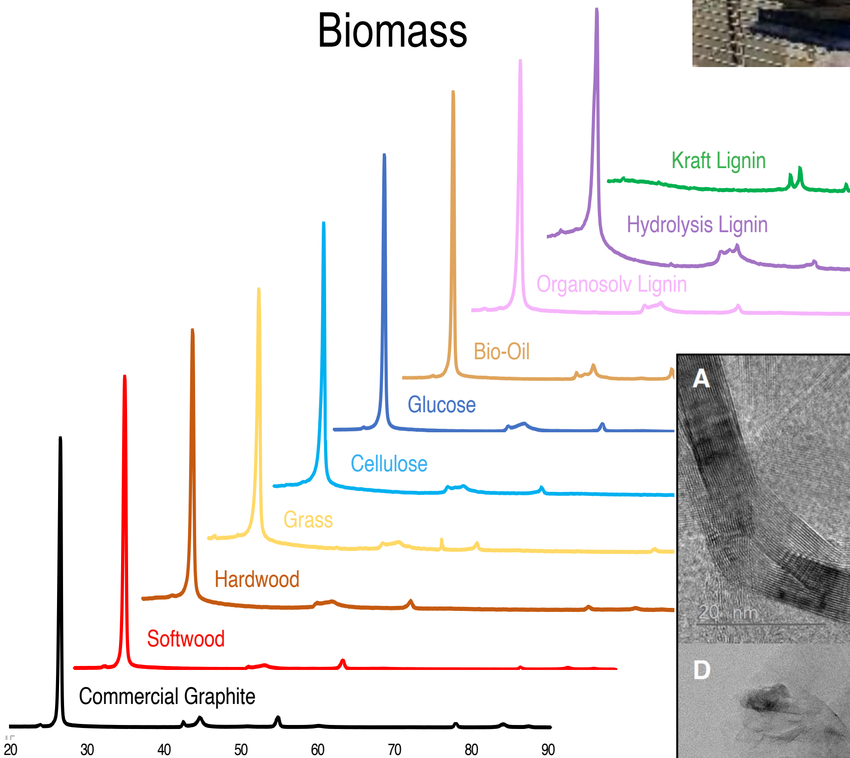
- Natural graphite
  - World: 1,300,000 ton production (2022)
  - US: 82,000 ton imported and no production (2022)
- Synthetic graphite
  - World: 1,800,000 ton production (2021)
  - US: Small amount from Phillips 66
- Graphite shortage is expected in LIB and EV market

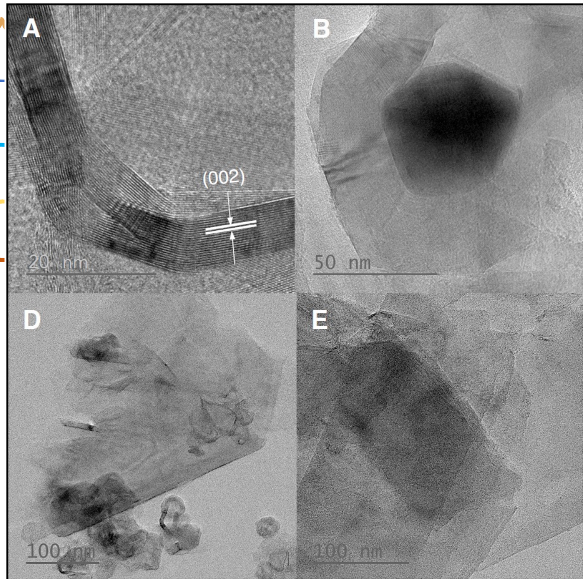


Prelim. Work: Graphite Synthesis from Biomass

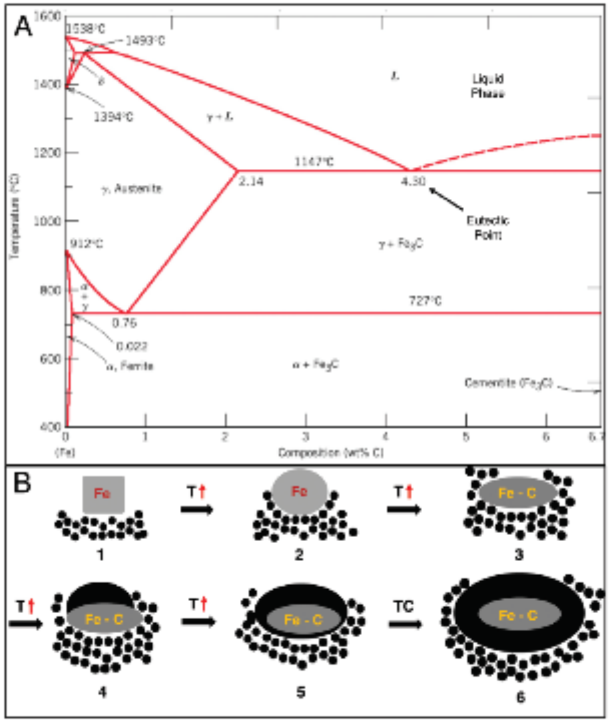
Biomass

Graphite





Sagues et al., Green Chem. 2020



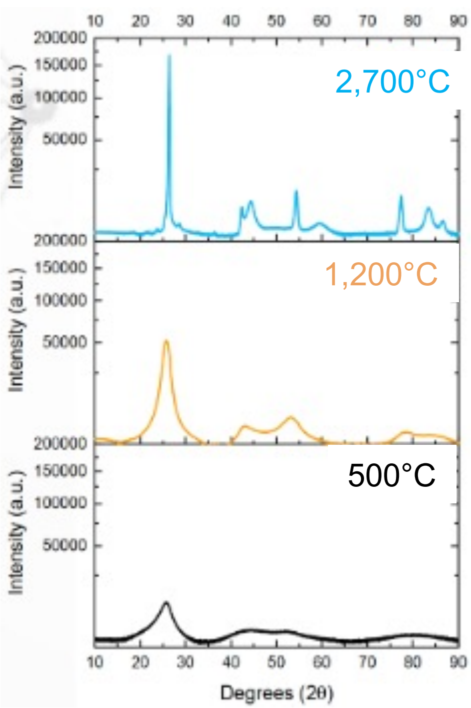
NREL Transforming ENERGY

NC STATE UNIVERSITY

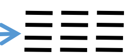
Prelim. Work: Graphite Synthesis from Bio-oil

Heavy crude from BioBTX (catalytic pyrolysis) was coked, calcined and graphitized to produce

XRD



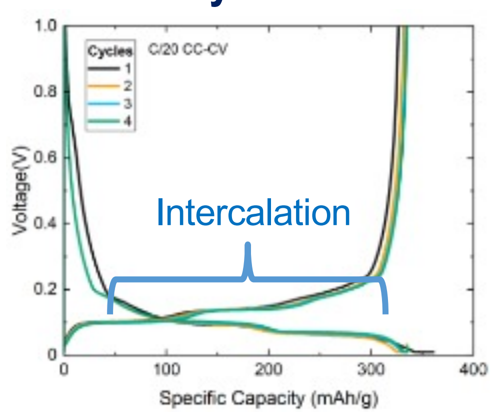
Catalytic Pyrolysis Crude (**BioBTX**) → Coking (500°C) → Calcine (1,200°C) → Graphitize (2,700°C) →

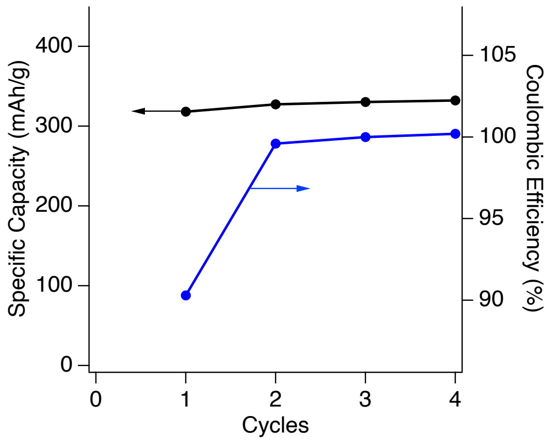


Michael Regula, Zachary Combs, **Birla Carbon**

Property	Unit	Coke	Calcined Coke	Bio-graphite	Comm. Graphite
(002) d-spacing	nm	0.3455	0.3471	0.3370	0.3365
L_C	nm	2.6	2.6	28.9	41.4

