Energy & Environmental Research Center (EERC)

Laboratory-Scale Coal-Derived Graphene Process

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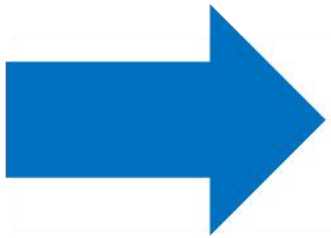
OUTLINE

- Project Overview
- Motivation
- Background
- Upgraded Coal-to-Products (UCP) Technology
- Project Technical Approach
- Progress and Current Status
- Technology Development Plans
- Summary and Conclusions

Project Overview: Objective and Duration

The goal of this project is to develop a technological process to convert domestic U.S. coals into high-value solid carbon products such as graphene and high-quality graphite.

Project Duration: 36 months, May 2020 to April 2023



Project Overview: Funding and Partners

U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY $744,064

Lignite Energy Council $162,000

NORTHAMERICAN COAL $25,000

EERC

UND UNIVERSITY OF NORTH DAKOTA

Total Funding = $931,564

Driving Force For The Study

New Coal Markets in Nonenergy Sectors – Revitalize Coal Communities

High-Value Products for Next-Generation Applications and Carbon-Free Energy Future

Big Market Opportunity

From

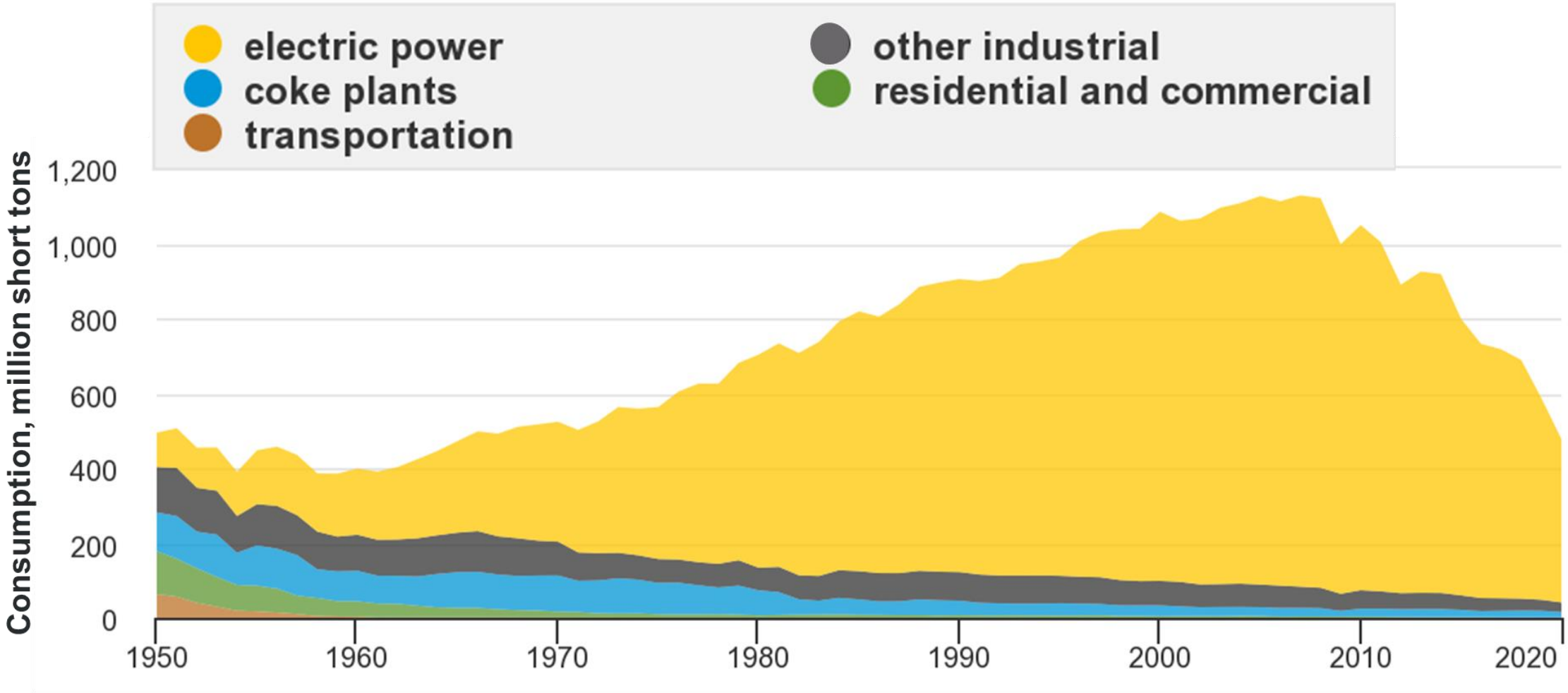
$14.3 billion (2019)

to

$21.6 billion (2027*)

*Allied Market Report, 2022

U.S. Coal Consumption By Major End Users 1950–2020



Source: https://www.eia.gov/energyexplained/coal/use-of-coal.php (accessed 9/7/2021).

The U.S. Coal Equation

Coal Equation For Decarbonized Energy Future

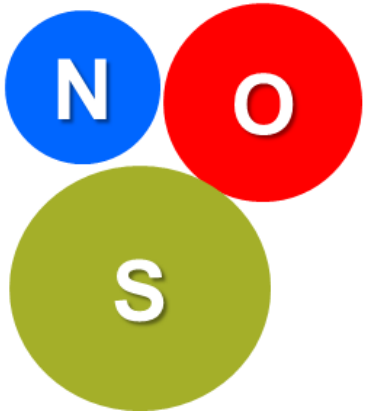
Keep everybody happy with a balanced coal equation.

Coal Challenges For High-Value Carbon Products

Ash impurities

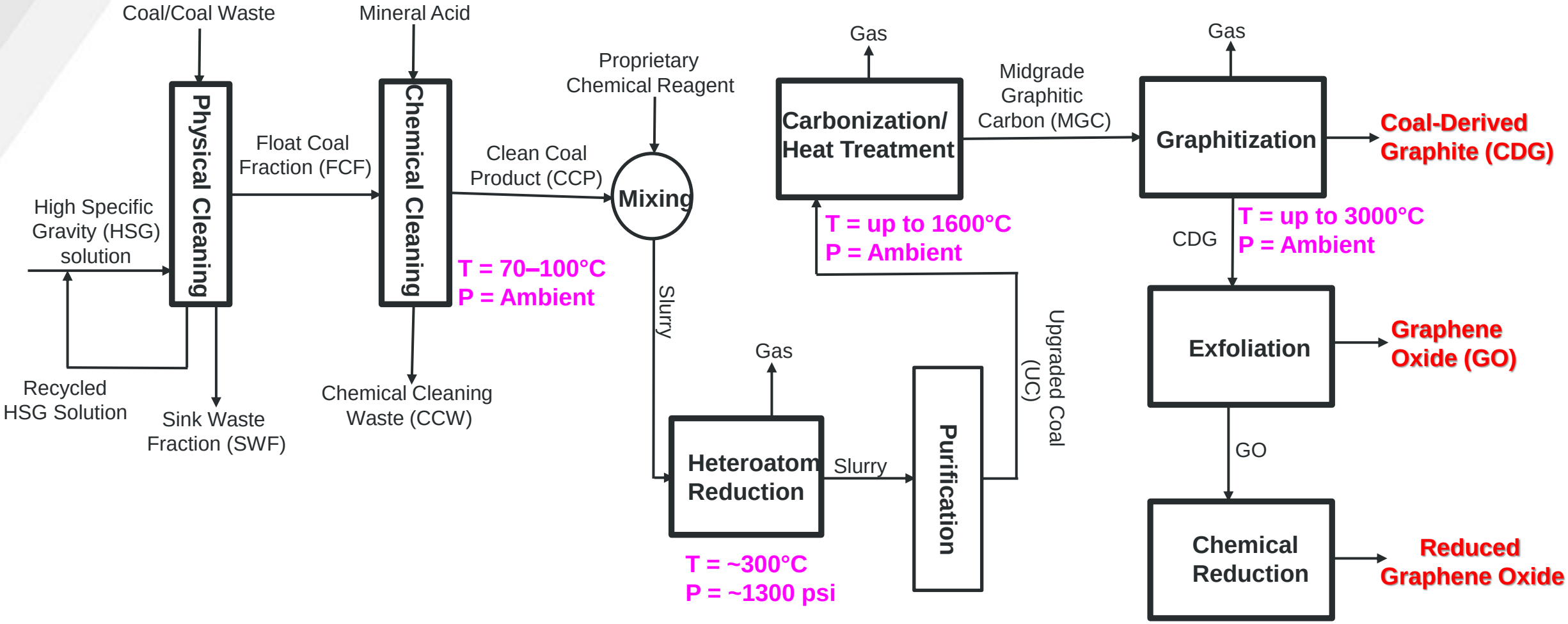
High VM (low rank coals)

Heteroatoms



Low FC (low rank coals)

Upgraded Coal-to-Products (UCP) Technology

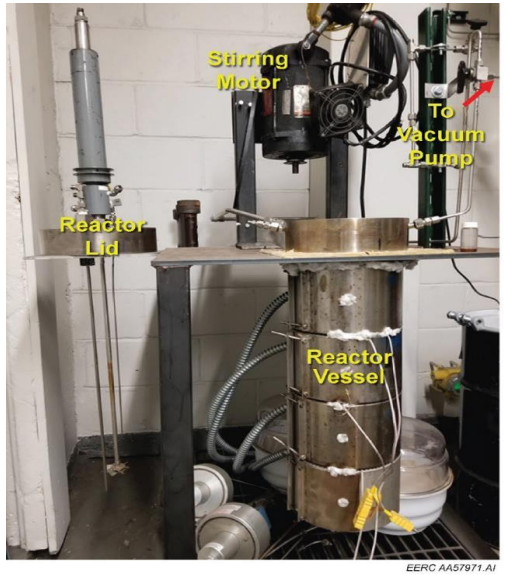


The UCP Technology is applicable to ALL coal ranks and their wastes

Scientific Principles of the UCP Technology

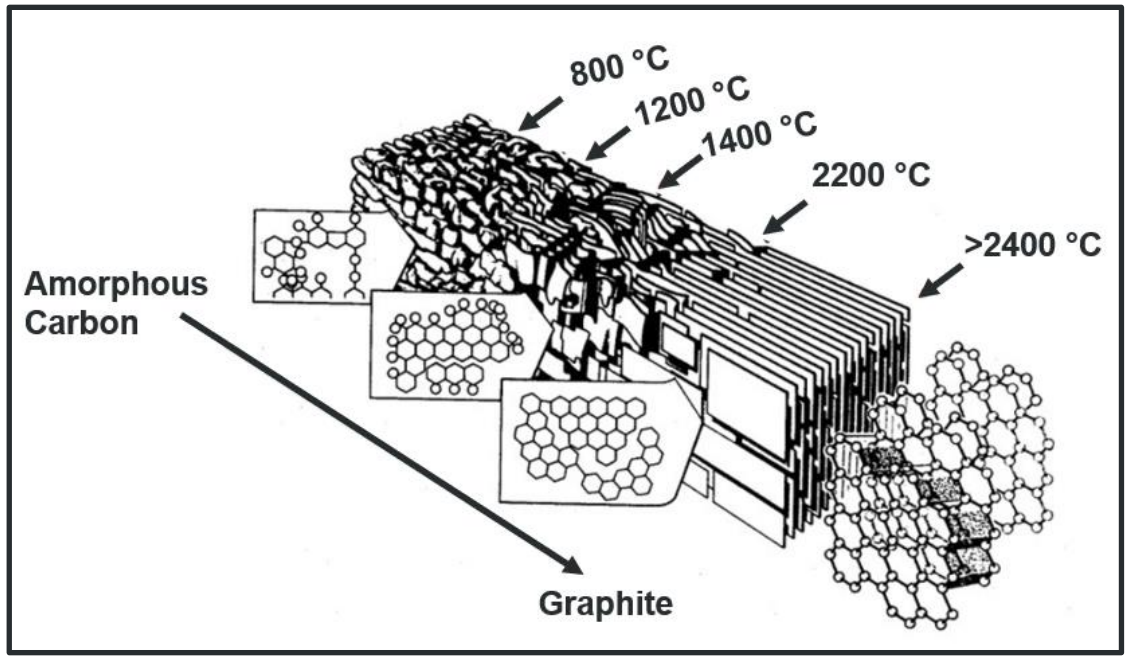
Simple Wet Chemistry Processes

- Physical Cleaning (Float–sink concept)
- Chemical Cleaning (with mineral acid, **No HF!**)
- Heteroatom Reduction Reaction (proprietary reagent)



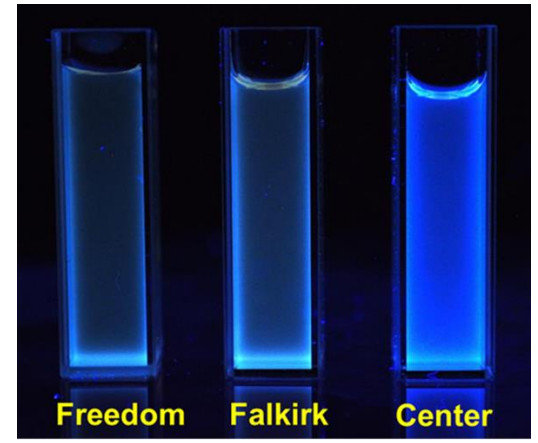
Controlled Heat Treatment

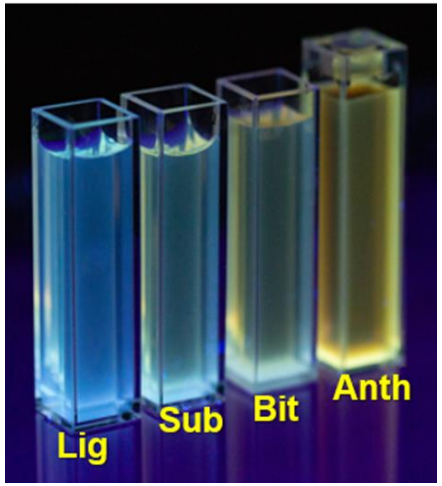
- Staged Carbonization (up to 1000 °C)
- Heat treatment (up to 1600°C)
- Graphitization (up to 3000°C)



