Coal and Petroleum “Co-Coke”:
A New Feedstock for Graphite Production

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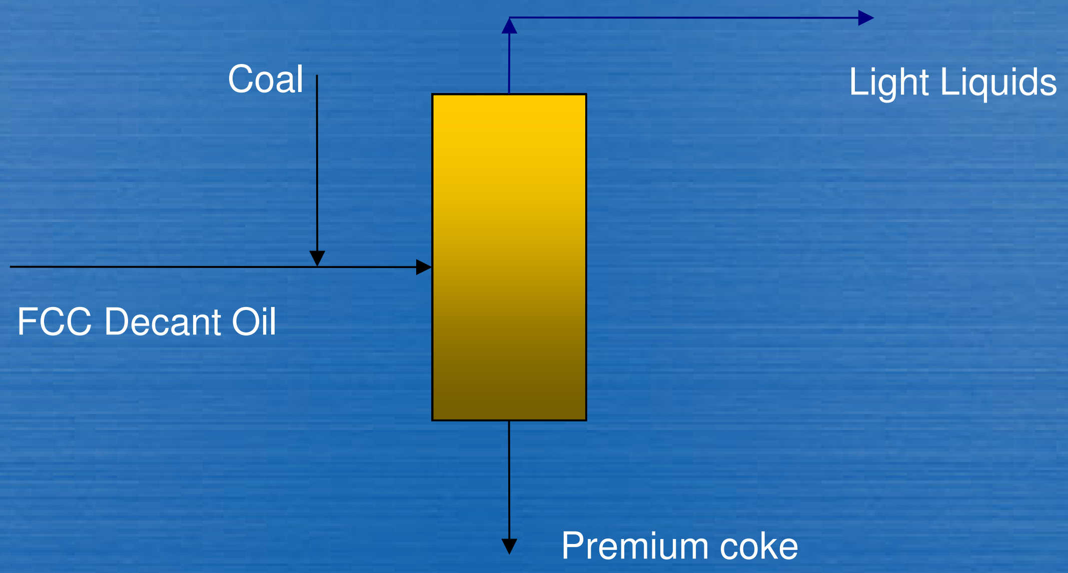
The Co-Coking Concept