Battery Performance





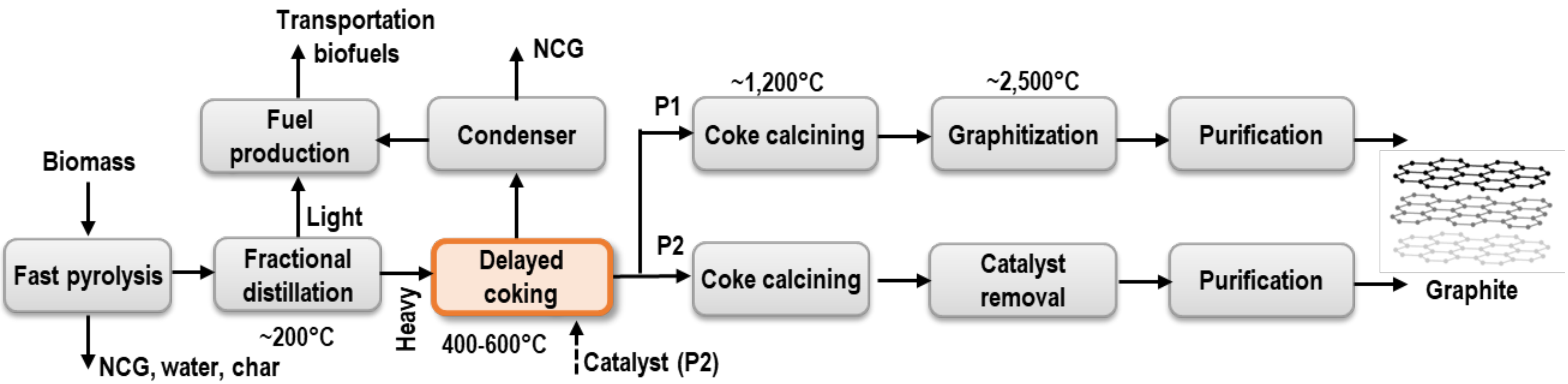
BETO funded: TCF (**WBS 6.6.0.2 Sustainable Graphite for Lithium-Ion Batteries**) and AOP (**WBS. 2.3.1.314 Catalytic Upgrading of Pyrolysis Products**)

Project Objectives

- The primary objective of this project is to scale up the key process ("delayed coker") for converting biocrude pyrolysis oil into high-quality graphite that is economically and environmentally preferred as anode materials in lithium-ion batteries.

BP	Key Milestones & Deliverables
1	Go/No-go #1, Initial verification
2	Lab-scale study of two pathways; Electrochemical performance in LIB; Process model and TEA; Metrics - $2.80/GGE fuels and technology down selection (Go/No-go #2)
3	Reactor design and construction; Process optimization; Systems analysis (TEA, LCA); Metrics - (a) $2.50/GGE fuels and (b) 60% reduction in GHG emission (Go/No-go #3)
4	Delayed coker operation; Electrochemical performance; Systems analysis; Metrics – (a) 500 hr operation (with 100 hr cont.), (b) $2.50/GGE fuels, (c) 60% reduction in GHG emission (Final verification)

Scale up to 3kg/h delayed coker



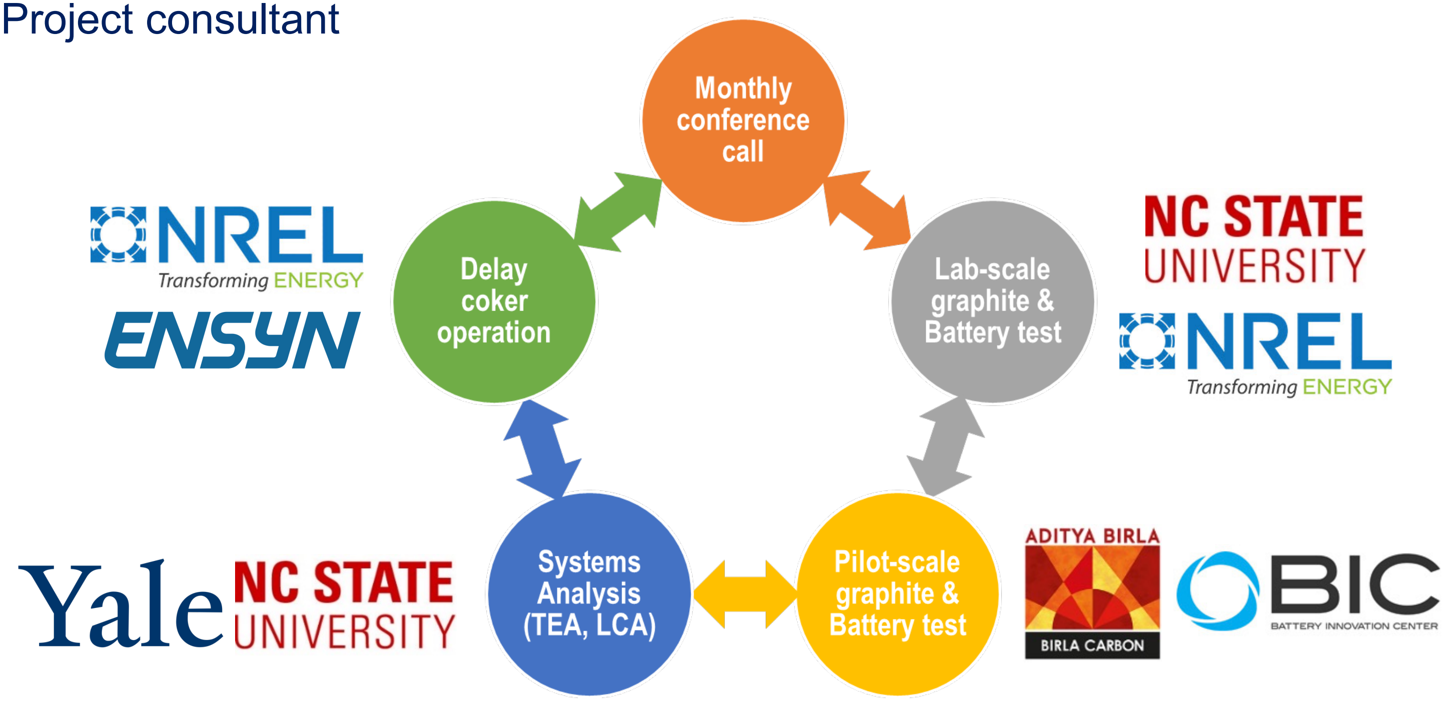
- Two pathways
  - Graphitization of catalytic pyrolysis oil (coking + calcination + graphitization)
  - Catalytic graphitization of pyrolysis oil (coking + calcination)
- Variables to optimize
  - Biomass: Softwood, hardwood
  - Fast pyrolysis: Catalytic, non-catalytic
  - Delayed coking: Temp, time, catalyst
  - Calcining, graphitization purification

pilot coker

Two approaches will be investigated to optimize operability and economics of graphite synthesis and reduce deployment risk

Management and Project Teams

- Project work breakdown
  - Bio-oil production – Ensyn, NREL, and BioBTX
  - Lab-scale graphite production and coin-cell battery test – NCSU and NREL
  - Pilot-scale graphite production and pouch-cell battery test – Birla and BIC
  - Delay coker construction and installation – Equipment company, Ensyn, and NREL
  - Systems analysis: TEA and LCA – NCSU and Yale
  - Project consultant



Project leverages the expertise of a highly diverse team, including Birla Carbon, BIC, Ensyn, and independent consultant.