Technology Development History

- **Summer 2019** – ND State Energy Research Center (SERC) seed funding for **~$200k**
  - GQDs made from lignite from 3 different mines
- **Summer 2020** – DOE award for **~$931k**
  - GQDs, GO, rGO, and graphite from lignite, subbituminous, bituminous, and anthracite
- **Spring 2022** – DOE award ~**$1.5m**
  - Lignite-derived graphite for LIB anode
- **Next Steps** – Scale-up & commercialization





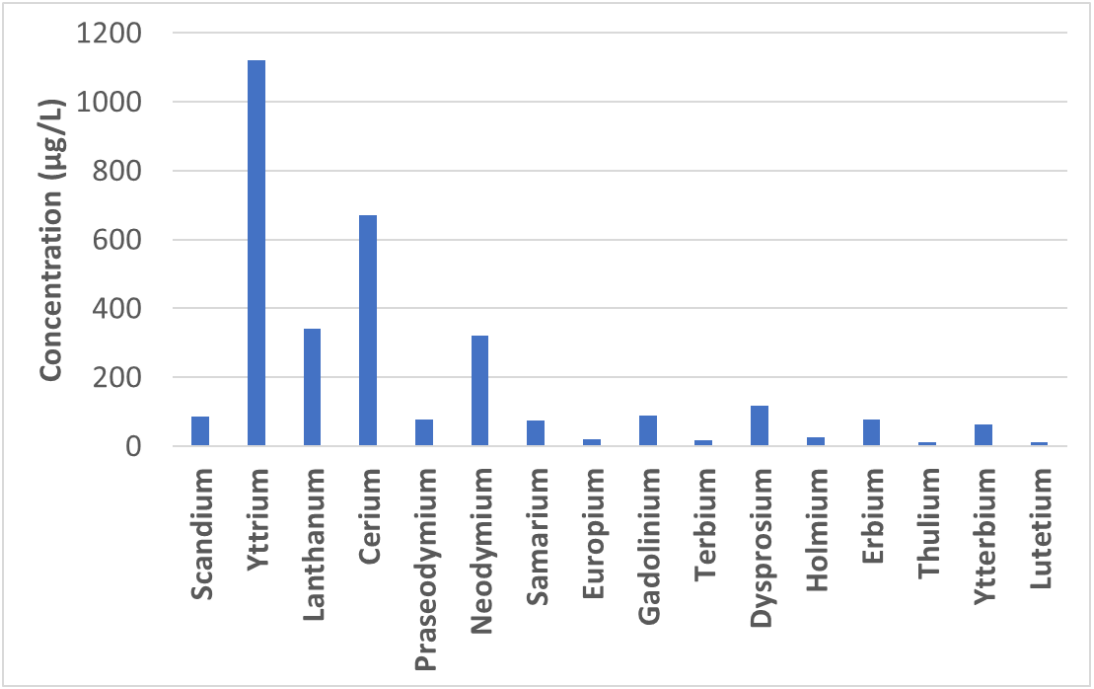
Technical/Economic Advantages and Challenges

Advantages

- **Environmentally Sustainable**
  - Processing under inert conditions
  - Significantly less gaseous emissions (CO_2,NO_x, SO_x)
  - Most toxic species recovered as aqueous wastes for easy handling
- Simple process
- Easily scalable
- Potentially economically feasible
- **Recovery of other critical minerals like REEs**
- **Byproducts from carbonization step**

Challenges

- Product filtration process (practical challenge)



Site Selection Criteria for Potential UCP Deployment

- Modular Deployment Units
- Co-location with coal mines
- Available water resources
- Potentially powered by wind and/or solar energy

Short ride
or conveyed to plant

Technical Approach

The technical approach included the following tasks:

- **Task 1.0** – Project management
- **Task 2.0** – Coal pre-treatment & equipment fabrication/acquisition
- **Task 3.0** – Graphitization of treated coals
- **Task 4.0** – Exfoliation of graphite to graphene
- **Task 5.0** – Techno-economic analysis
- **Task 6.0** – Analysis of product target markets and technology gaps

Project Schedule and Success Criteria

Schedule of Milestones

- **M1** – Project kickoff meeting, Due 7/31/20
- **M2** – Equipment fabrication, Due 8/31/20
- **M3** – Coal pretreatment, Due 12/31/20
- **M4** – LTHG furnace installation/training, Due 8/31/21
- **M5** – Coal graphitization, Due 12/31/21
- **M6** – Graphene products, Due 5/31/22
- **M7** – Initial economic analysis results, Due 8/31/22
- **M8** – Analysis of product target markets, Due 10/31/22
- **M9** – Analysis of technology gaps, Due 12/31/22

Success Criteria

- **BP1 (24 months, 4/30/2022)**
  - Residual ash content 5% or less
  - 10–20% reduction in O_2 content
  - 5–10 g of coal-derived graphene
- **Go/no-go DP (4/30/22)**
  - Demonstrate production of GQDs, GO, rGO.
- **BP2 (12 months, 4/30/2023)**
  - Estimated selling price of coal-derived graphene materials
  - Product target markets
  - Technology gaps

Risk Identification and Mitigation Strategies

Risk Category	Impact Level	Mitigation Strategy
Financial risks - Equipment cost increases after award	low	Detailed initial quote estimates were built into the budget
Cost/Schedule - Budget overrun	low	Overall budget structured by task and subtask
Technical/Scope risks - Challenges getting GO or rGO from low rank coals	medium	Pursue other graphene products such as GQDs
Management & Planning - Overall planning & oversight risks	low	- EERC senior management oversight - Regular updates with DOE
ES&H Risks - Chemical/material exposure to personnel & environment	low	Follow established EERC safety procedures

Progress and Current Status of Project

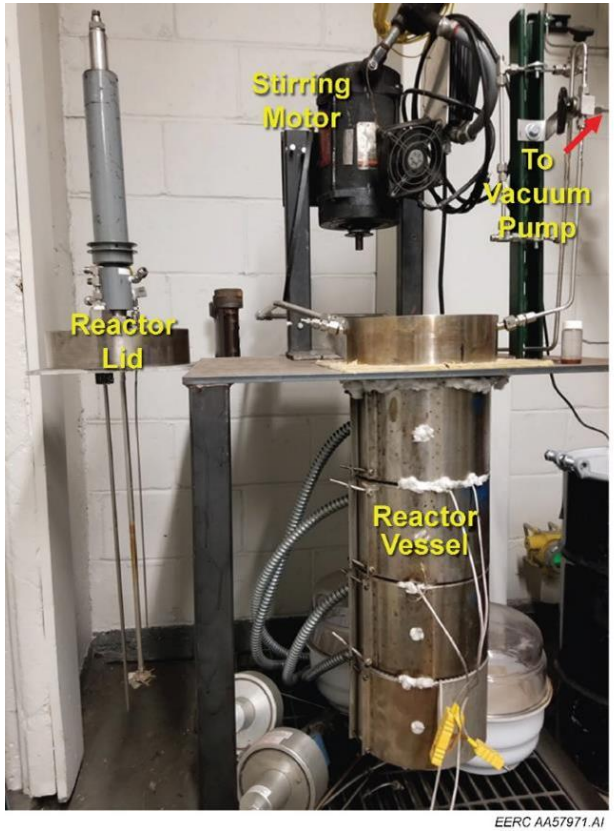
- The project is due to be completed in the next 6 months on April 30, 2023. The key accomplishments to date include:
  - Acquisition, installation, training, and successful operation of the graphitization furnace
  - Tunable optical properties of GQDs made from all four coal ranks
  - Croissant graphite made by the UCP process
  - Coal-derived GO and rGO
  - Preliminary economic analysis and analysis of product target markets
- Results of preliminary economic analysis and analysis of product target markets are discussed.

Critical UCP Technology Equipment Needs – Graphitization

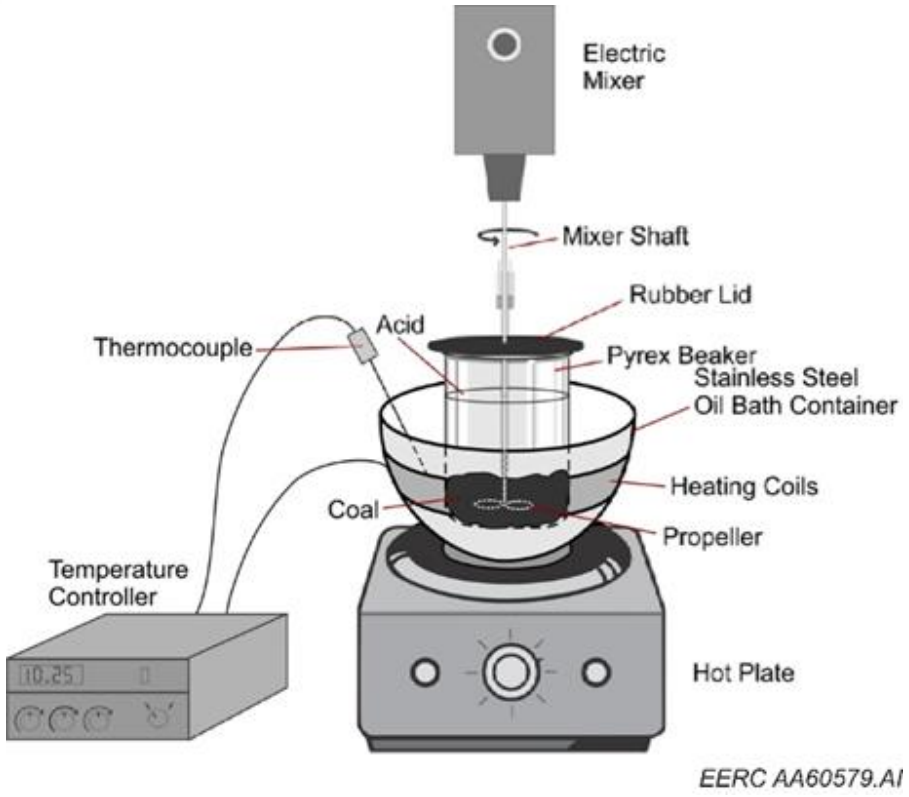
Critical Equipment Needs – HRR and Carbonization