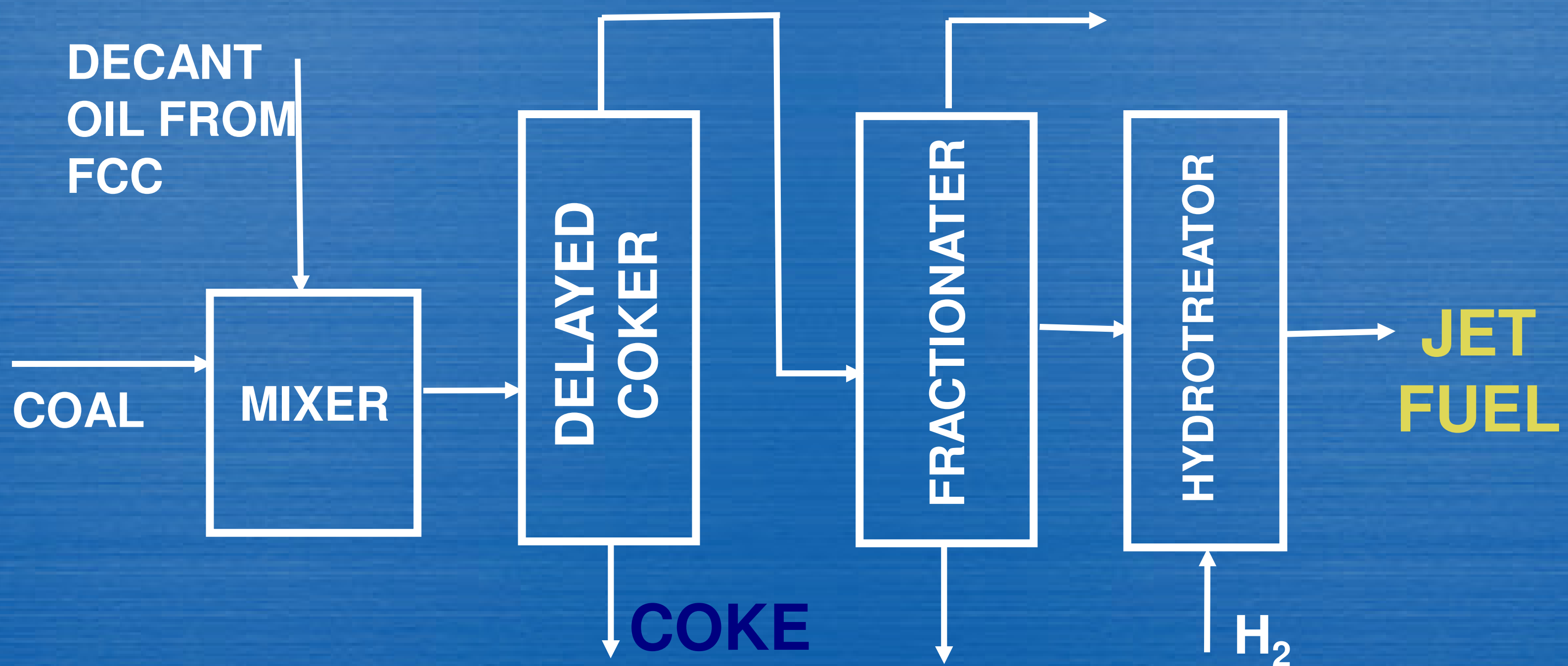
Background on Co-Coking

- One of two coal-to-liquids processes being developed at Penn State.
- Objective is to find ways to add coal to refinery unit operations.
- Production of a premium-quality coke by-product could have significant economic impact.

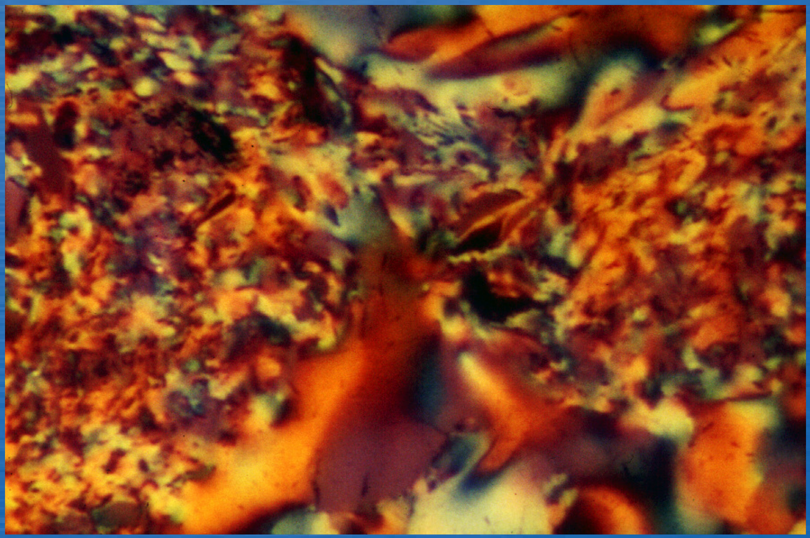
The Co-Coking Process Concept

- Co-coking is the simultaneous coking of coal with a petroleum feedstock (e.g., decant oil or resids).
- The process objectives are to “skim” coal-derived structures into the liquids, giving in situ stabilization to the jet fuel, and to produce good-quality coke.
- The process involves adding pulverized coal to the feed to a delayed coker.
- Original idea: E. T. “Skip” Robinson, BP Oil, 1996

Co-coking Block Flow Diagram



Coal-Petroleum Mixing in Co-Coking

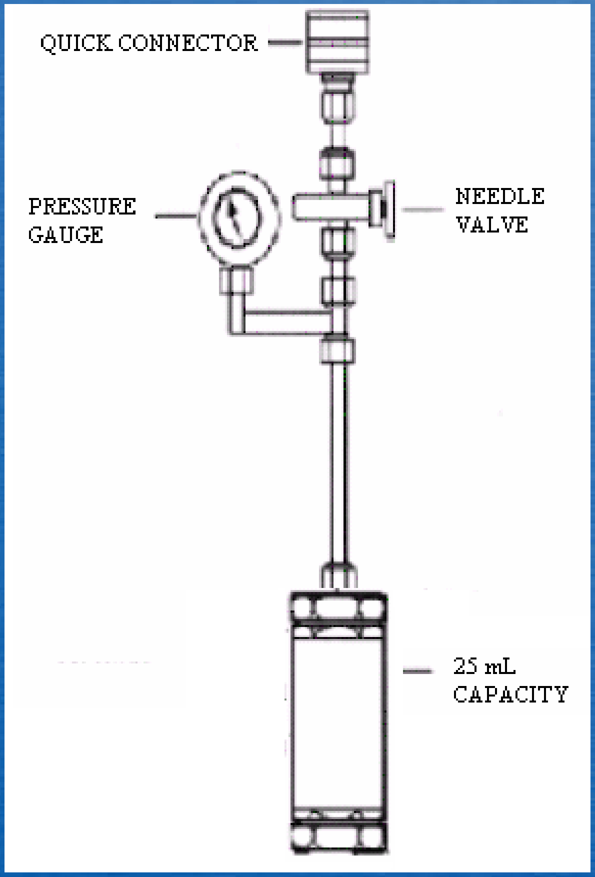


- To assure successful coal-petroleum interactions in co-coking, we want to have both the coal and the petroleum in a highly fluid state at reaction temperature.
- Thus, our coal selection has focused on high-volatile A bituminous coals with fluidities ≥ 20,000 ddpm.