Milestones and Go/No-go

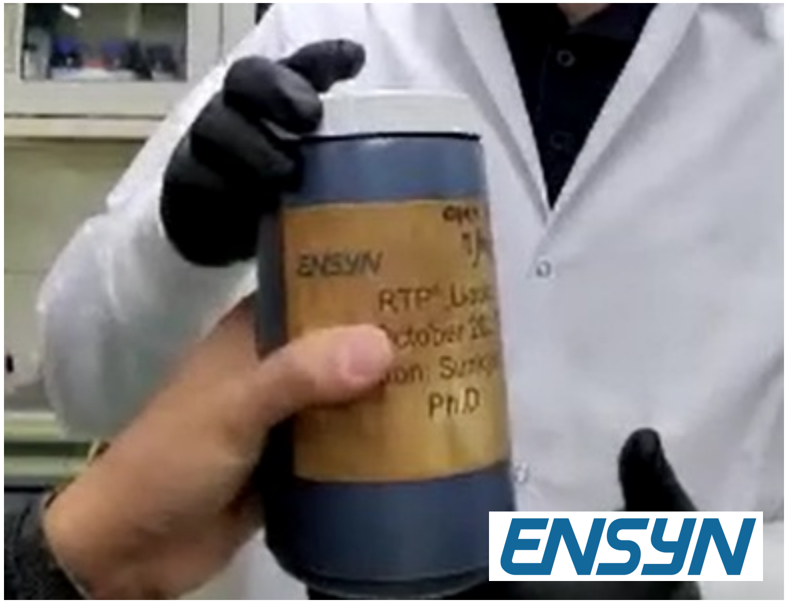
Milestone	Topic	Date	Target	Progress
Task 1, GNG1	Initial Verification	6/30/22	Initial verification completion	Completed
Task 2, M1	Biocrude production	9/30/22	20+ kg of bio-oil production	Completed
Task 3, M2	Develop design parameters for needle coke	12/31/22	Evaluate the parameters in lab-scale	In progress
Task 4, M4	Develop design parameters for catalytic graphite	3/31/23	Evaluate the parameters in lab-scale	In progress
Task 4, M5	Develop design parameters for catalyst removal	9/30/23	Evaluate the parameters in lab-scale	In progress
Task 5	Deleted		-	-
Task 6, M6	Electrochemical analysis of Graphite	6/30/23	Coin cell battery test	In progress
Task 7	Deleted		-	-
Task 8, M9	Building model for Preliminary TEA	3/31/23	Process model for prelim TEA	In progress
Task 8, M10	Finishing Preliminary TEA based on lab data	9/30/23	Prelim TEA completion	-
Task 9, M11, GNG2	Intermediate verification	12/31/23	Intermediate verification	-
Task 10, M12	Reactor design specs	3/31/24	Identification of reaction design specs	In progress
Task 11, M13	Pilot reactor construction by commercial partner	3/31/25	Pilot coker construction	-
Task 12, M14	Continuation of lab work to optimize the process	3/31/24	Process optimization	-
Task 12, M15	Completing experiments for selected pathway	9/30/24	Process optimization	-
Task 13, M16	Develop model for delayed coker feeding	6/30/24	Process model for prelim LCA	-
Task 13, M17	Preliminary LCA and update preliminary TEA	12/31/24	Prelim LCA completion	-
Task 14, GNG3	Intermediate verification	3/31/25	Intermediate verification	-
Task 15, M18	Production of FB biocrude for pilot test	6/30/25	Pilot scale bio-oil production	-
Task 15, M19	Delayed coker operation with FP biocrude	9/30/25	500 hours of operation	-
Task 16, M20	Pilot test with CFP Biocrude	9/30/25	24 hours of operation	-
Task 17, M21	Electrochemical analysis of anode materials	9/30/25	Coin and pouch cell battery test	-
Task 18, M22	Validation of fuel performance	9/30/25	Fuel performance test	-
Task 19, M23	Completing TEA and LCA for FP-based graphite	9/30/25	Process model update for TEA and LCA	-
Task 19, M24	Completing TEA and LCA for CFP-based graphite	9/30/25	TEA and LCA completion	-
Task 20, M25	Final report	9/30/25	Final ppt and/or report	-
Task 21	Final verification	9/30/25	Final verification	-

Progress and Outcomes

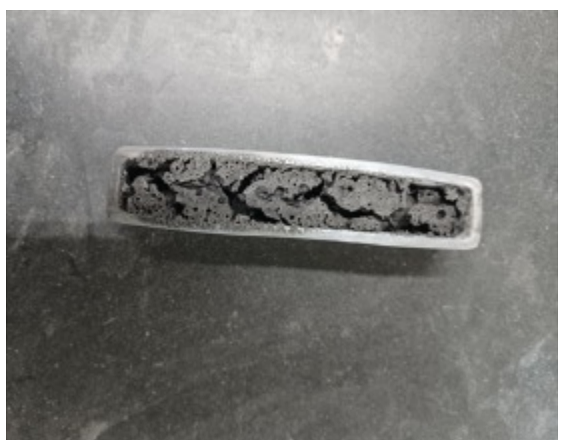
- BP1
  - Initial Verification successfully completed

- BP2
  - Held Kick-off meeting on November 8, 2022
  - Received pyrolysis oils from Ensyn (non-catalytic) and BioBTX (catalytic)
  - Investigated catalyst loading for catalytic graphitization
  - Investigated heating rates and hold times for catalytic graphitization
  - Measure coking rates for BioBTX oil
  - Building models to allow design of pilot coker
  - Constructing system to collect volatiles from coking/hydrotreating to SAF

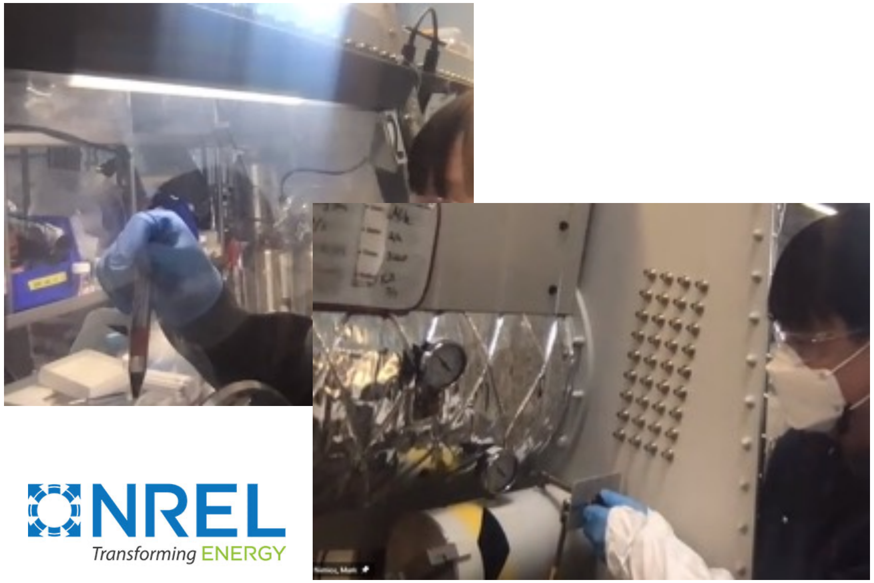
Initial Verification: (1) Graphite Production