Carbonization System

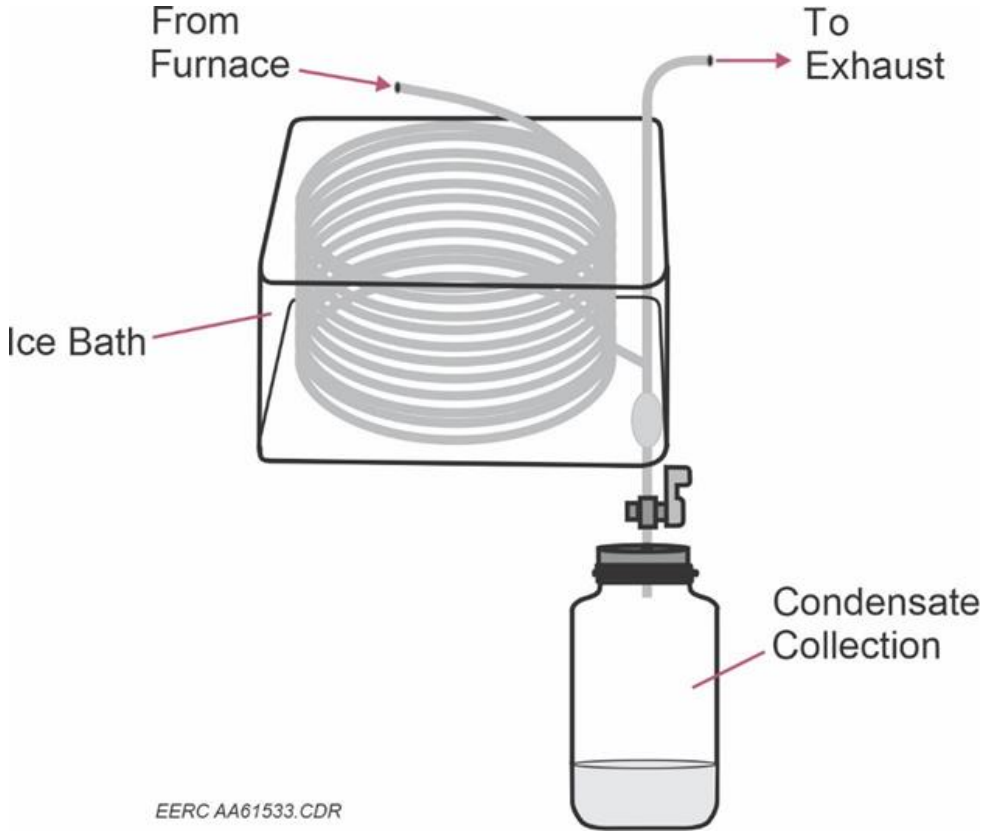
HRR Reactor



Demineralization and Condensate Trap Systems

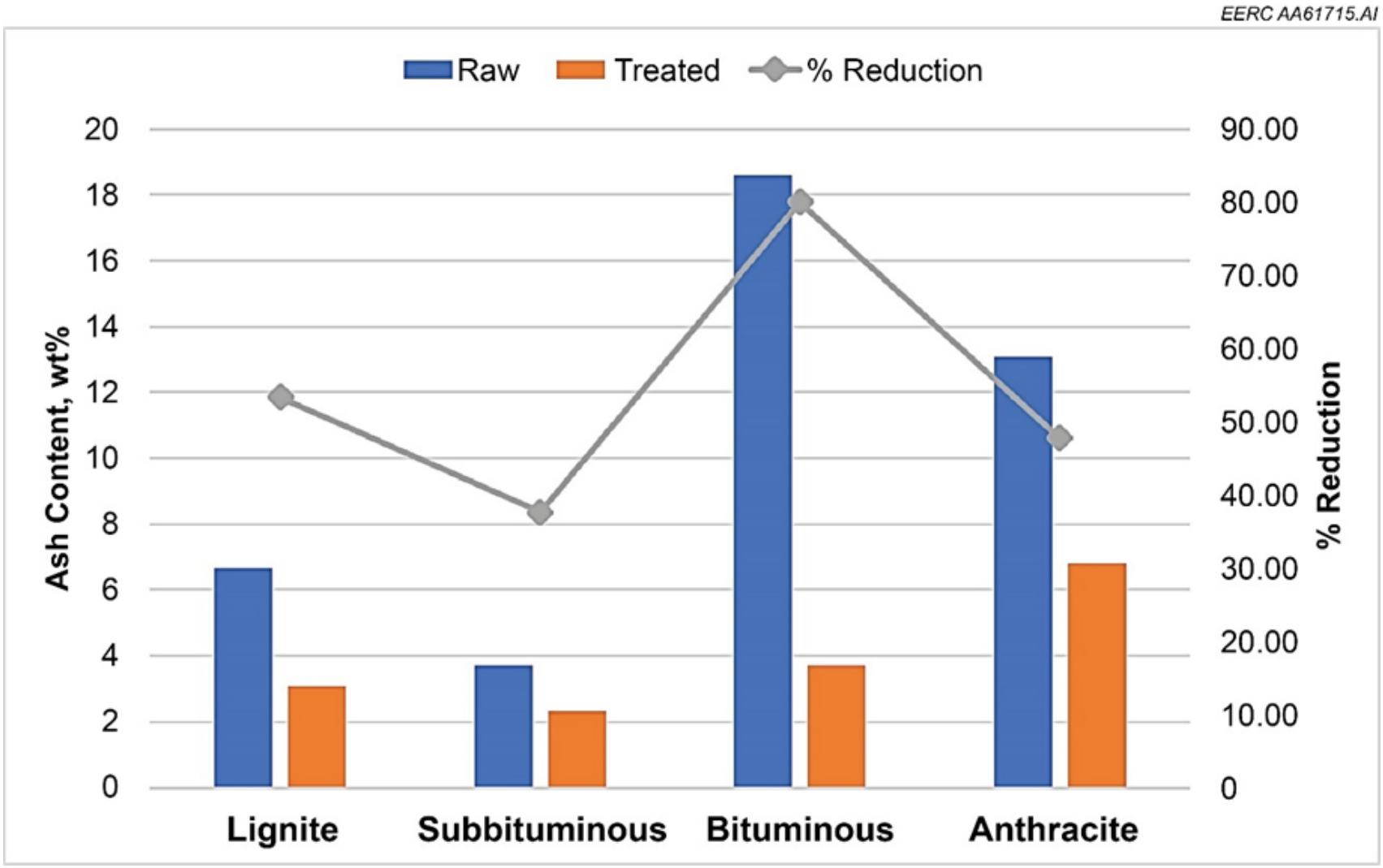


Demineralization System

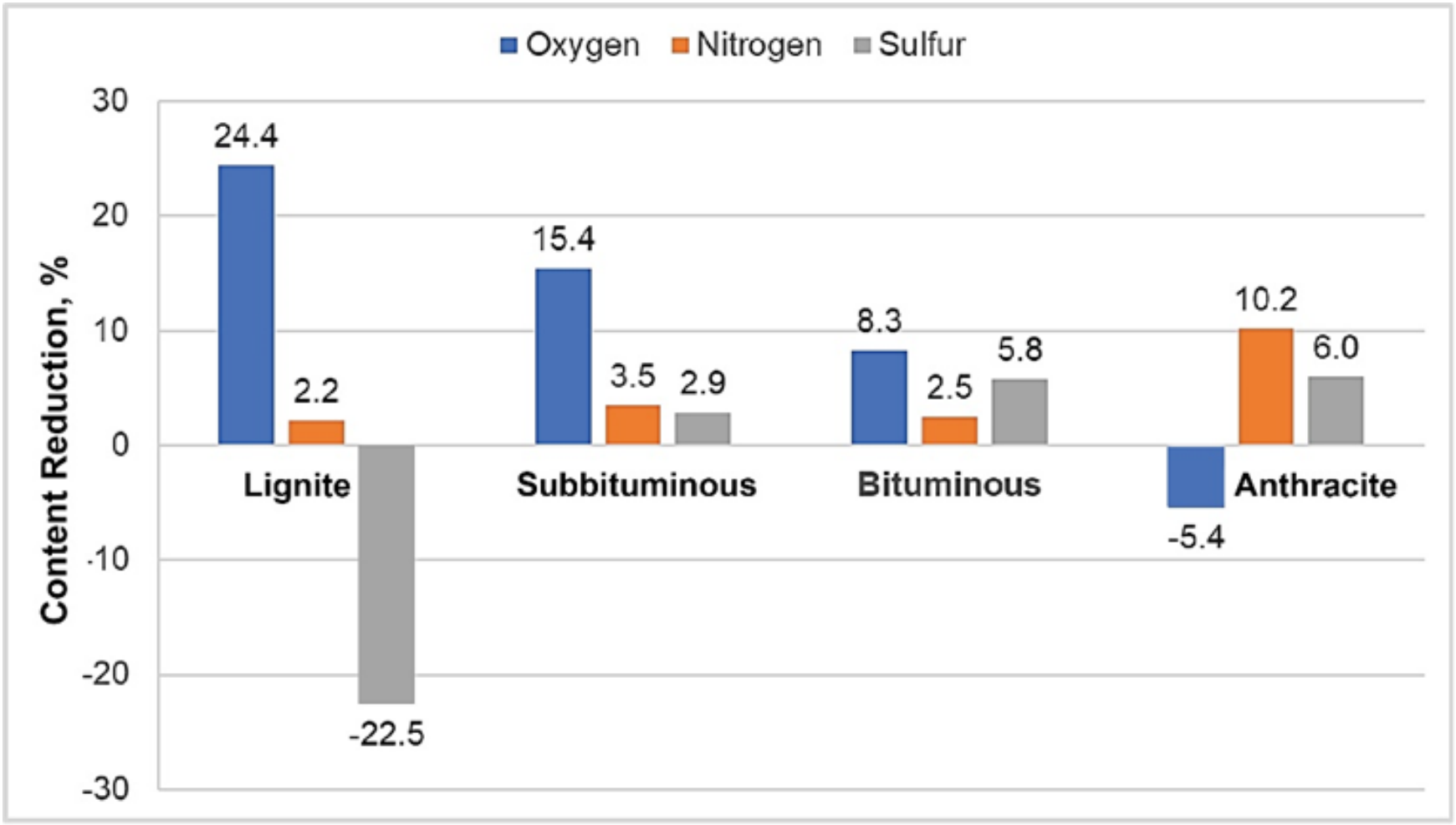


Condensate Trap

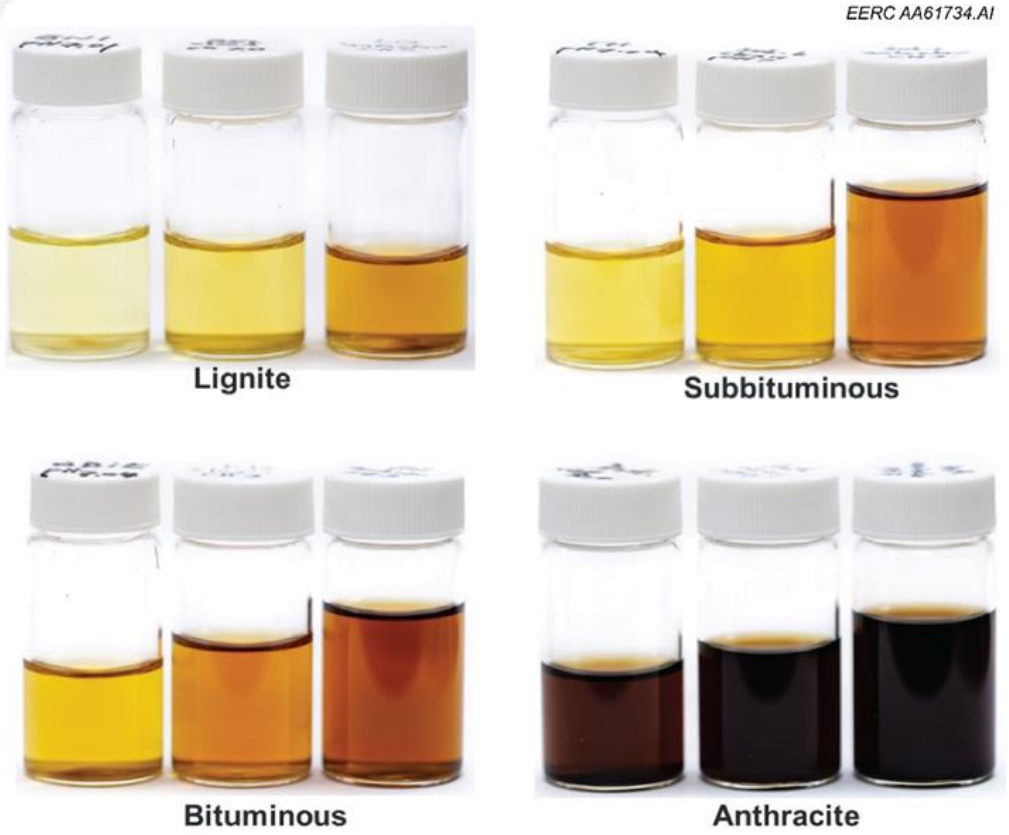
Ash Content Reductions

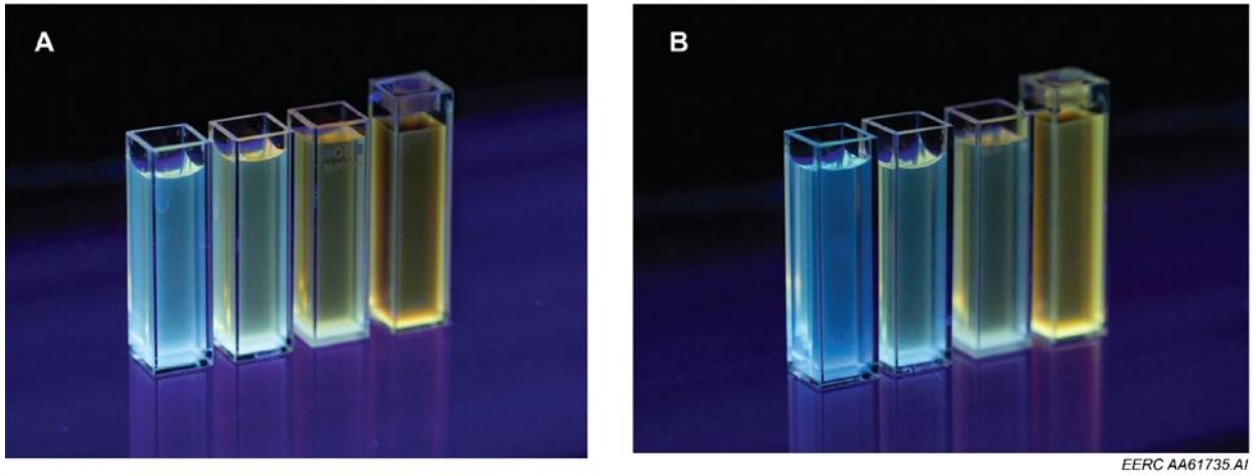