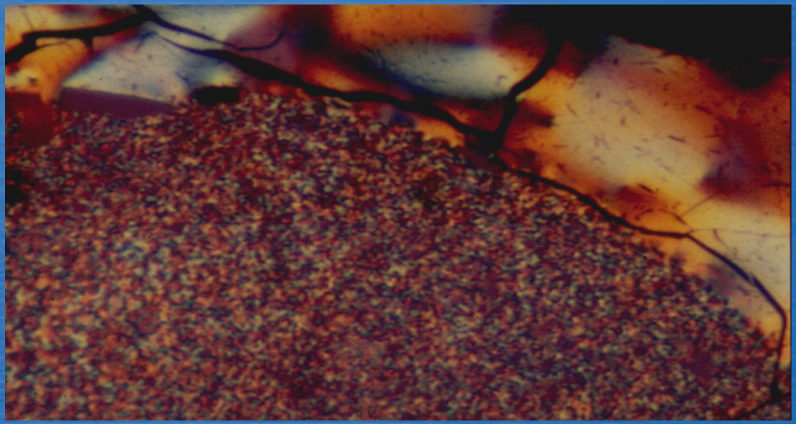
Co-coking Laboratory-scale Reactors

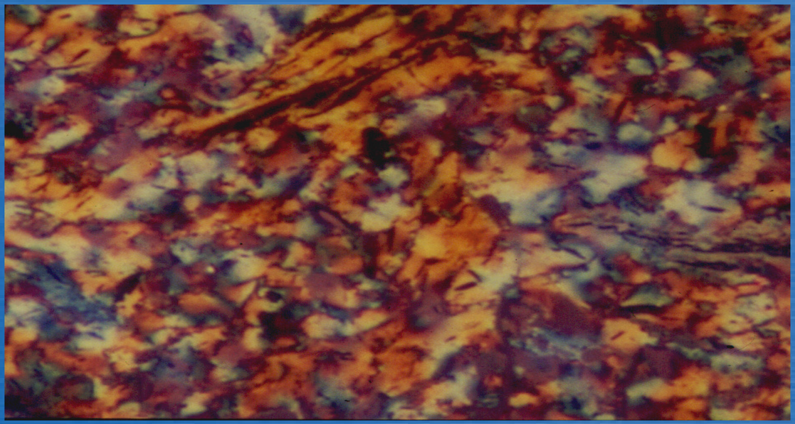
Typical experimental conditions:

- Autogenous pressure
- 465°
- 6–18 hours



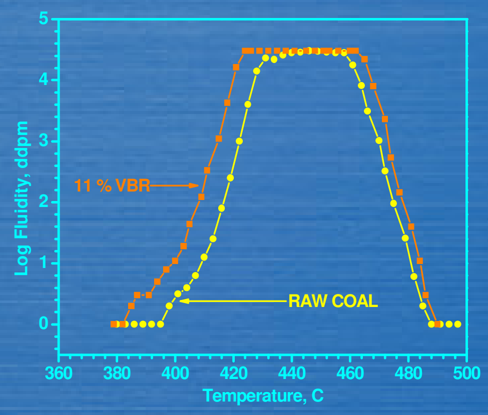
Results from Decant Oil and Vacuum Resid

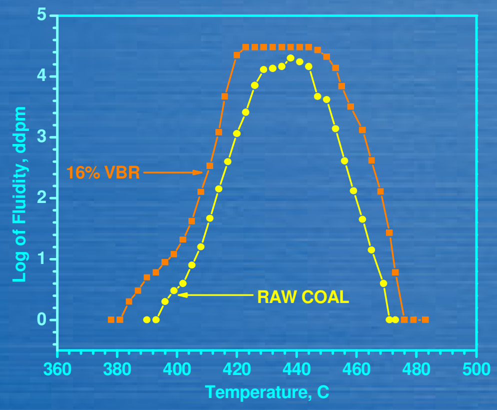




- Co-coking of coal/vacuum resid blends (left) indicates that each component cokes separately.
- Co-coking of coal/decant oil blends (right) shows excellent mixing of the two materials.
- Our current research focuses on use of decant oil as the liquid vehicle.

Influence of Blending on Fluidity





- Blending of highly fluid coals with petroleum fraction (in this case, vacuum resid) enhances fluidity.
- Powellton seam coal shown on left; Pittsburgh seam coal on right.