Initial Verification: (2) Graphite Purification



Initial Veri.: (3) Slurry Preparation for Battery Test



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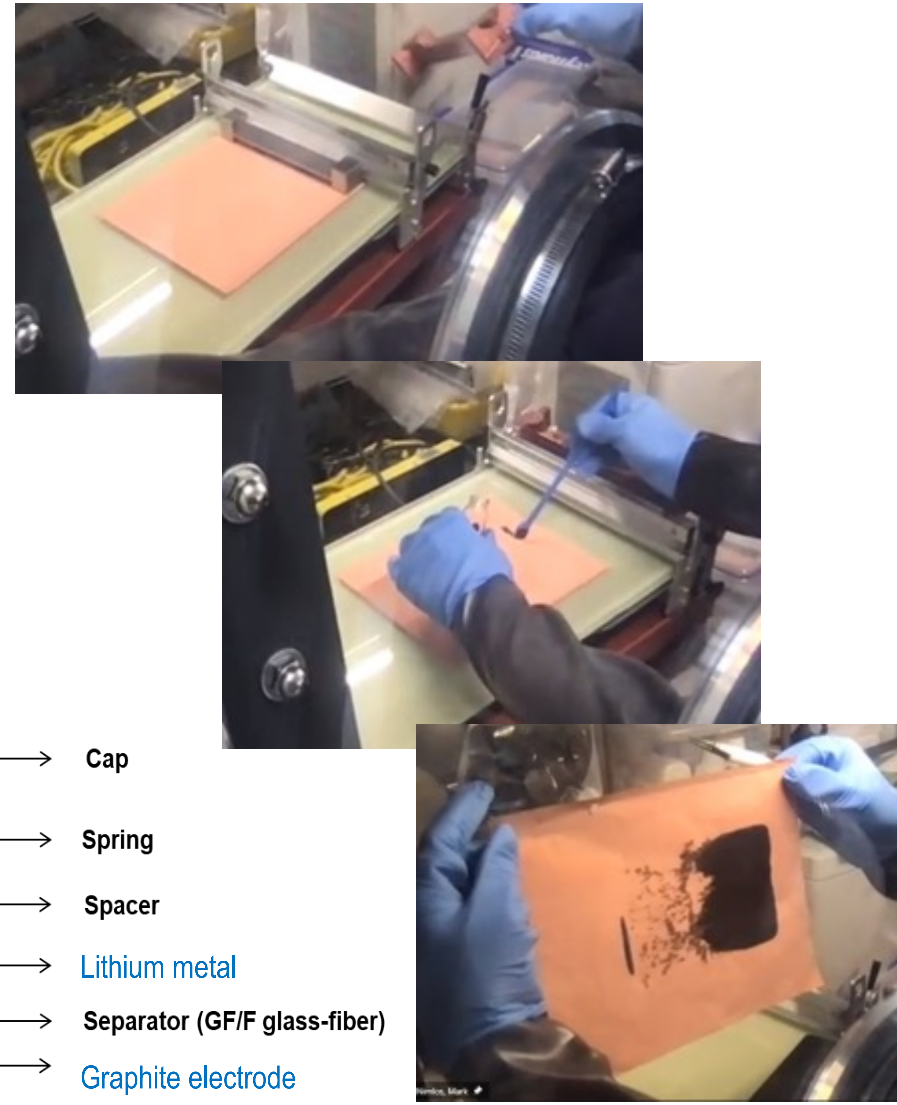
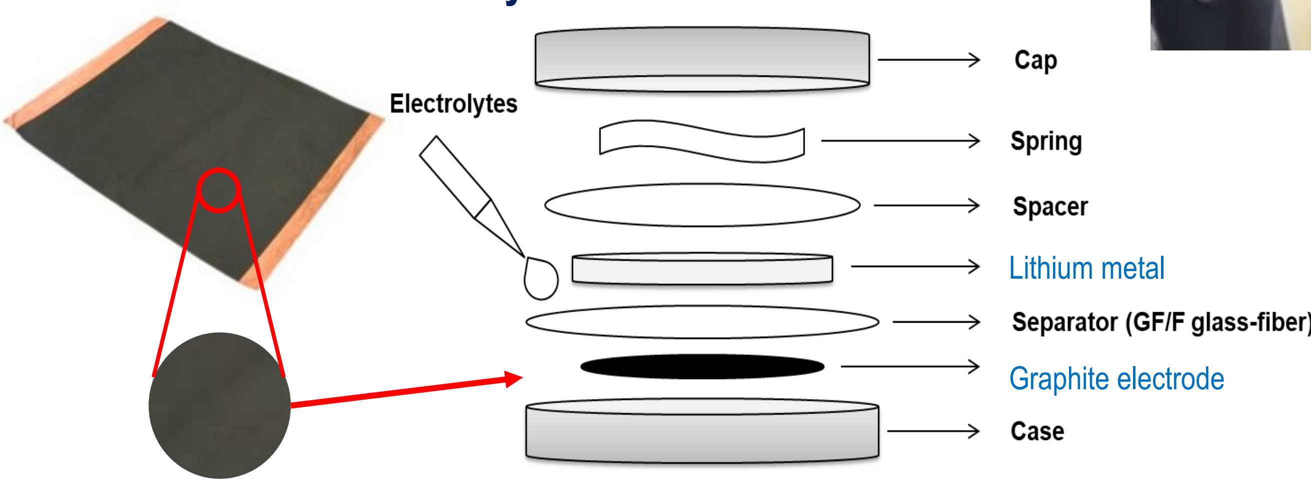
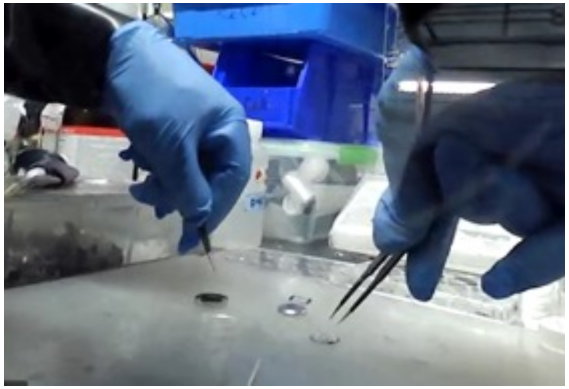


Assembly of Half Cell LIB



Initial Verification: (4) Battery Performance Test



NREL
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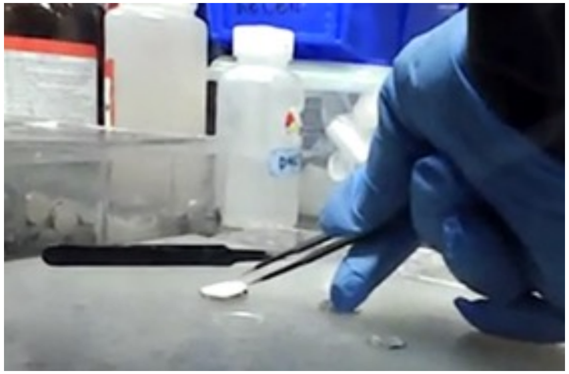