Heteroatom Reductions



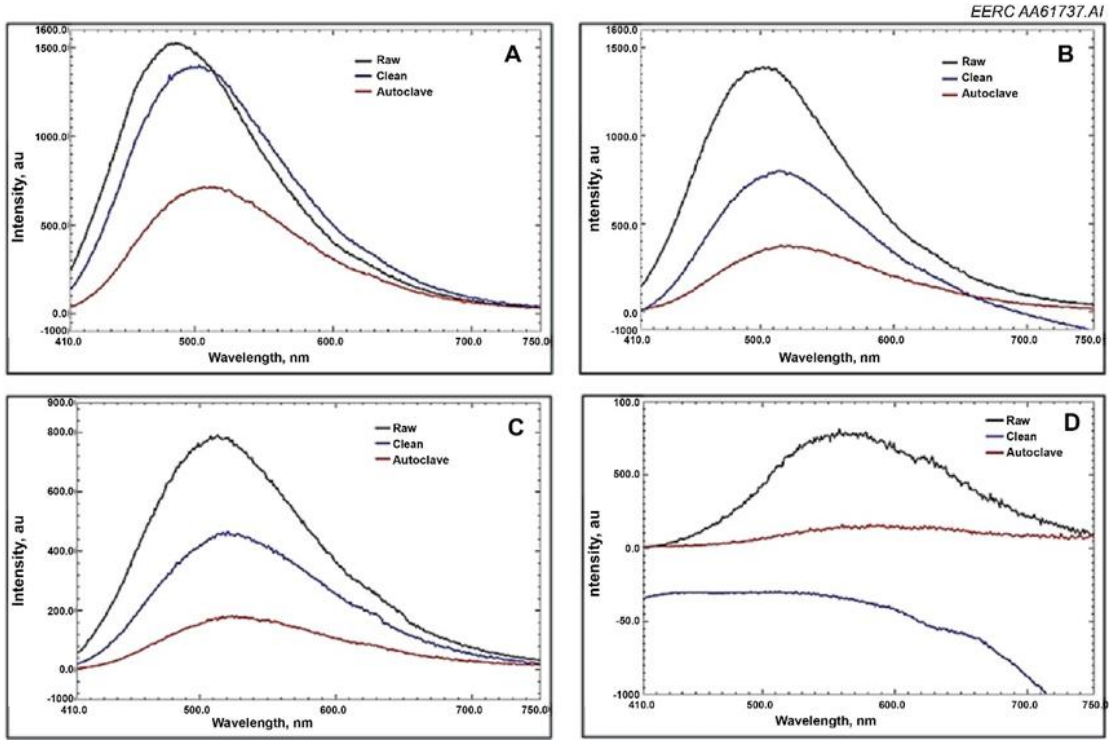
Coal-Derived Graphene Quantum Dots



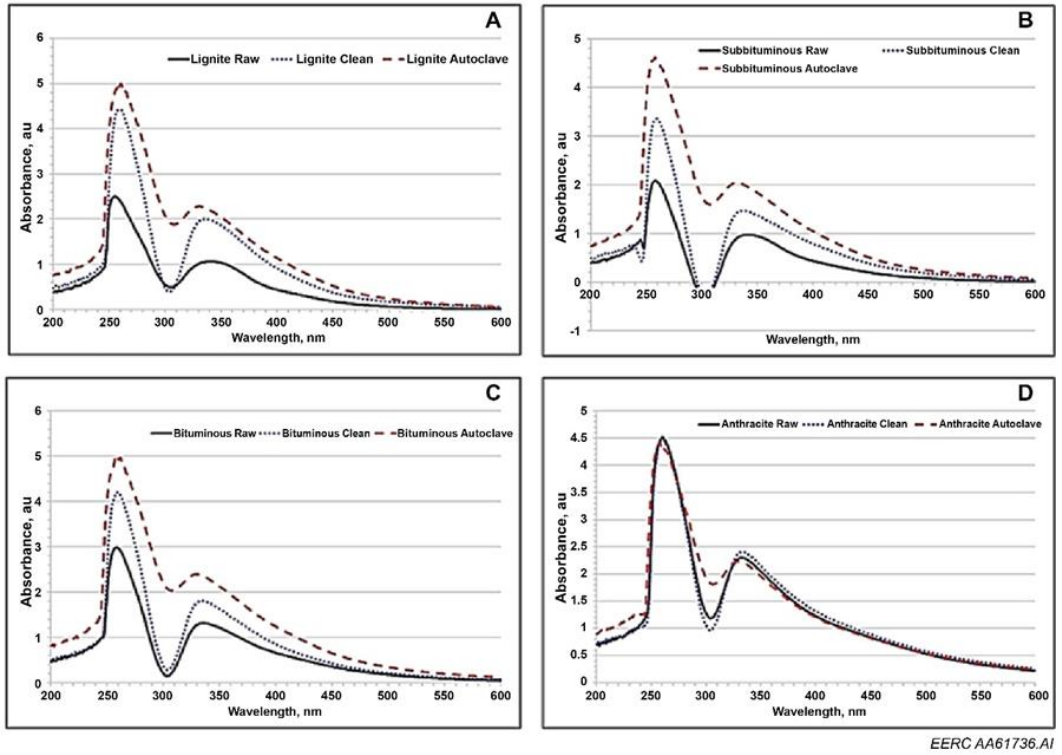


UV-F and UV-vis Analyses

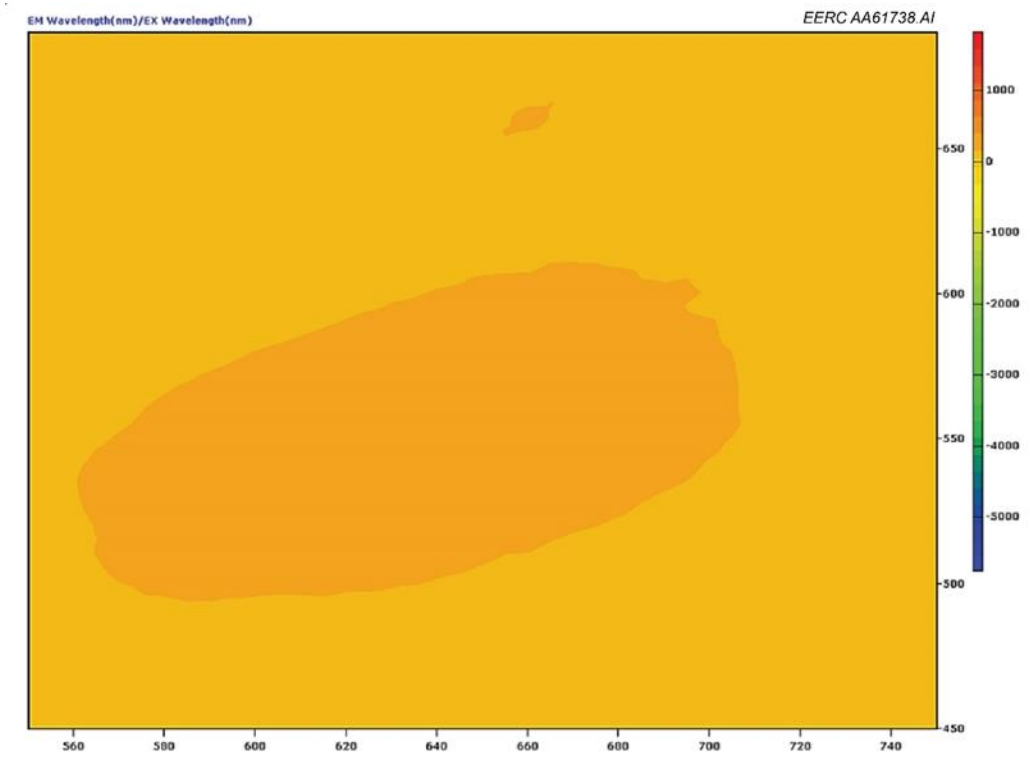
UV-Fluorescence Spectroscopy

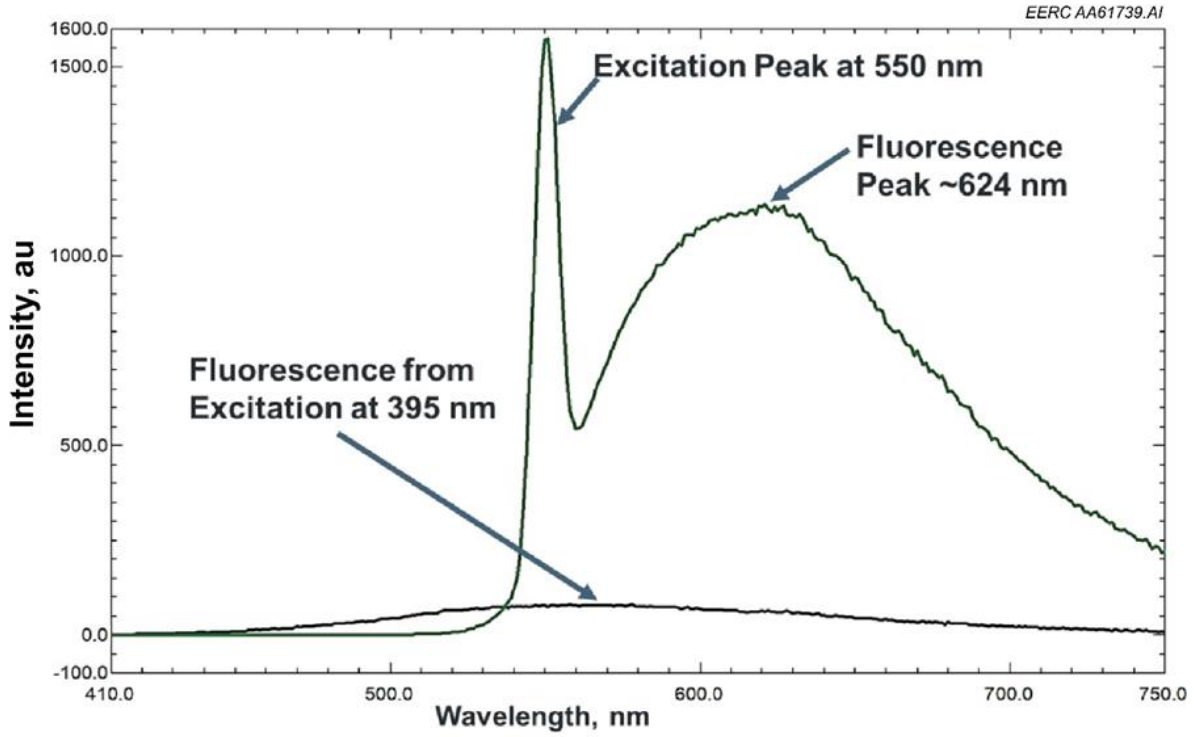


UV-vis Spectroscopy