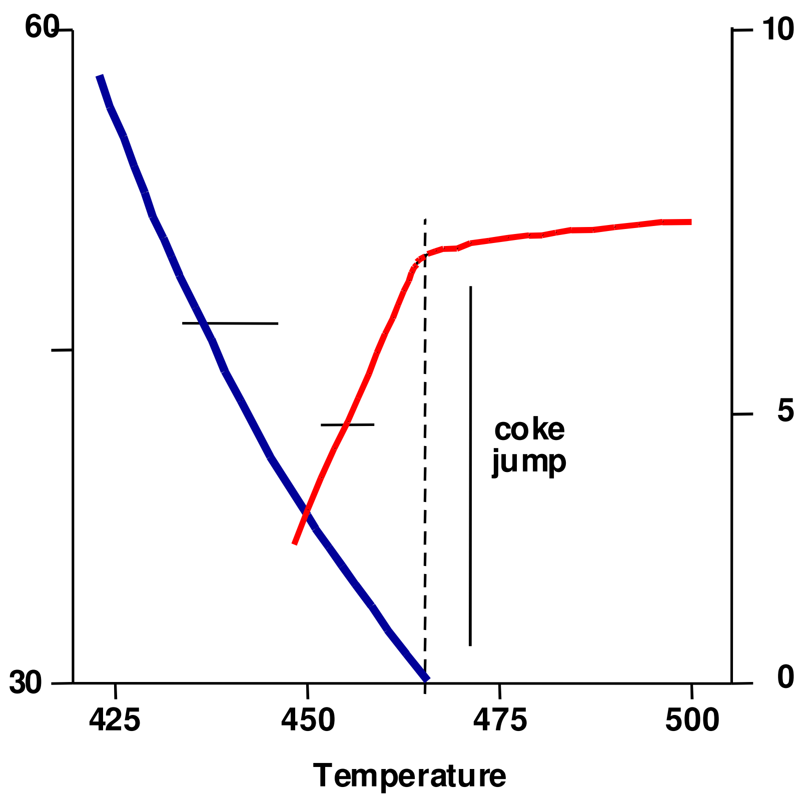
Characteristics of Coals

	Pittsburgh No. 8	Powellton
%C	83.3	87.6
%H	5.7	5.8
%N	1.4	1.6
%S	1.3	0.9
%O	8.4	4.1
%Ash	10.3	4.1
%VM	36.0	29.9
%FC	53.7	65.1

Chemical Composition of Decant Oil

- $f_a = 0.71$
- $H_{ar}/C_{ar} = 0.84$
- Polycyclic aromatics: two-ring <5%; three+four ring ≈88%; four-ring <5%
- Cycloalkanes (naphthenes) = 1%
- Hydroaromatics = 0

Coke Yield as a Function of Temperature

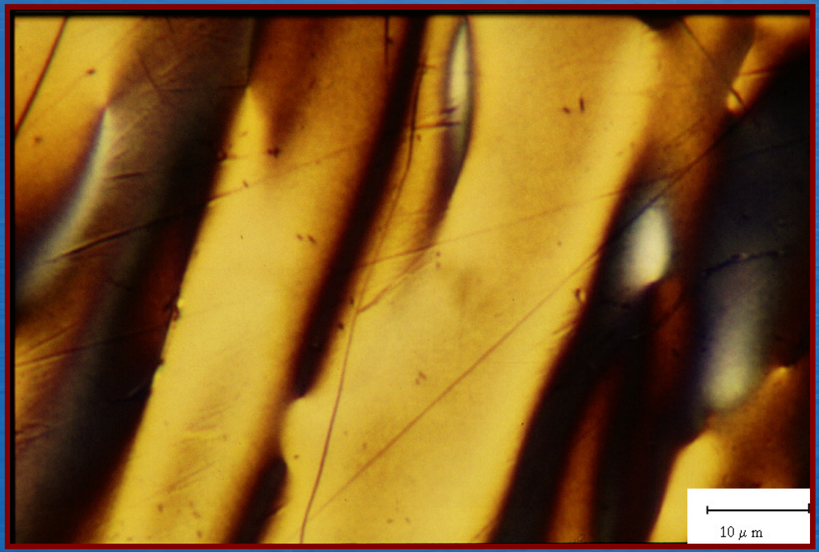


Coke Yield as a Function of Reaction Time

- Control experiments using only decant oil show an increase in yield as 6 h < 12 h ≈ 18 h. At 18 h yield is 55-60%.
- We selected 18 h to better simulate a delayed coker.
- Addition of coal enhances coke yield to ≈70% at 18 h.