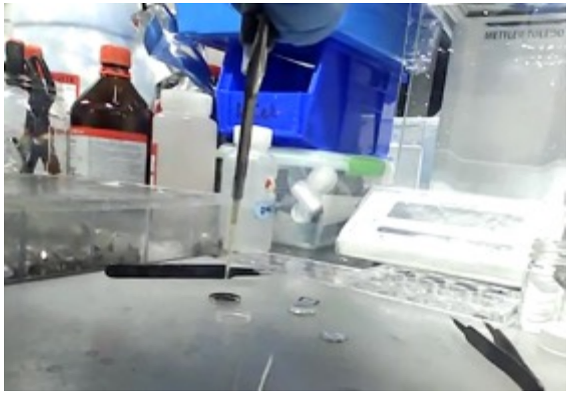

Initial Verification Results: Graphite from Bio-oil

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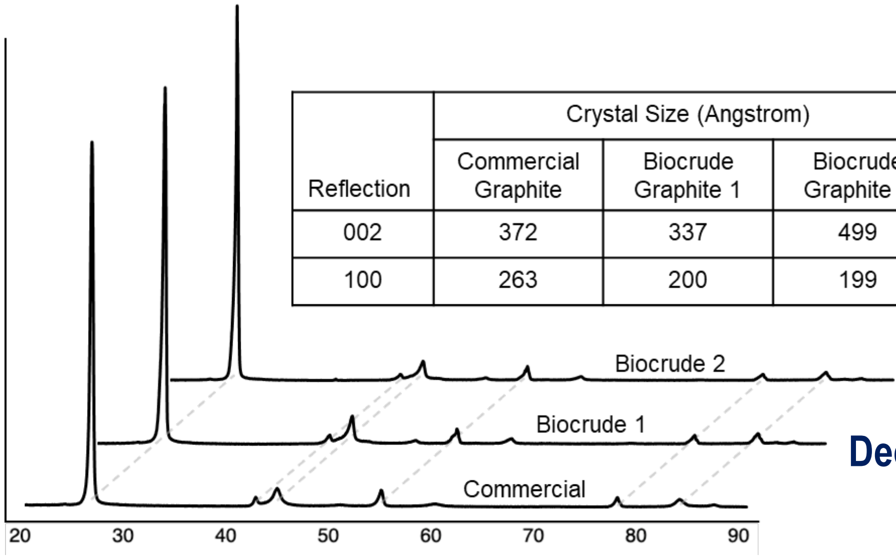
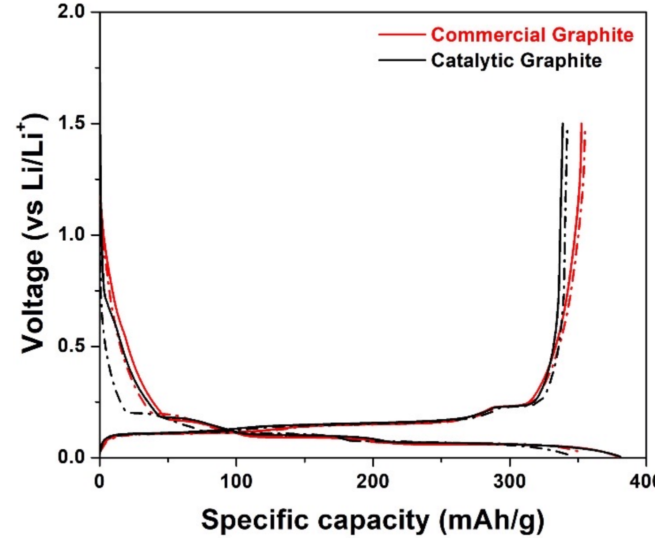


Reflection	Crystal Size (Angstrom)		
	Commercial Graphite	Biocrude Graphite 1	Biocrude Graphite 2
002	372	337	499
100	263	200	199



			2nd			
		charge	discharge	charge		
Proposal		335	344	338	84	98
Verification		339	347	342	90	99

[a] Coulombic Efficiency; [b] Discharge/charge at 15 mA/g and cycled at 150 mA/g (voltage range: 0.001-2.0 V).

The performance of graphite from bio-oil is comparable to a commercial graphite

Project Kick-Off Meeting

- November 8, 2022
- NCSU Campus
- 19 participantes (15 in-person)

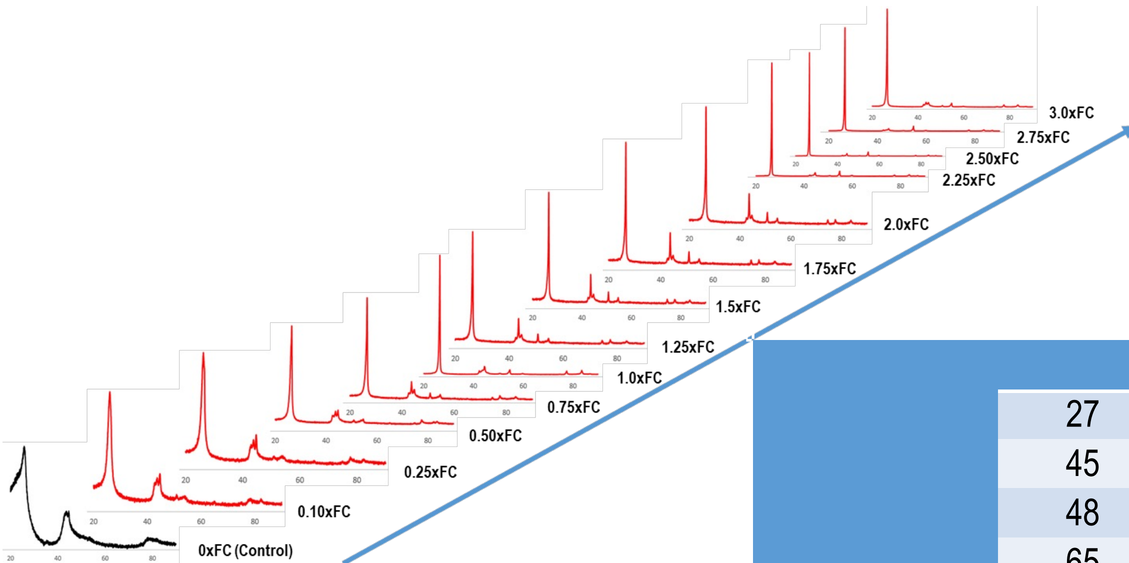
	Topic	Presenter
8:30 am	Welcome	Myron Floyd
8:45 am	Introduction	All
9:00 am	Project overview	Sunkyu Park
9:15 am	Industry perspective I – Ensyn	Ensyn
10:00 am	Industry perspective II – Birla Carbon	Birla Carbon
10:45 am	Industry perspective III – BIC	BIC
11:30 am	Reporting and cost-share documents	Research Office
11:45 pm	Lunch – Panera catering	
12:30 pm	Synthetic graphite production	Brian Worfolk, Consultant
1:30 pm	Previous work on graphite I	Mark Nimlos
2:00 pm	Previous work on graphite II	Shaikat Dey
2:30 pm	Previous work on graphite III	Joe Sagues
3:00 pm	Pilot reactor	Spencer Everitt, Xytel
3:30 pm	Future work discussion	Nimlos and Park
4:00 pm	Walk to Forest Biomaterials	
4:15 pm	Facility tour	Sunkyu Park

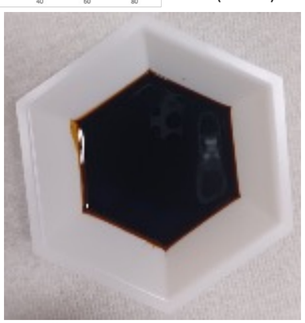
Bio-oil from Ensyn (non-catalytic bio-oil)

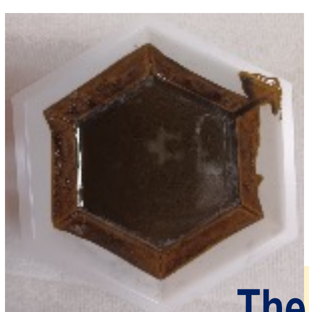
ENSYN

Rapid Thermal Processing plant, Renfrew, ON (3 million gallons/year)

Effect of Catalyst Loading







		L_a (Å)	d_{002} (nm)	I_D/I_G
	27	122	0.3419	1.03
	45	179	0.3410	1.22
	48	238	0.3381	1.13
	65	375	0.3356	1.07
0.75 x FC	89	428	0.3347	0.77
1.00 x FC	160	403	0.3361	0.64
1.25 x FC	134	532	0.3355	0.69
1.50 x FC	180	644	0.3350	0.78
1.75 x FC	179	706	0.3341	0.40
2.00 x FC	179	615	0.3348	0.35
2.25 x FC	240	370	0.3351	0.32
2.50 x FC	233	390	0.3344	0.19
2.75 x FC	218	416	0.3347	0.28
3.00 x FC	177	418	0.3352	0.43
Commercial	197	385	0.3347	0.17

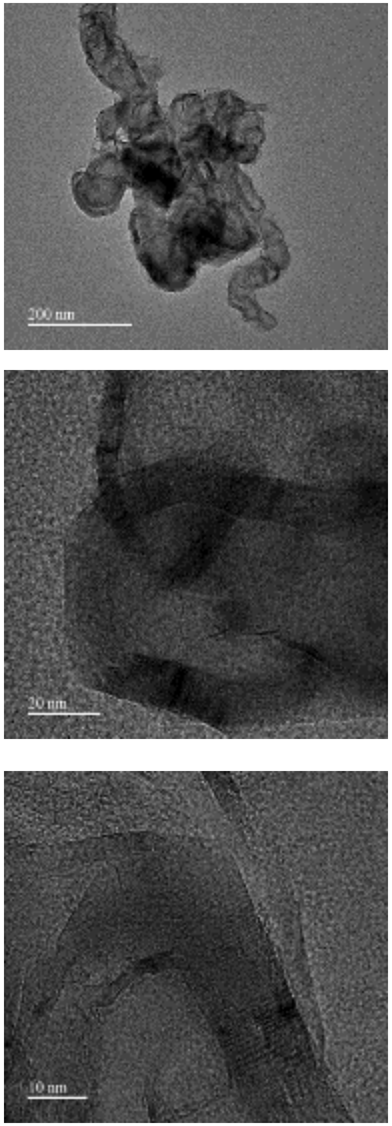
The optimal catalyst loading was identified based on XRD