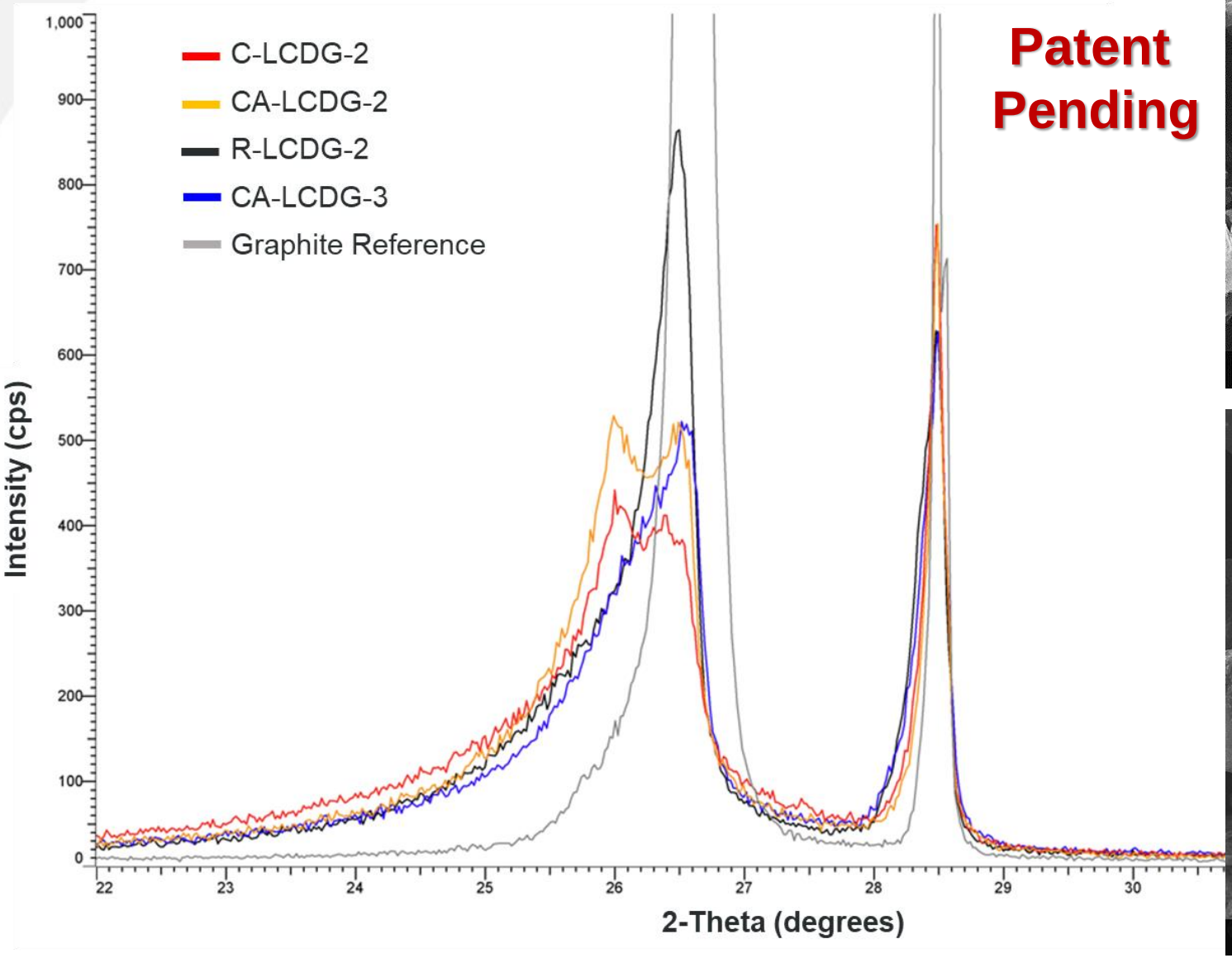


Anthracite-Derived GQDs Excited by Visible Light

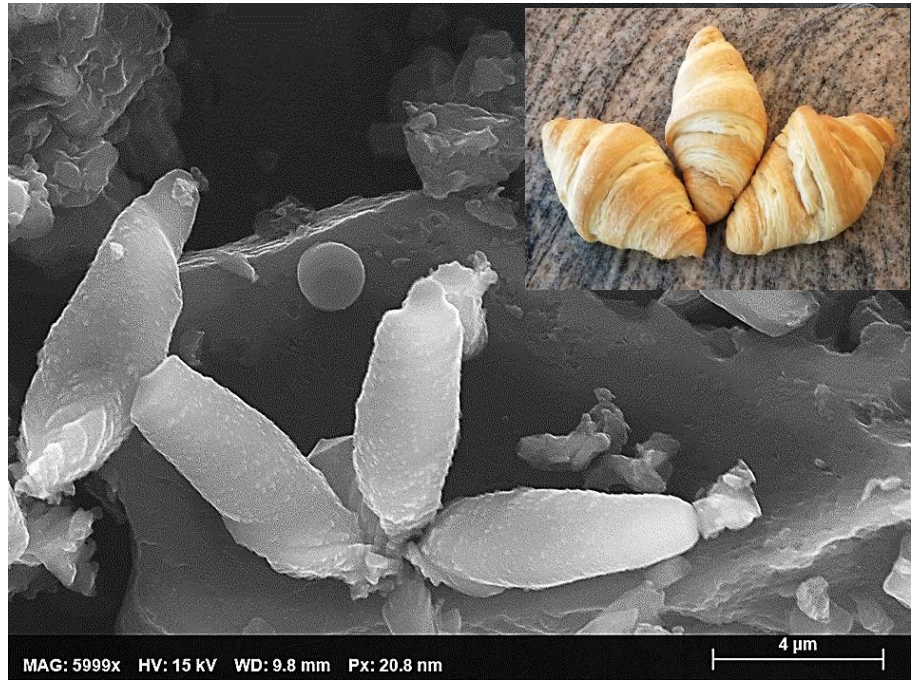


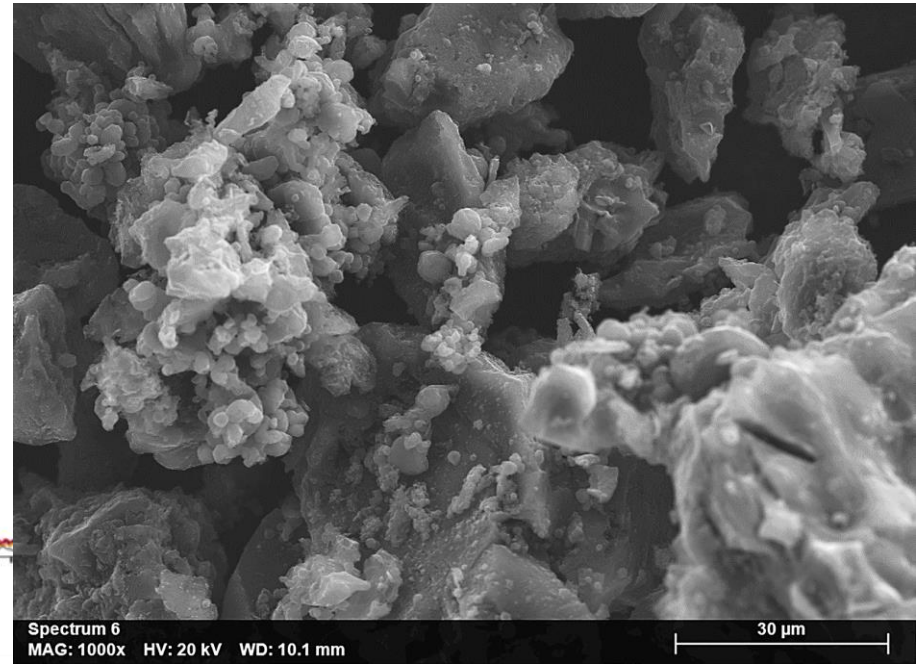


Coal-Derived “Croissant” Graphite

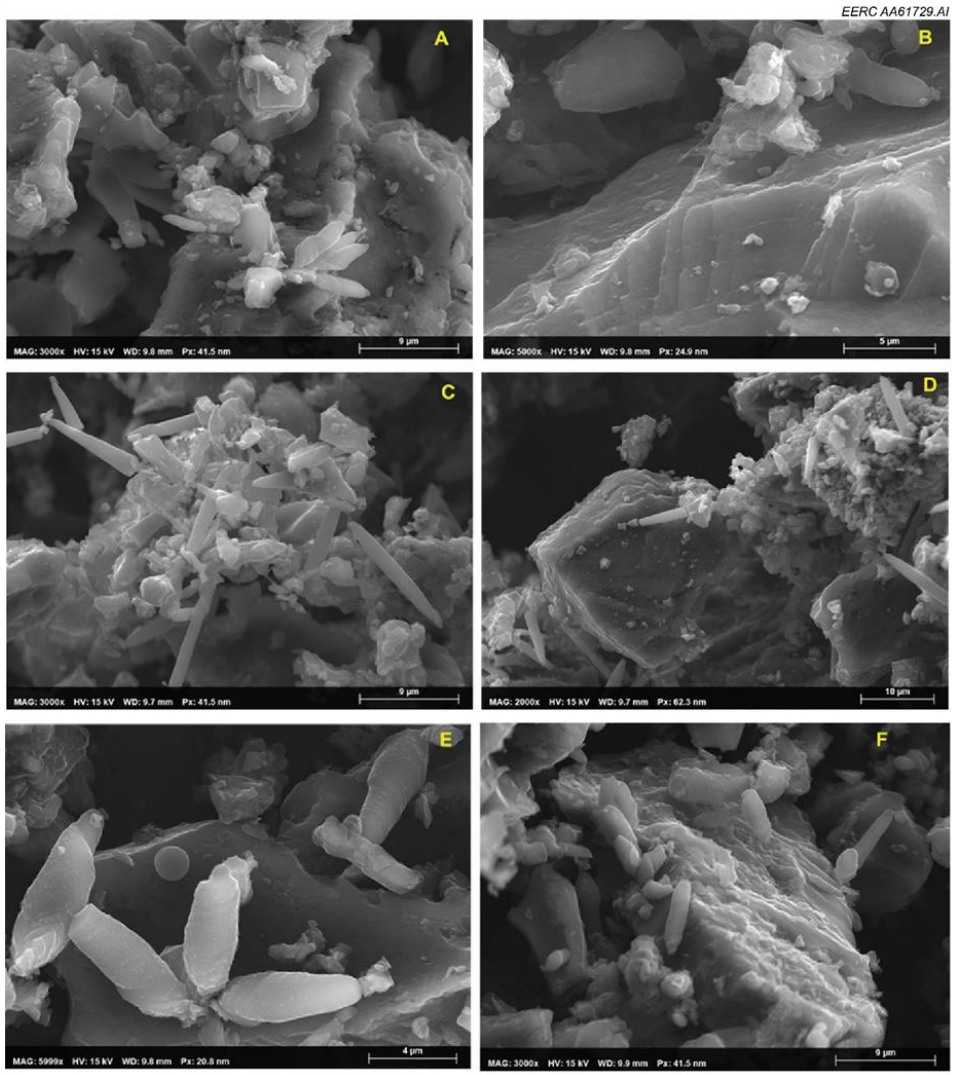


Patent Pending

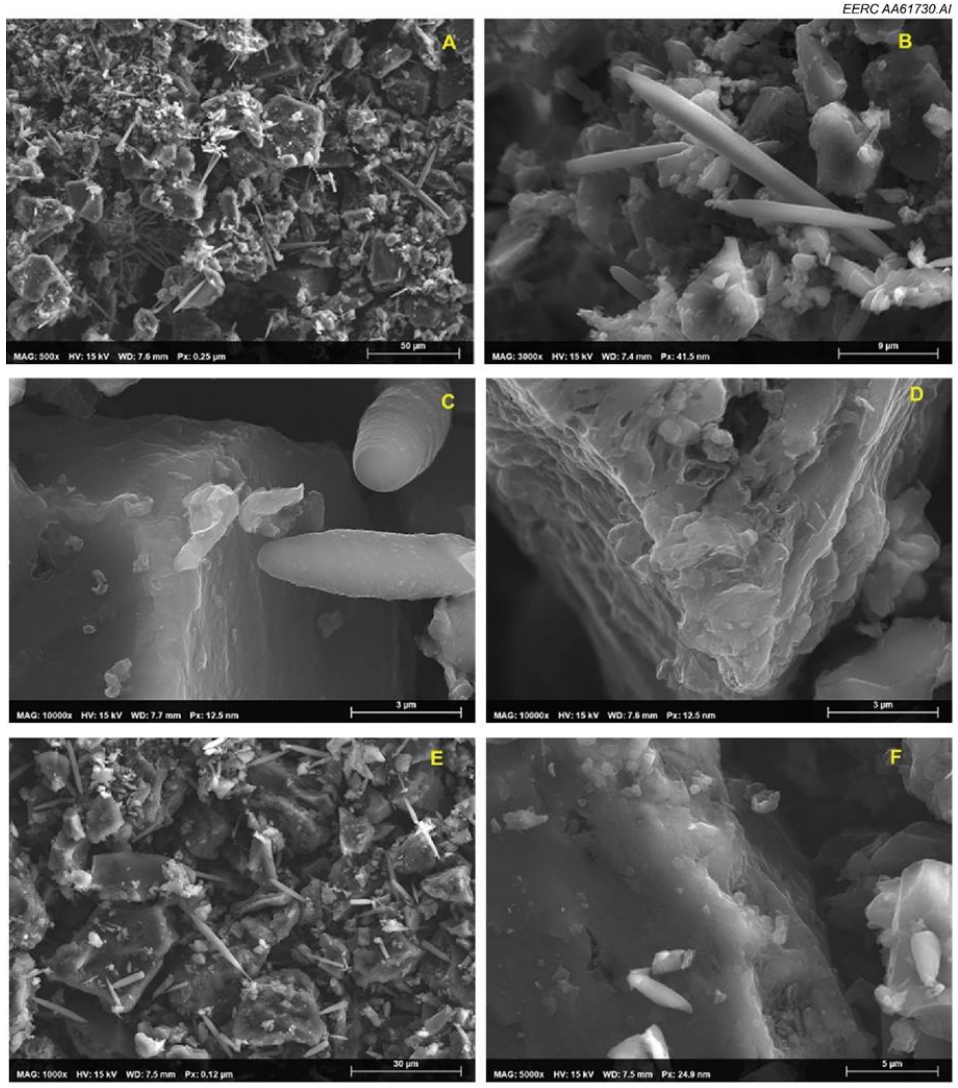




Coal-Derived “Croissant” Graphite Cont.