Optical Texture: Domains

- Domain structures are >60 μm long and >10 μm wide.
- Domain texture is higher when coking decant oil alone than in co-coke (17% vs. 3%)

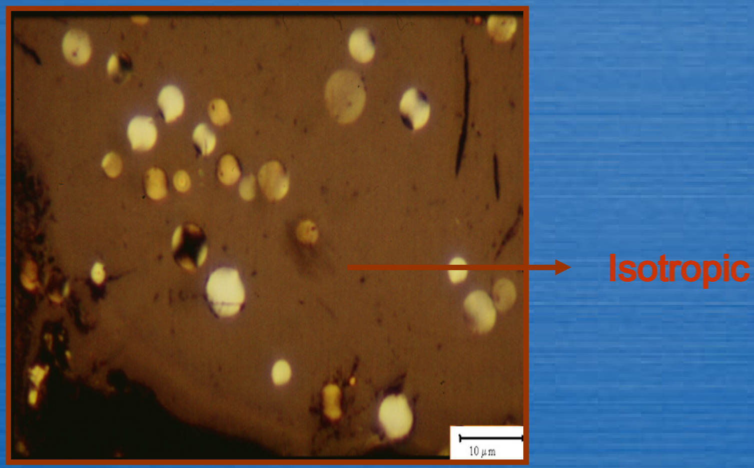


Optical Texture: Flow Domains

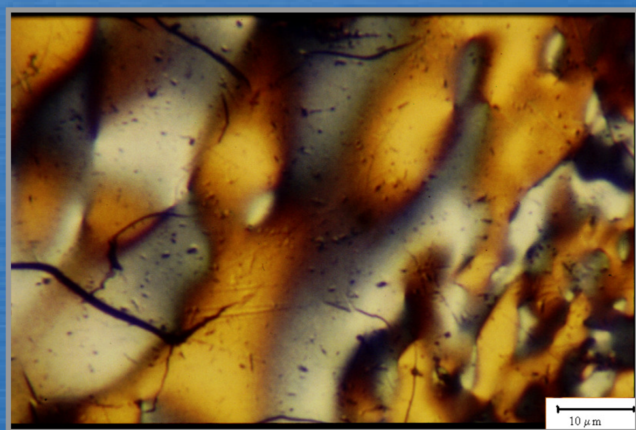
- Flow domains are > 60 µm long and < 10 µm wide.
- Flow domain texture is also less in the co-coke than in the control from decant oil (15% vs. 5%).

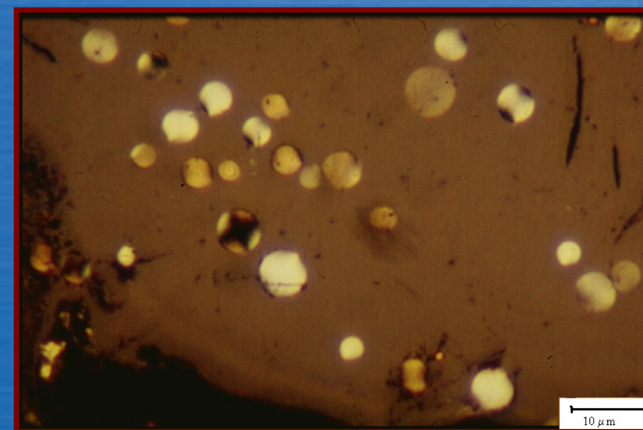
Optical Texture: Isotropic (?) Carbon

- Material tentatively identified as isotropic carbon is lower in co-coke than in control cokes from decant oil (27% vs. 8%).