Morphology and Inorganic Analysis of Biographite

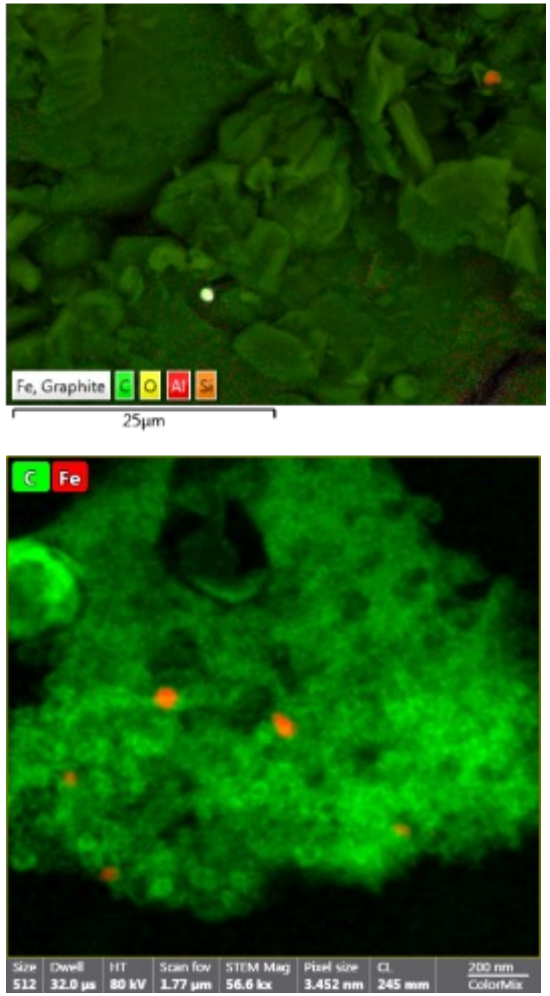
Low

Magnification

High



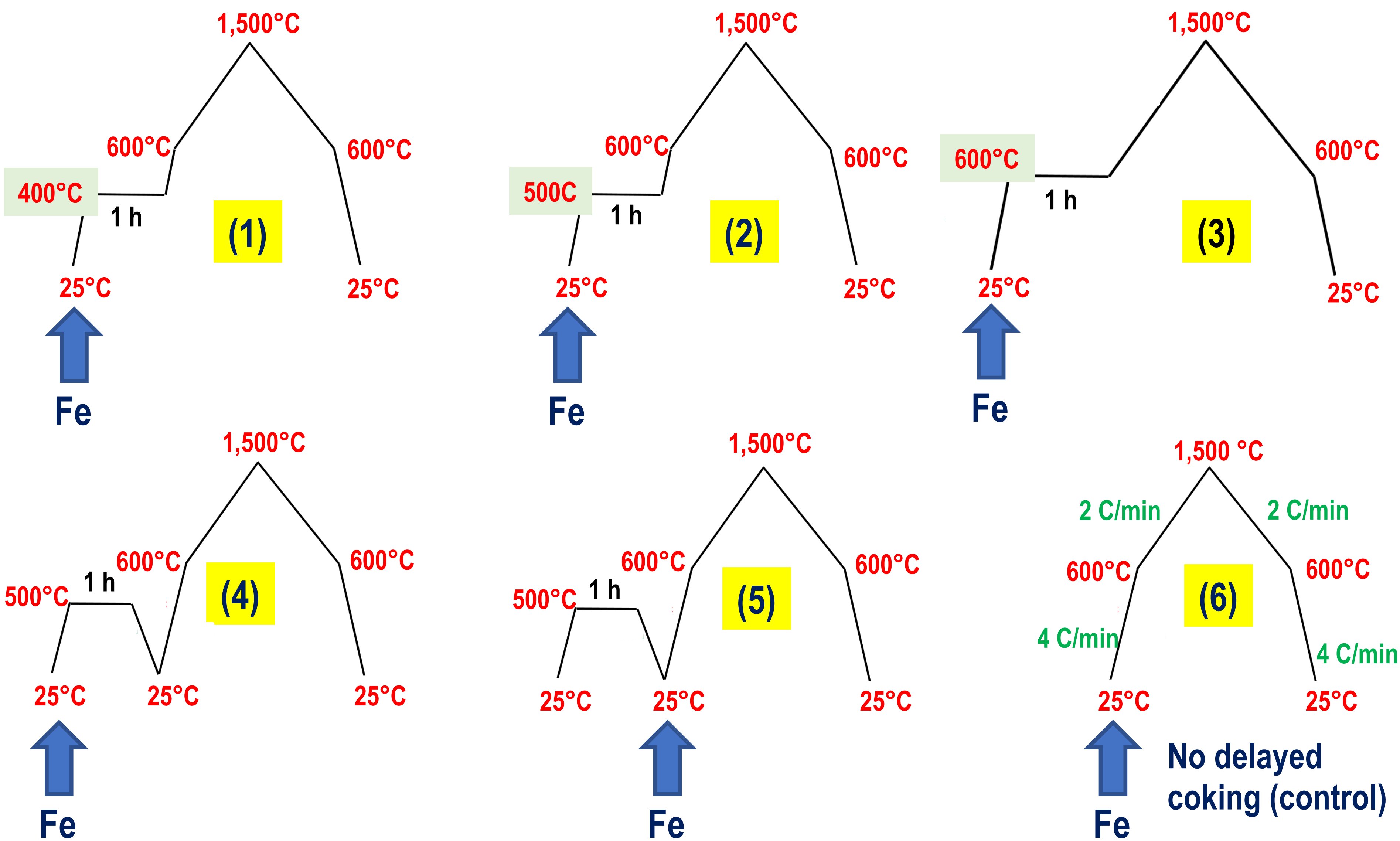
Elemental mapping



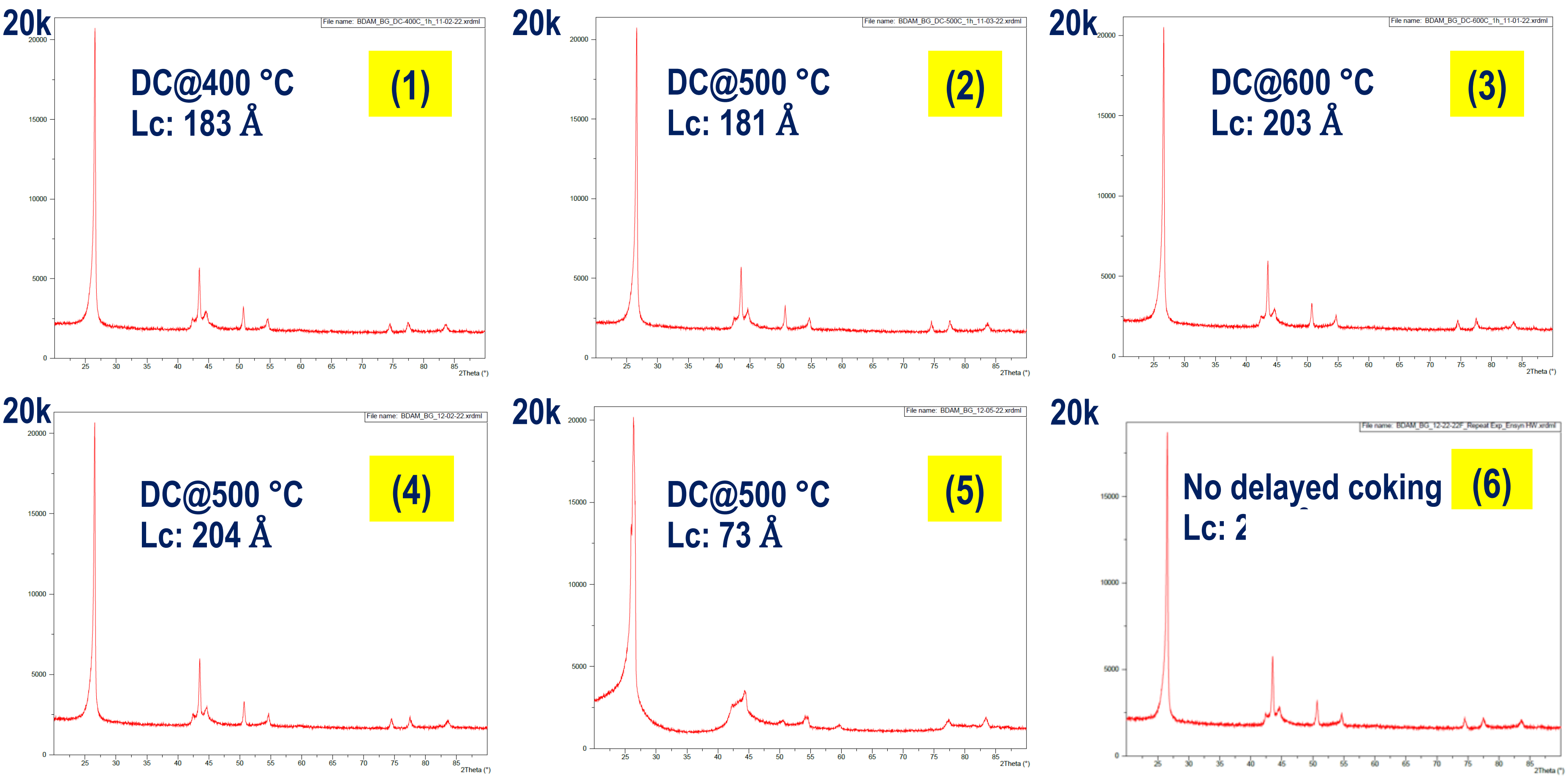
Element	HW Bio-oil	Bio-graphite
Organics (C)	99.817	99.861
Al	0.009	0.027
Si	1.5 ppm	0.012
P	0.031	0.018
S	0.115	0.009
Cl	--	0.009
Ca	0.009	0.007
Ti	--	5.5 (ppm)
Fe	1.7 (ppm)	0.049
Ni		1.1 (ppm)
Cu	2.8 (ppm)	1.2 (ppm)
Zn		0.3 (ppm)
Br	--	5.1 (ppm)
Sn	0.002	0.003
Te	0.003	0.004
Mg	0.0 (ppm)	--
K	0.012	--
Sb	0.001	--
Hf	1.7 (ppm)	--
Cr	--	--

Higher purity graphite can be produced with further acid and/or heat treatment

Simulated Delay Coking Experiments

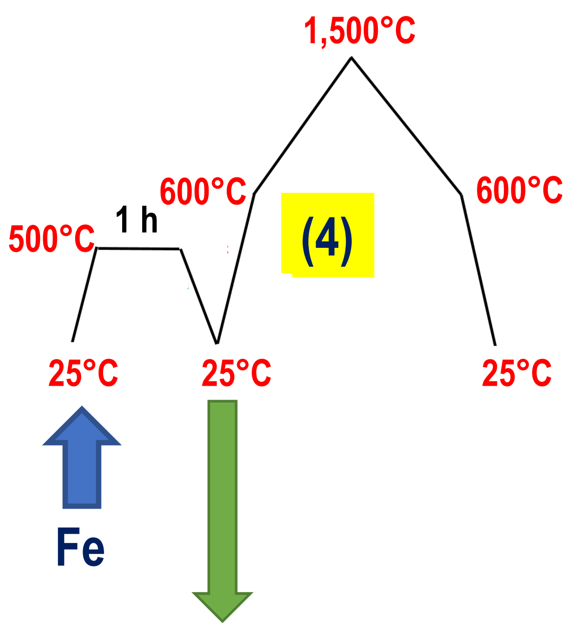