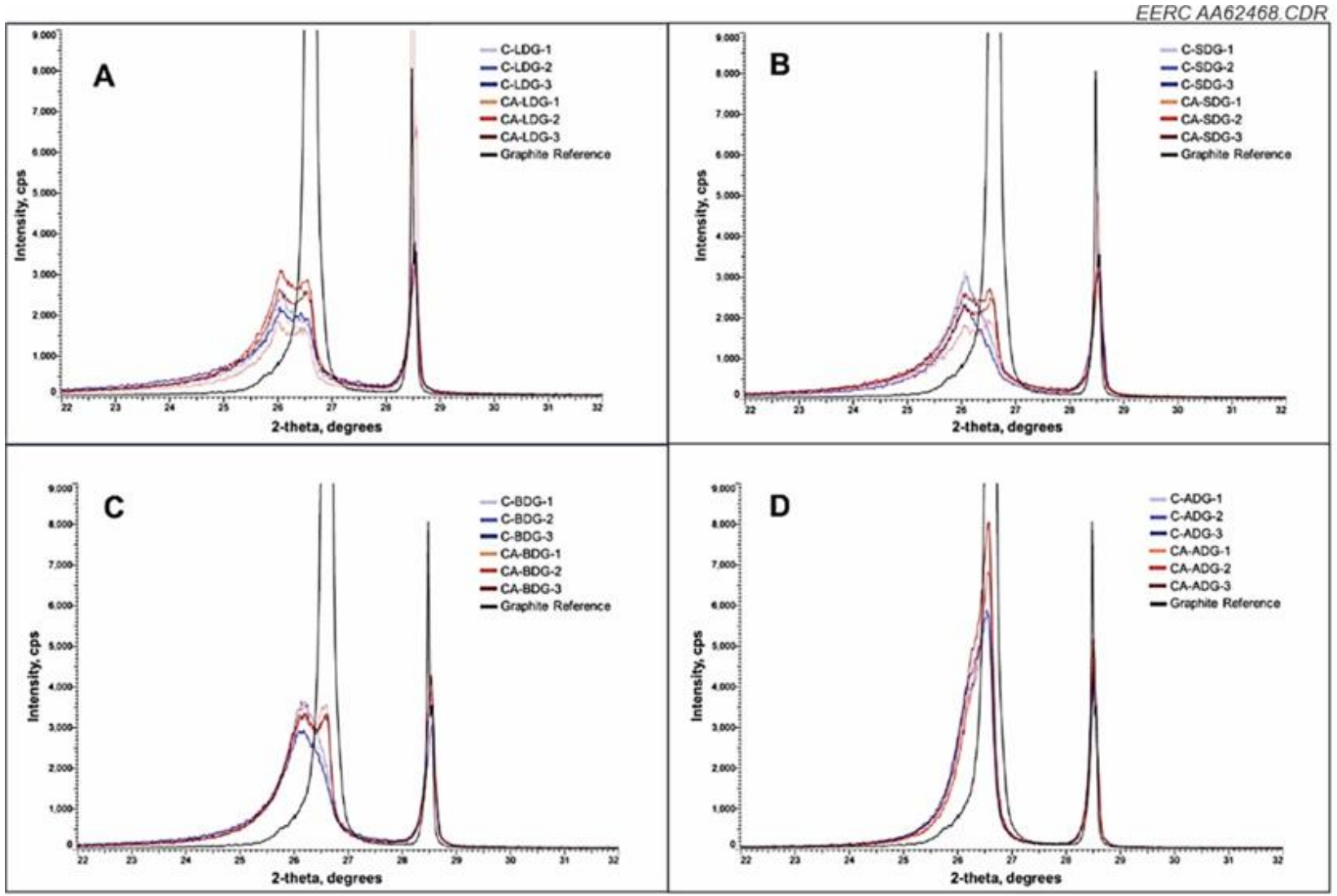


Lignite



Subbituminous

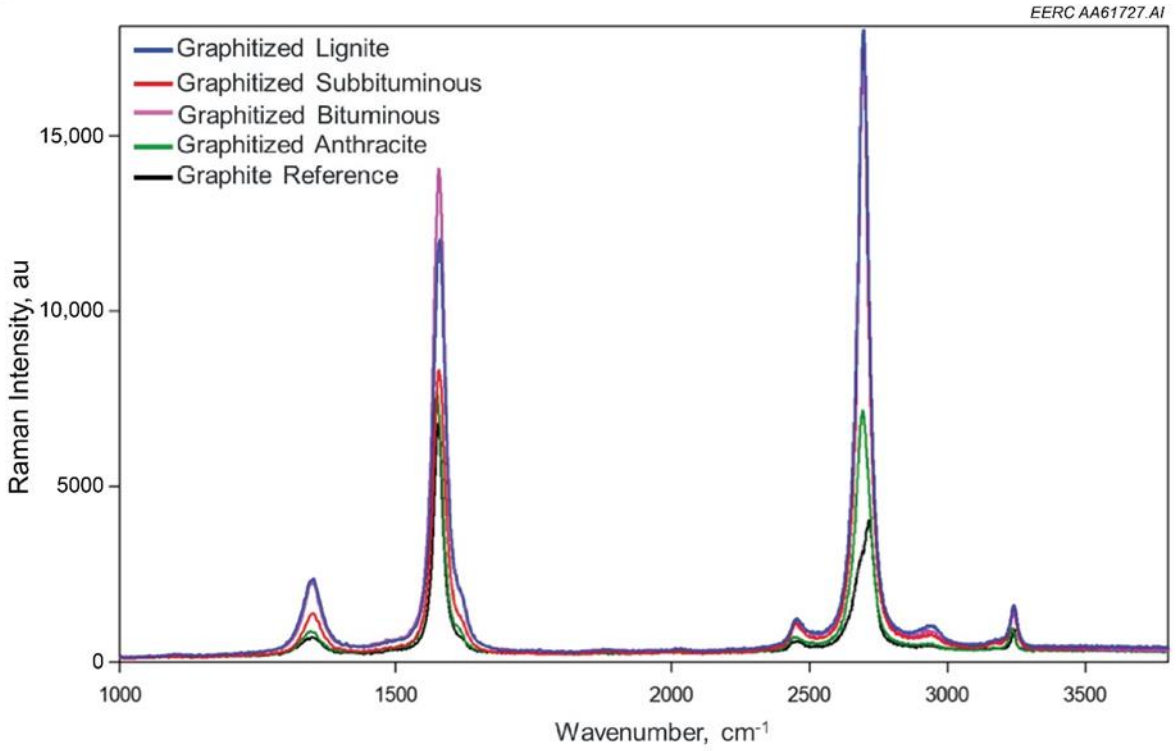
XRD Analysis of Coal-Derived Graphite (CDG)



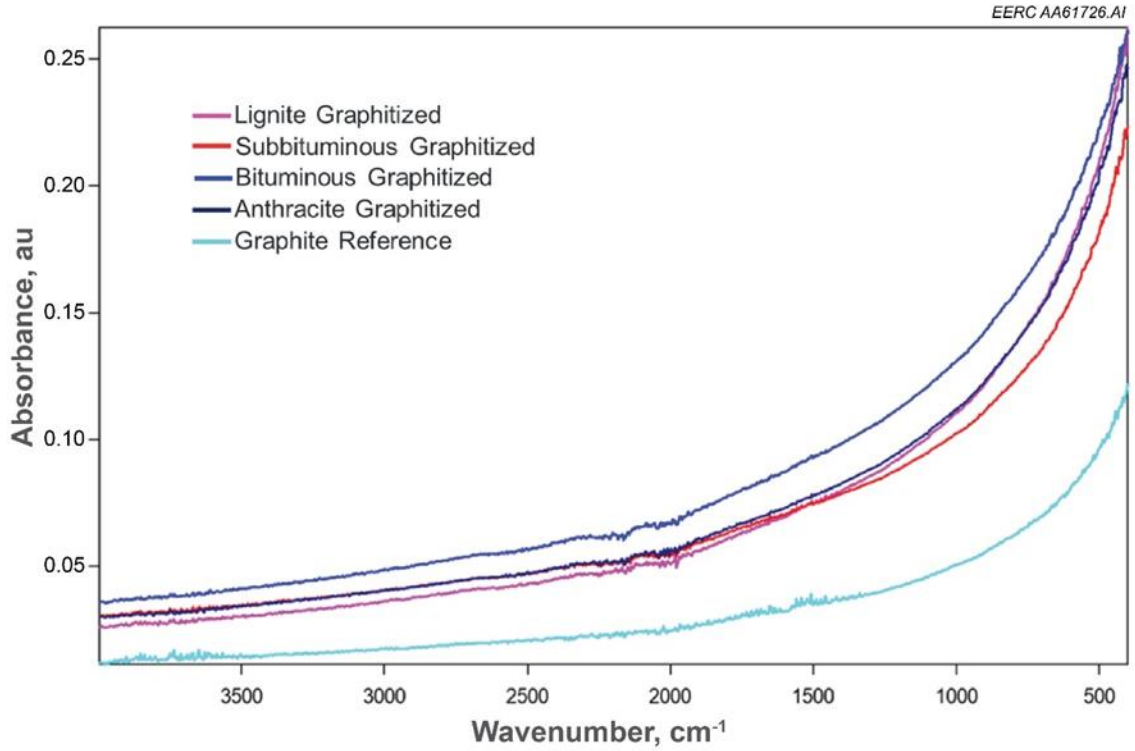
A – Lignite
B – Subbituminous
C – Bituminous
D – Anthracite

Raman and FTIR Analyses of CDG

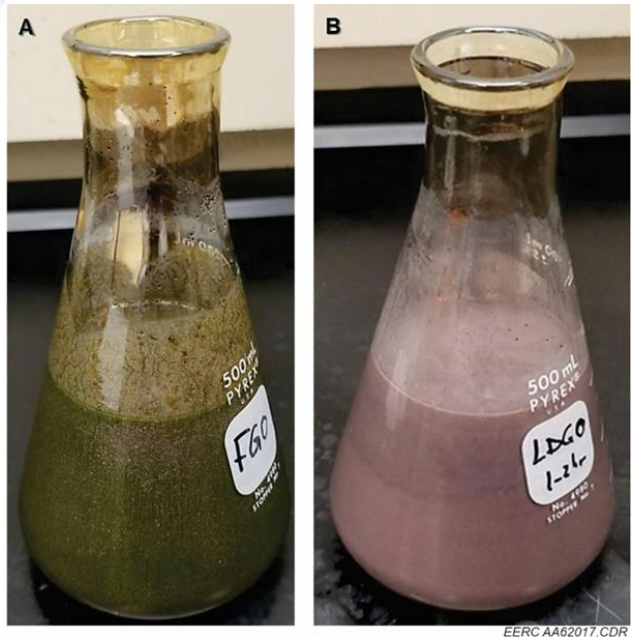
Raman



FTIR



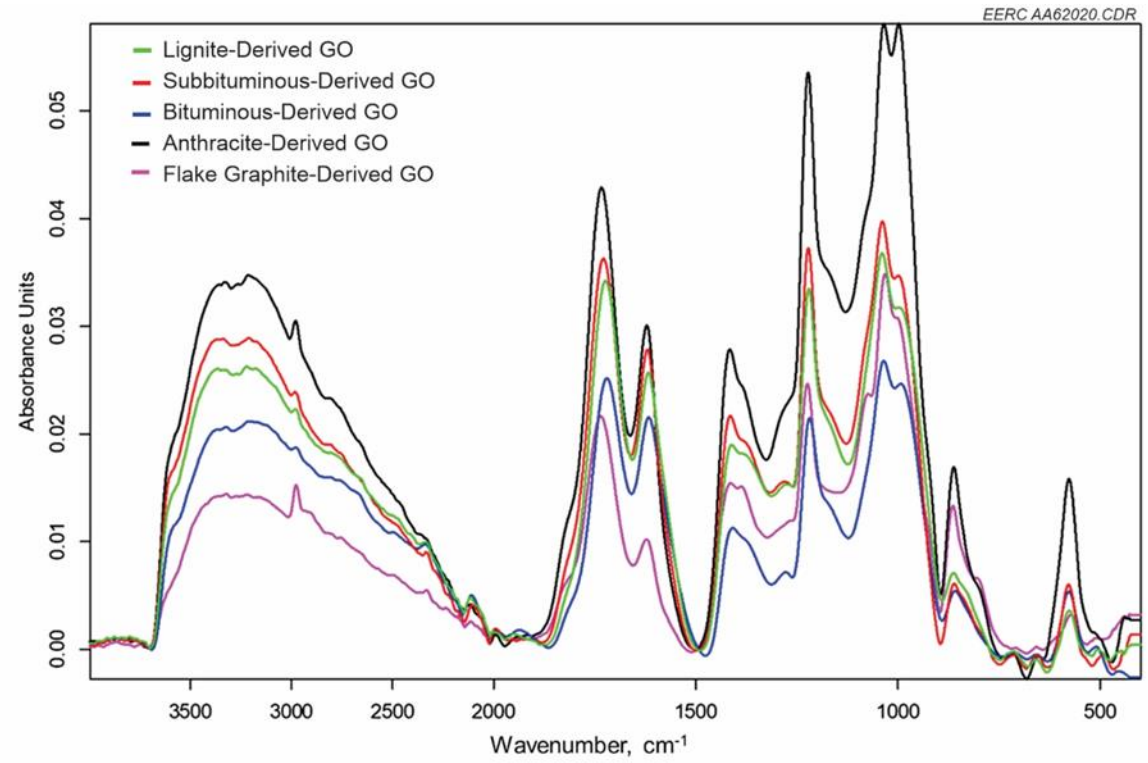
Coal-Derived Graphene Oxide



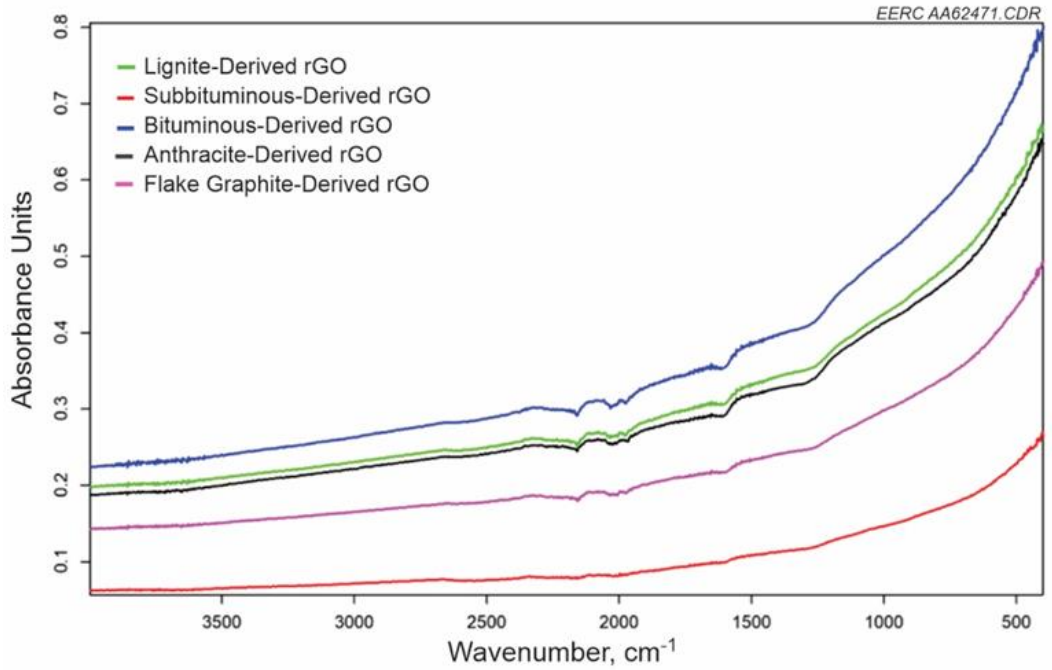
Sample	Starting Mass (g)	Recovered Mass (g)
FGO	3.0	5.678
ADGO	3.0	4.684
BDGO	3.0	3.636
SDGO	3.0	2.566
LDGO	3.0	2.539

FTIR Analysis of GO and rGO

GO



rGO



Analysis of Products Target Markets

- **Graphite**
  - Batteries for Electric Vehicles
  - Industrial electrodes
  - Nuclear Energy Generation

- **Graphene (GO, rGO, etc)**
  - Clean energy technologies (wind turbines, photovoltaics, fuel cells, etc)
  - Lithium batteries (Li-metal, Li-S, etc)
  - Composites
  - Conductive inks
  - Sensors (e.g. biosensors, electrochemical sensors, gas, etc)
  - Coatings and sealants
  - 3D printing/Additive manufacturing

- **Graphene Quantum Dots**
  - Optical display applications
  - Bioimaging
  - Light-emitting diodes
  - Flash memories