Dominant Optical Textures in Co-cokes

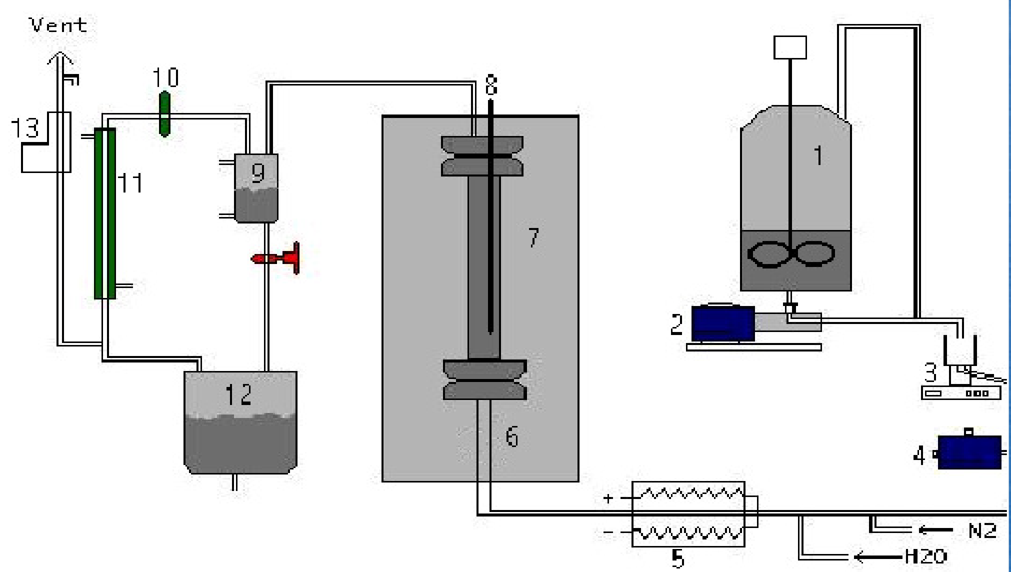




- The dominant optical textures in the co-cokes are small domains (left) and mosaics (right).
- Mosaics could be precursors to flow domains on further heat treatment.

Optical Texture of Extruded Green-Mix for Graphite Electrode from Petroleum Coke

Co-Coking Process Diagram



1. Heated Feedstock Tank
2. Feedstock Pump
3. Balance
4. Metering Pump
5. Superpreheater
6. Preheater
7. Coker Drum
8. Thermocouple Well
9. DP Cell
10. Back Pressure Regulator
11. Condenser
12. Receiver Tank
13. Mass Flow Meter

Co-Coking Pilot System

Typical Co-Coking Conditions

- 465° C coke drum inlet temperature
- 1.7 atm (17.5 kPa) system pressure
- 16.7 g/min feed rate
- 6 h run duration
- 6 h further soak time at 465° C
- 12 h total run duration

Products of Coking and Co-coking

Products from decant oil

Products from co-coking coal and decant oil

Typical Yields from Co-Coking– Similar to Yields from Delayed Coker Operation

Coke	25–30%
Liquids	60–65%
Gases	6–12%

Comparison of Coking Conditions and Product Distributions

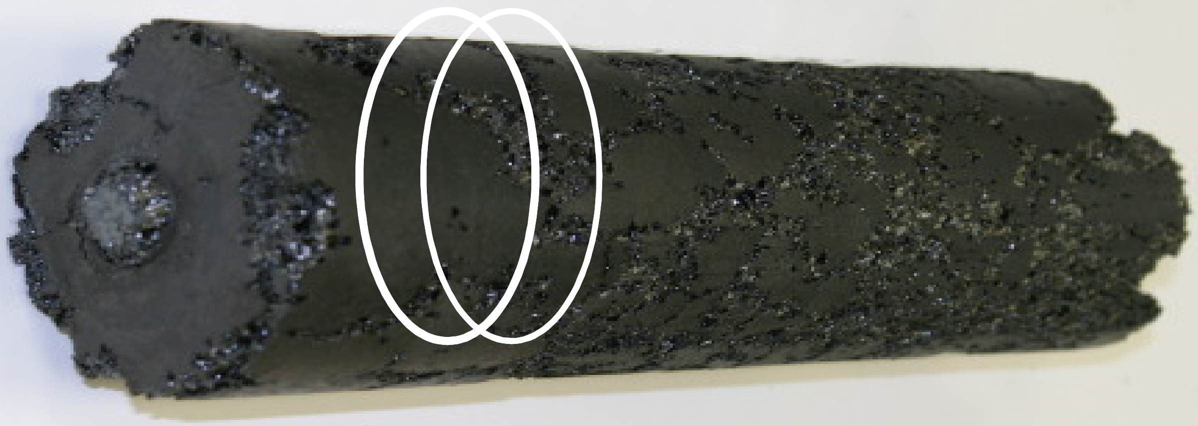
Components	Decant Oil	4:1 Decant Oil/ Powellton Coal	4:1 Decant Oil/ Powellton Coal
Feed, hrs	6	6	6
Steam Strip 500ºC, hrs	0	0	1
Held at 500ºC, hrs	6	6	5
Feed Rate, g/min	16.7	16.7	16.7
Total Feed, g	6028	6054	6012
Coke Product, g , (%)	860 (14.3%)	1917 (31.7 %)	1770 (29.4 %)
Liquid Product, g, (%)	4800 (79.6%)	3989 (65.9 %)	3838 (63.8 %)
Gas Product, g , (%)	368 (6.1%)	148 (2.4 %)	404 (6.7%)

Premium Carbon Products from Co-coking

- In addition to coal-based distillate fuels, we also aim to produce a premium coke product.
- The value of the by-product coke could be a sufficient economic benefit.
- Coke applications being evaluated at present are for synthetic graphite and aluminum-smelting anodes.
- Future evaluation may include activated carbon and carbon black.