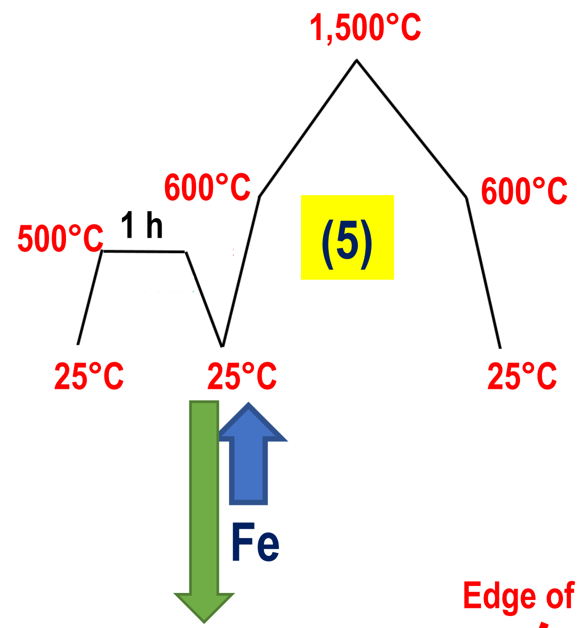
Simulated Delay Coking Experiments

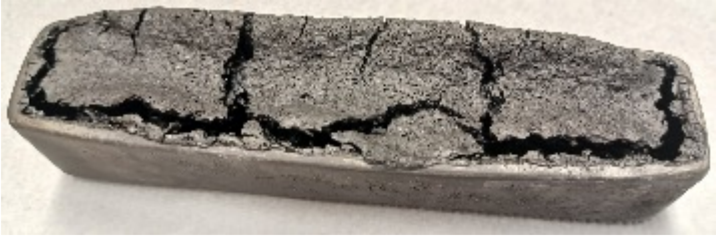


- Not much difference was observed when treated 400~600 °C (delayed coking) – (1, 2, 3, 6)
- XRD for (5) (catalyst mixed after delayed coking) was not as sharp as others – Mixing issue

Bio-oil Foaming





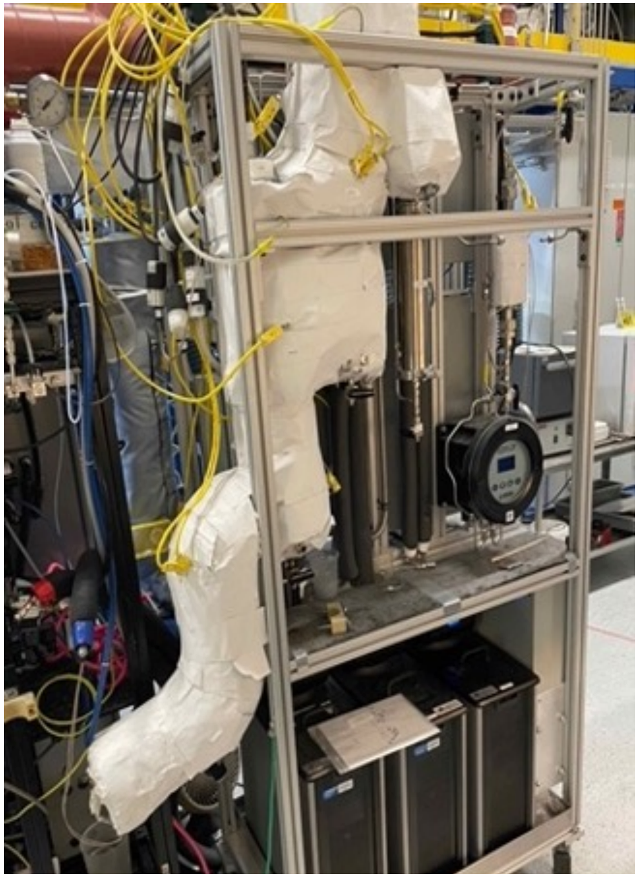


After Delayed Coking (Exp. 4)

After Delayed Coking (Exp. 5)

When bio-oil is heated without catalysts (5), carbon structure is swollen

Measurements of Coking Products



Picture of the condensation system at NREL for collecting vapors from coking pyrolysis oils (cold finger, condenser, electrostatic precipitator, GC analyzer).