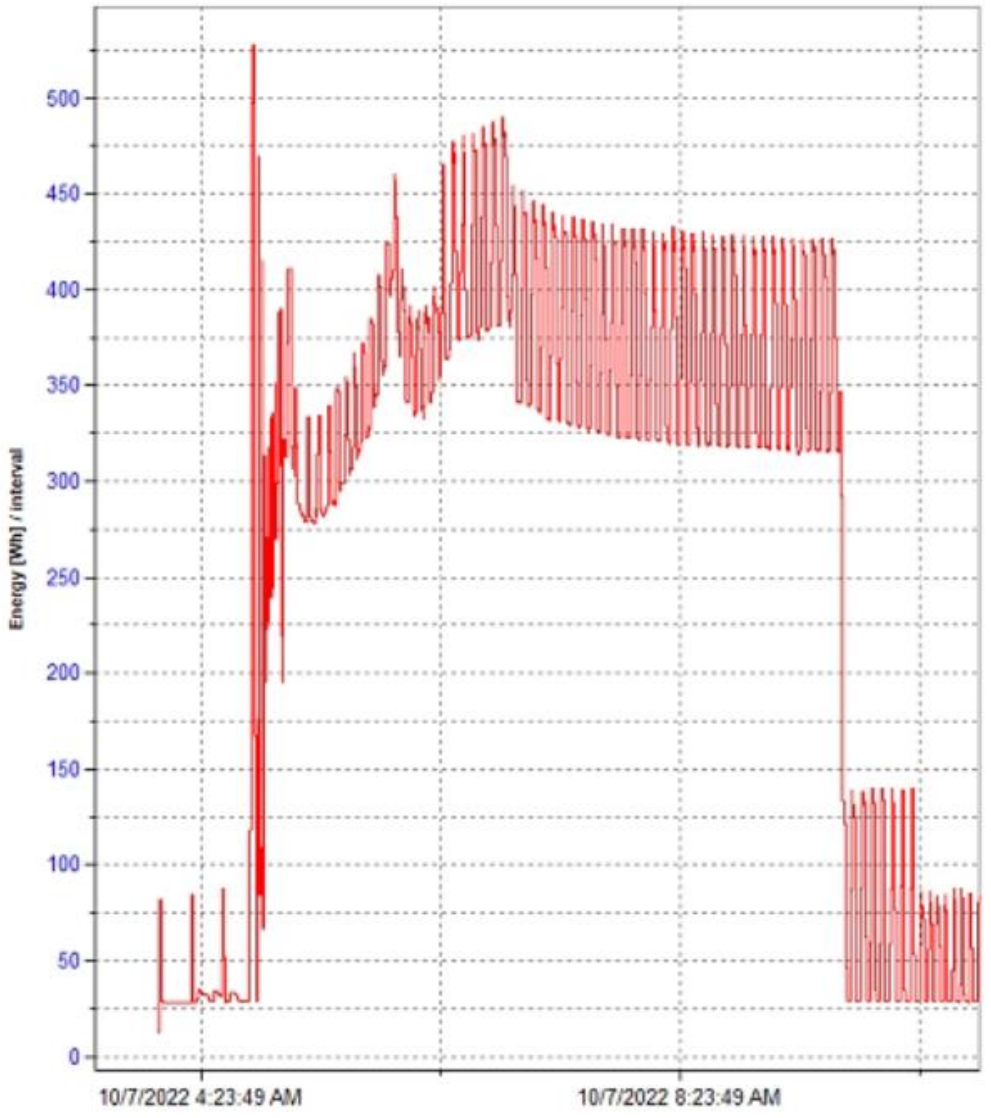
Preliminary Economic Feasibility Analysis

Developing spreadsheet model from first principles for batch processing

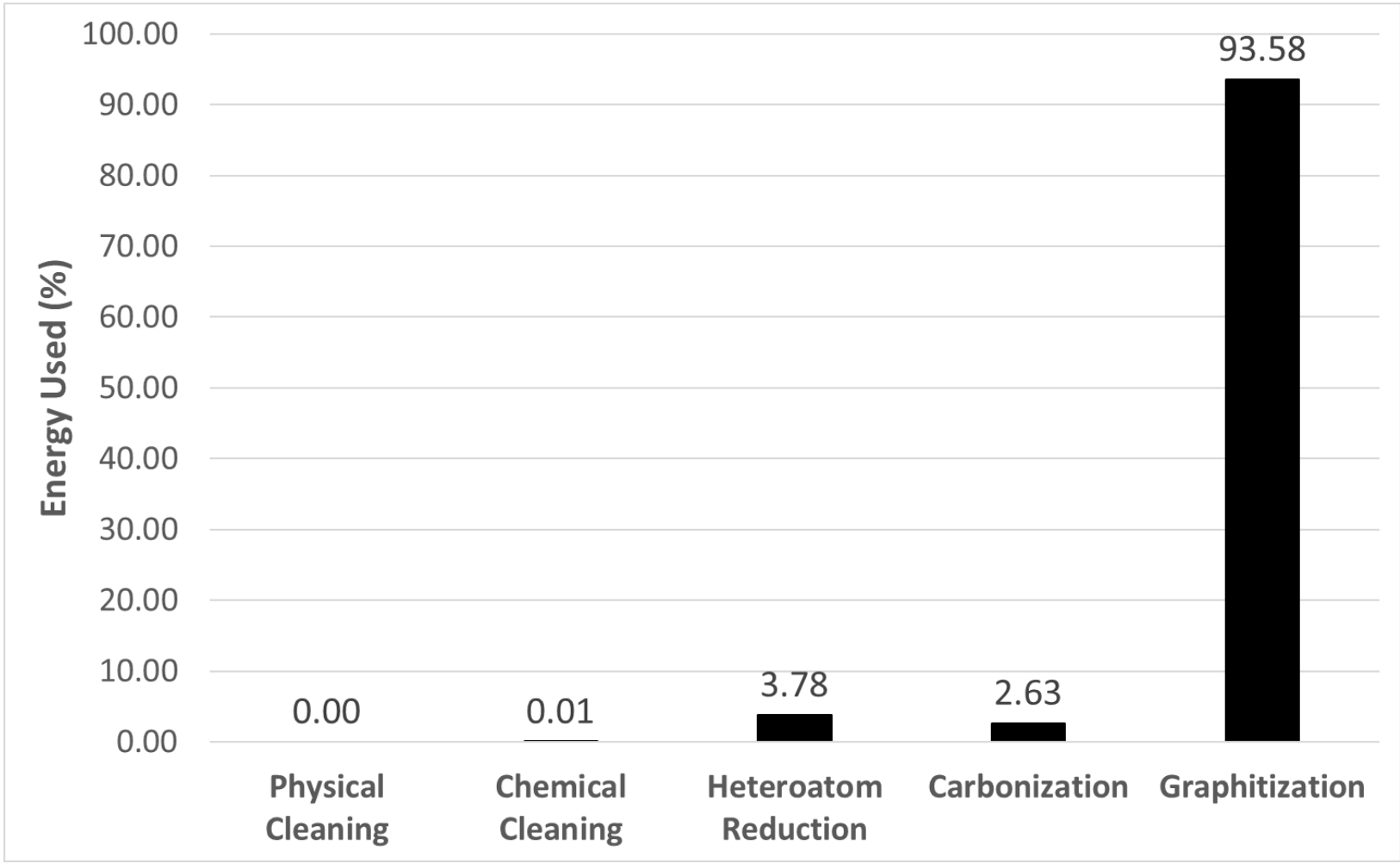
- **Key Parameters:**
  - Feedstock batch size
  - Capital cost
  - Energy cost
  - Operational cost
  - Labor cost
  - Raw material cost

- **Key Assumptions:**
  - 1 kg batch of coal
  - 50 batches per year
  - 75% energy efficient
  - 50% labor efficient

Measure Energy Usage by Power Logger



Energy Use Breakdown



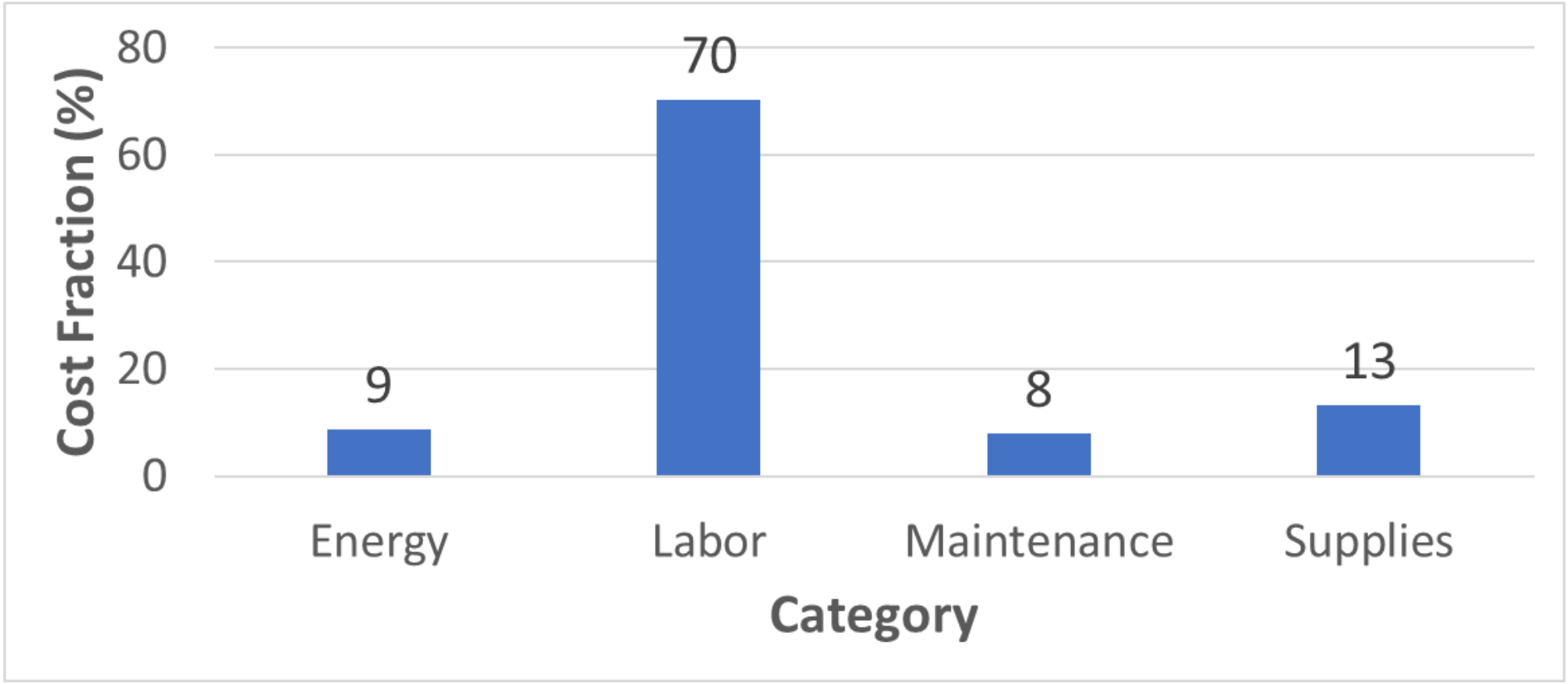
Approximate Labor Per Process Per Person

Process	Time (hrs)
Physical Cleaning	0.10
Chemical Cleaning	0.13
Heteroatom Reduction	1.50
Carbonization	6.17
Graphitization	2.93

Cost Analysis

Coal Type	Raw Material ($)	Capital ($)	Operational ($)	Total Costs ($)
Lignite	1.11	261,855	38,018	299,874
Subbituminous	0.78	261,855	38,018	299,873
Bituminous	3.40	261,855	38,018	299,876
Anthracite	5.90	261,855	38,018	299,878

Operational Cost Breakdown



Graphite Yields By Coal Type

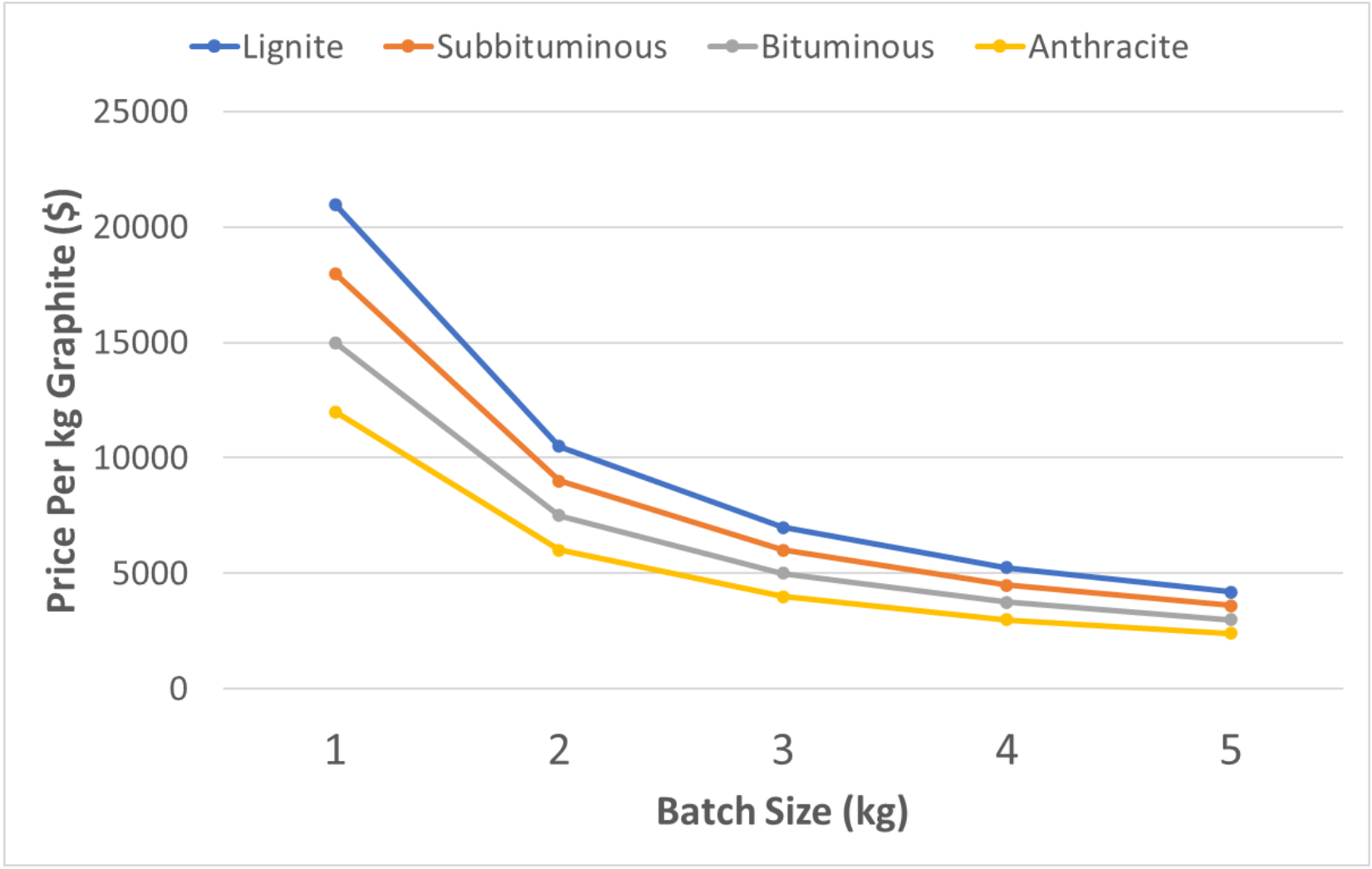
Coal Type	Graphite Yields (%)
Lignite	30
Subbituminous	30
Bituminous	40
Anthracite	50