Preparation of Coke for Optical Microscopy

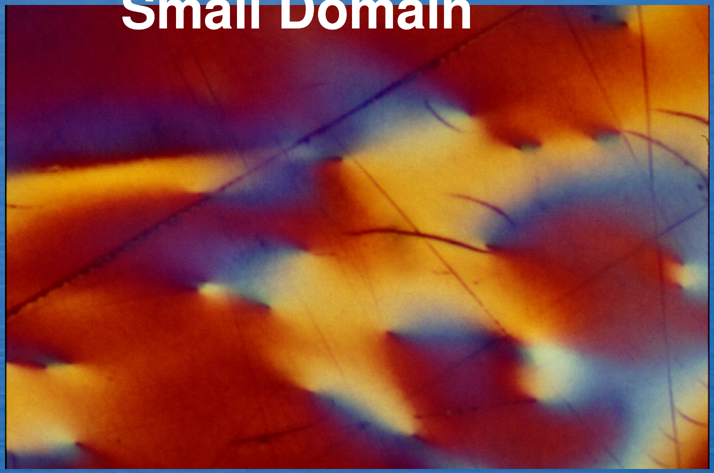
What has become of the coal?



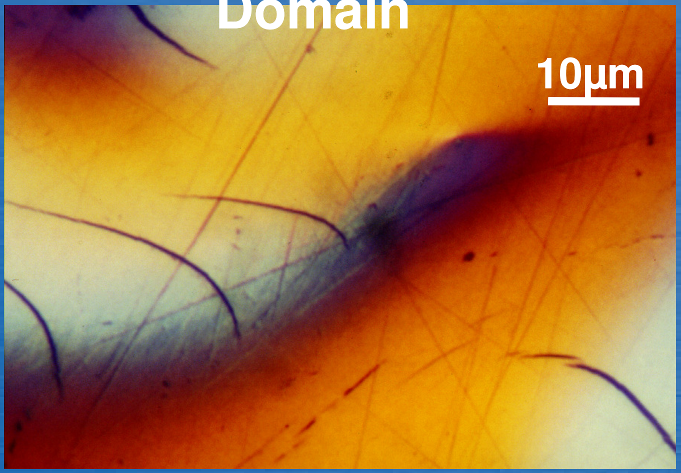
1 cm slices removed between 1-2, 6-7, 12-13, 18-19 and 24-25 cm