Trickle bed reactor system at NREL for hydrotreating biocrude oils.

Collaboration with (**WBS. 2.3.1.314 Catalytic Upgrading of Pyrolysis Products**)

NREL Transforming ENERGY

Lab-scale Graphite Reactor and Pilot Delay Coker

- Graphite reactor from Centorr
  - ~3,000°C graphitization
  - Facility modification in progress
  - Equipment purchase and installation (BP2)

- Pilot delay coker from Xytel
  - ~500°C coking
  - Hired a project consultant
  - Engineering study (BP2)
  - Equipment purchase and installation (BP3)

Project Impact

- Development of **a less-severe, cost-effective process** for producing anode materials for battery applications from domestically sourced biocrude has the potential to impact the market for electric vehicles, thereby boosting the US bioeconomy.

- **Graphite is a critical material for Lithium Ion Battery (LIB)**
  - Graphite is imported from other countries, where it is mined and upgraded using energy- and chemical-intensive processes with severe environmental burdens
  - Supply chain issues in US.

- The successful production of **value-added co-products is critical to biorefinery commercialization** by lowering the production costs of renewable liquid transportation fuels.
  - Heavy components of biocrudes will be utilized for graphite, which are low value for fuel and chemical streams

Graphite for EV batteries

- Bipartisan Infrastructure Law
  - $2.8 billion for domestic supply chains for battery manufacturing
  - Graphite considered a critical material
  - 90% produced outside US

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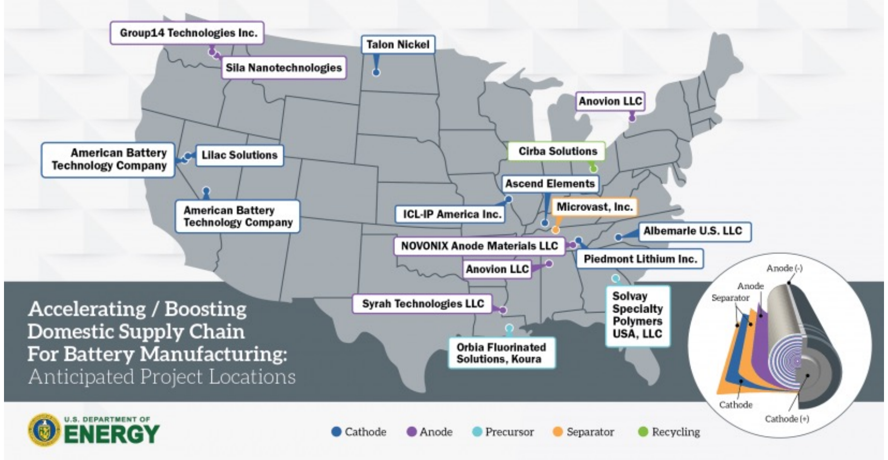
Department of Energy

Biden-Harris Administration Awards $2.8 Billion to Supercharge U.S. Manufacturing of Batteries for Electric Vehicles and Electric Grid

OCTOBER 19, 2022



- EPA considering RIN credits for EV
  - 50-100 kg graphite in EV
  - GHG emissions from synthesis might impact credits

U.S. EPA Rule Making Set Grants Exclusive E-RIN Production Right to EV Automakers

21 December 2022 | Dashboard Insights | Blog

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Summary

- Accomplishments
  - Completed initial verification
  - Kick-off meeting with all member institutes
  - Biocrude production (Ensyn and BioBTX)
  - Preliminary experimental results for catalytic graphitization
- Project future work (BP 2, until Dec 31, 2023)
  - Identify and develop design parameters for graphite
  - Coin-cell battery performance test
  - Vapor condensing and hydrotreating to hydrocarbons
  - Preliminary TEA
  - Engineering study for pilot delay coker
  - Intermediate verification in December 2023

Quad Chart Overview

Timeline

- BP1: Initial Verification
- **BP2: 7/1/2022 ~ 12/31/2023**
- BP3: 1/1/2024 ~ 3/31/2025
- BP3: 4/1/2025 ~ 9/30/2025

	FY23 Costed (Start ~ 12/31/2022)	Total Award
DOE Funding	$199,542	$3,999,937
Project Cost Share		

Project Partners

- DOE NREL, Ensyn, Yale Univ.
- Birla Carbon, Battery Innovation Center

Project Goal

The primary objective of this project is to scale up the key process ("delayed coker") for converting biocrude pyrolysis oil into high-quality graphite that is economically and environmentally preferred as anode materials in lithium-ion batteries.

End of Project Milestone

- Delayed coker operation (500 hr operation with 100 hr continuous)
- Electrochemical performance (comparable to commercial graphite)
- Systems analysis; (a) $2.50/GGE fuels and (b) 60% reduction in GHG emission

Funding Mechanism

- FY20 DE-FOA-0002203 SCale Up of Bench Applications (SCUBA), Topic Area 1
- WBS: 3.7.3.005

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BIOENERGY TECHNOLOGIES OFFICE

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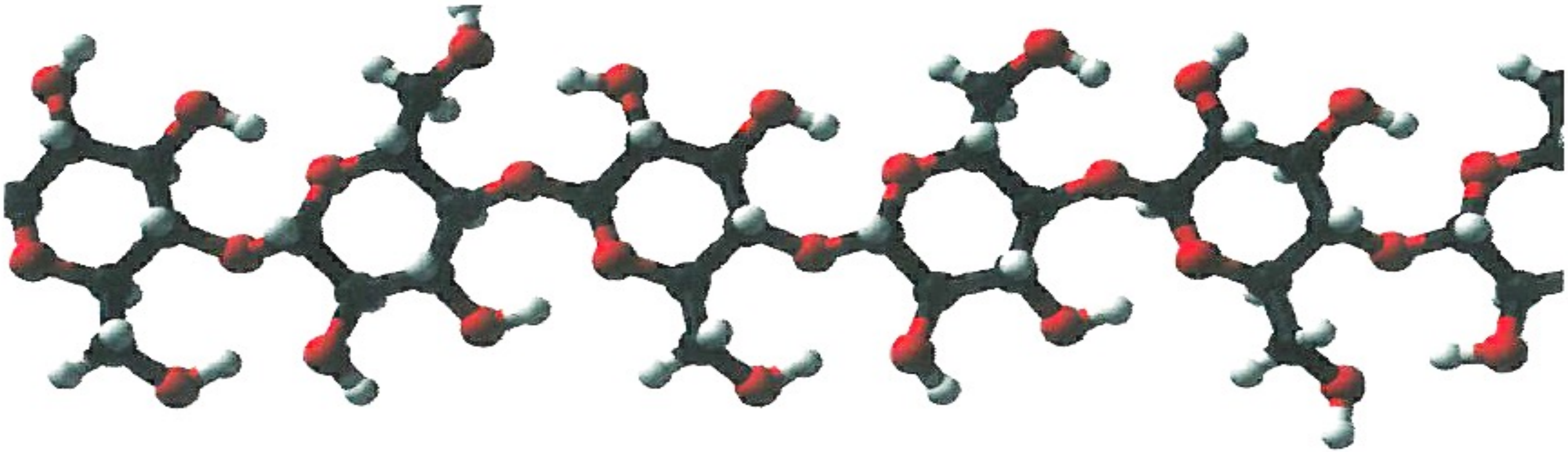
Additional Slides



Publications and Presentations

- **Publications**
  - Multiple manuscripts are in preparation

- **Oral Presentations**
  - Mark Nimlos, et al., Carbon Anode Material from Biomass Pyrolysis Oil, ACS Fall Meeting, Chicago, Illinois, Aug 2022
  - Shaikat Dey, et al., Cataytic Conversiion of Bio-oil into Rechargeable Battery Anode, 2022 Frontiers in Biorefining, King and Prince Beach & Golf Resort, St. Simons Island, Georgia, USA, Oct 2022.