Estimated Selling Price for Graphite

Coal Type	Cost Per Kg ($)
Lignite	21,000
Subbituminous	18,000
Bituminous	15,000
Anthracite	12,000

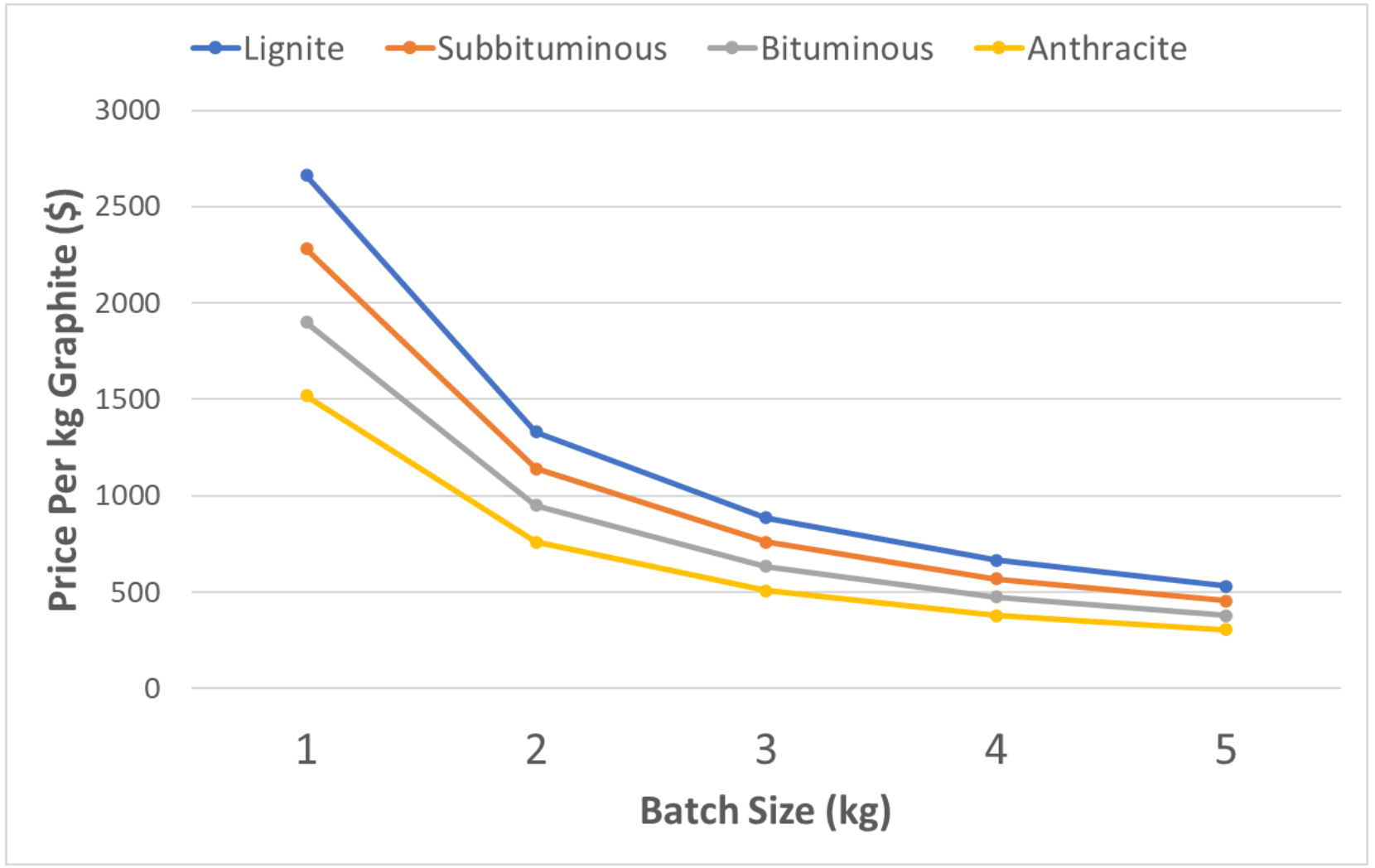
This is shocking but makes sense based on the scale and upfront capital-intensive nature of the process.

Sensitivity Analysis By Batch Size With Capital Cost



Price goes down roughly exponentially with batch size

Sensitivity Analysis By Batch Size Without Capital Cost



2nd and future years assuming capital cost are paid upfront in 1st year

Technology Development and Commercialization Plans

- **Current Plans**
  - The project is coming to an end in the next 6 months but has validated a laboratory-scale process that is being optimized (DE-FE0032139) to make graphite for LIB and other applications.
  - Finalize the economic analysis model to refine the estimated selling price for graphite, GO, rGO, and GQDs.
- **Next Steps**
  - Bench-Scale system for 5–10 lbs feedstock per batch
  - Scale-up process parameters optimization
  - Process control, Equipment, and Data Acquisition & Management
- **Scalability/Commercialization Potential**
  - Simple process, easily scalable, **upfront capital intensive**

Community Outreach and Workforce Development Efforts

Workforce Development

- Limited to internal staff cross-training because of covid-19 concerns

Community Outreach

- Public seminar at UND

Summary and Conclusions

- High-value carbon products such as graphene oxide, reduced graphene oxide, graphene quantum dots, and graphite can be made from coals of all ranks using the UCP process.
- Preprocessing conditions are key to achieve high quality, particularly croissant graphite.
- Coal pretreatment processes can be used to tune the optical properties of GQDs
- Additional process optimization and post-graphitization processing are needed to further improve graphite performance for LIB applications.
- **The UCP technology is an emerging environmentally sustainable process for efficient conversion of coal or coal wastes to high-value carbon products.**

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THANK YOU!

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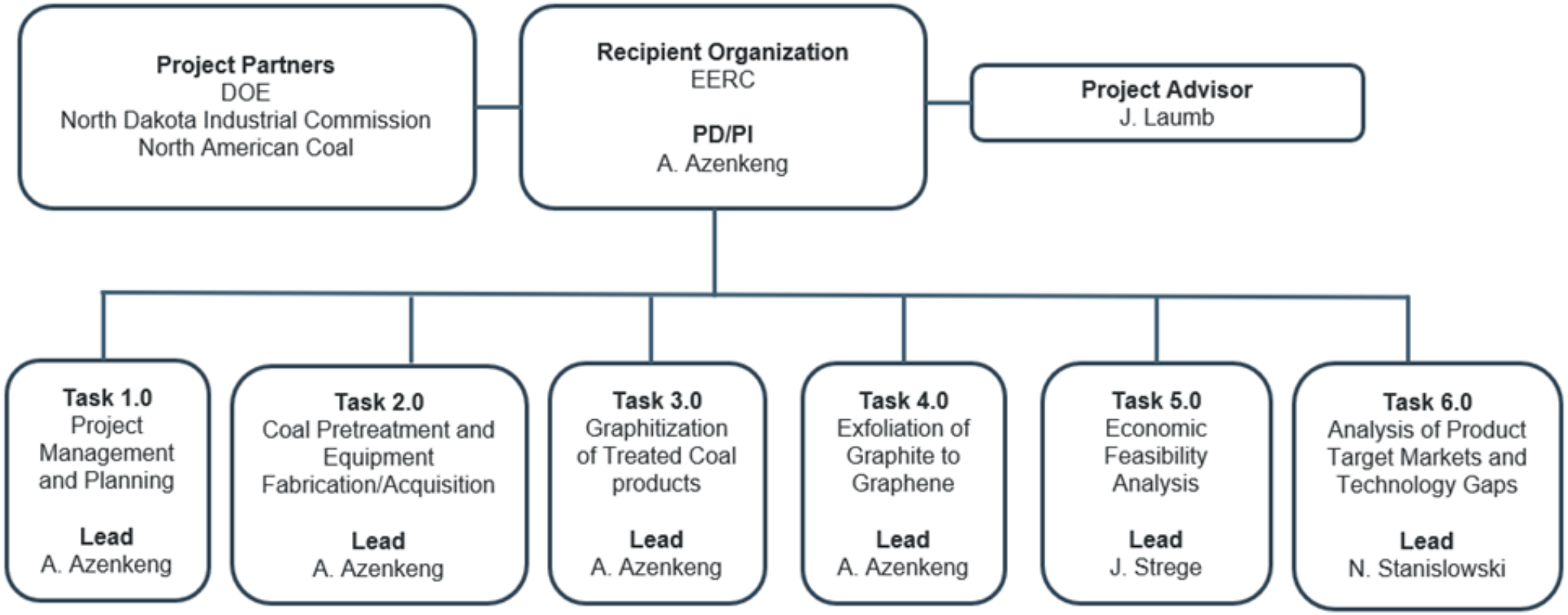
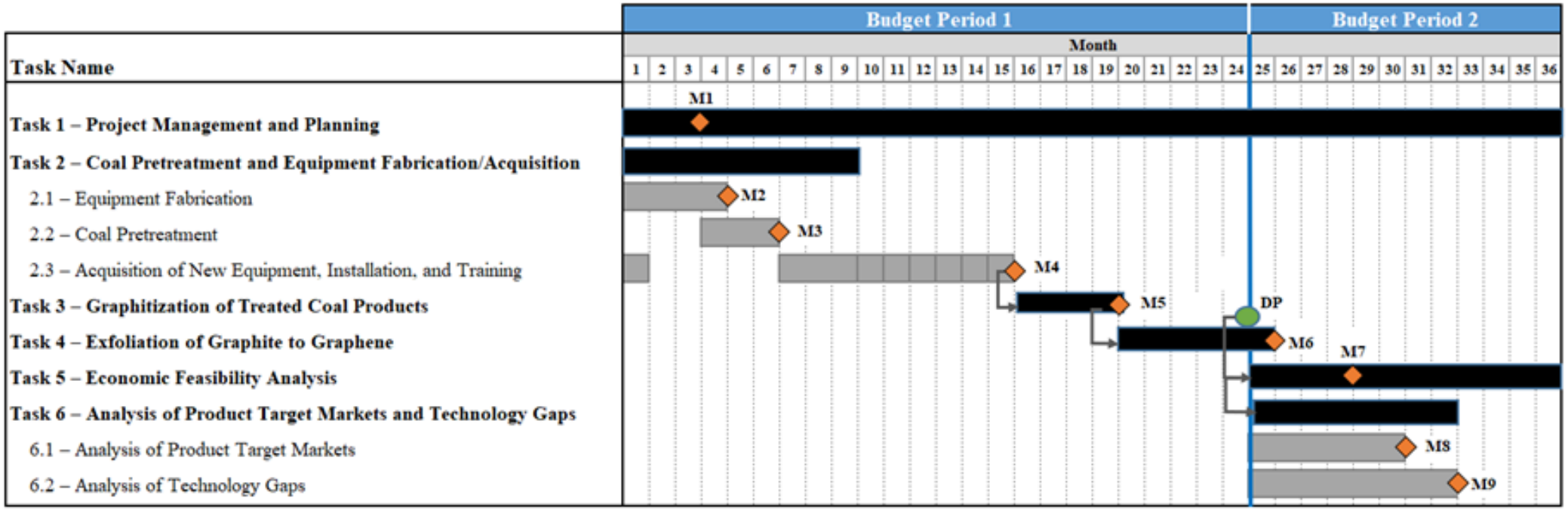
Organization Chart



Gantt Chart



Summary Task — Critical Path

Activity Bar — Decision Point (DP)

Milestone (M)

Key for Milestones (M)

M1 – Project Kickoff Meeting

M2 – Completion of DR, FBR, and CT Fabrication

M3 – Completion of Coal Pretreatment

M4 – Completion of LHTG Furnace Installation and Training

M5 – Completion of Coal Graphitization

M6 – Completion of Graphene Products

M7 – Initial Economic Analysis Results Available

M8 – Completion of Analysis of Product Target Markets

M9 – Completion of Analysis of Technologies Gaps

LR 6/11/20