Carbon Textures from Decant Oil

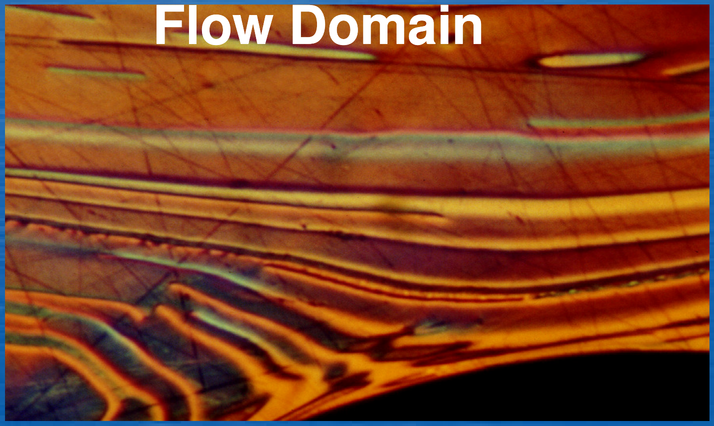
Small Domain



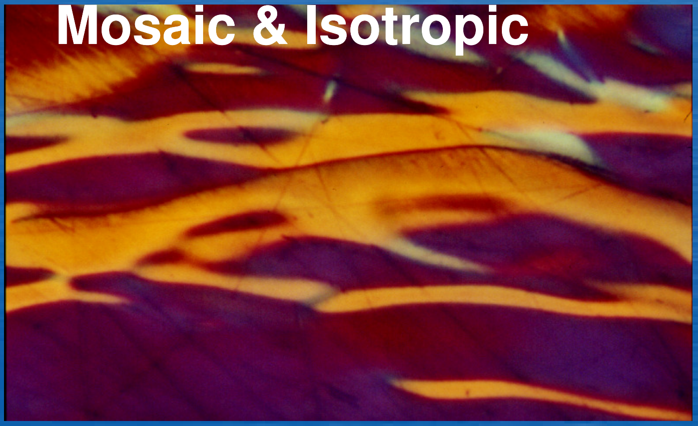
Domain



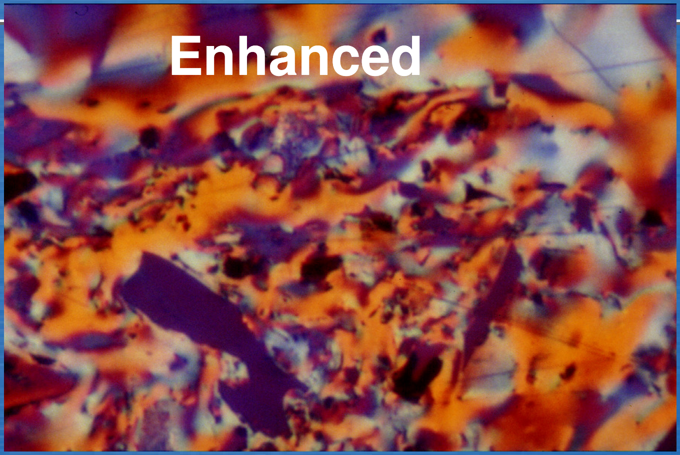
Flow Domain

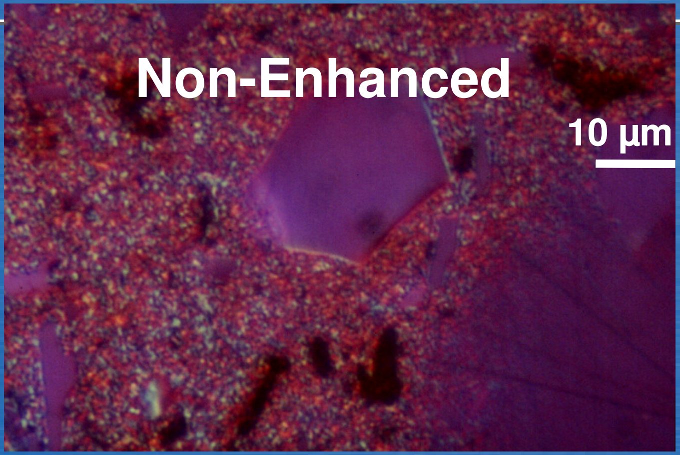


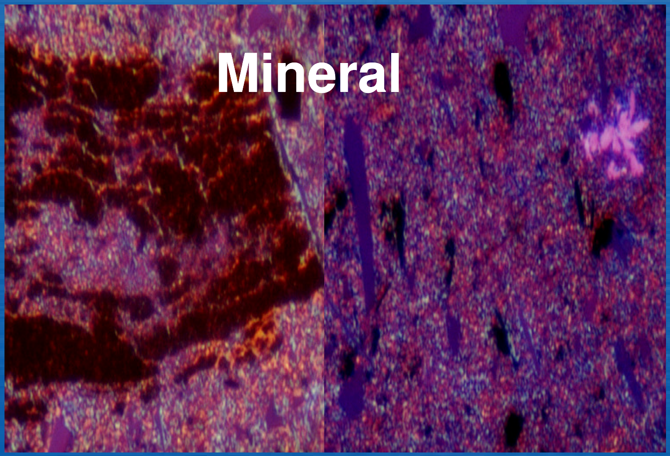
Mosaic & Isotropic



Carbon Textures from Coal







Distribution of Textural Components:
4:1 Decant Oil : Powellton

Location	% Coal-derived	% Petroleum-derived
From Bottom, cm		
1 - 2 cm	80.1	19.9
6 - 7 cm	80.9	19.1
12 - 13 cm	80.1	19.9
18 - 19 cm	68.7	31.3
24 - 25 cm	74.5	25.4
Radial Section, mm		
0 - 13, mm	40.9	59.1
13 - 29, mm	75.8	24.2
29 - 54, mm	96.2	3.8

Distribution of Optical Textures:
4:1 Decant Oil : Powellton

Location	% Coal	% Petrol.	Domain >60µm	Flow Domain >60L; <10W, µm
From Bottom, cm				
1 - 2 cm	80.1	19.9	1.8	0.0
6 - 7 cm	80.9	19.1	1.6	0.0
12 - 13 cm	80.1	19.9	1.5	0.5
18 - 19 cm	68.7	31.3	3.4	1.4
24 - 25 cm	74.5	25.4	2.8	0.4
Radial Section, mm				
0 - 13, mm	40.9	59.1	7.4	1.0
13 - 29, mm	75.8	24.2	1.2	0.7
29 - 54, mm	96.2	3.8	0.0	0.0

Distribution of Optical Textures:
Control Experiment with Decant Oil Only

Location	Isotropic	Mosaic <10µm	Small Domain 10-60µm	Domain >60µm	Flow Domain >60L; <10W µm
From Bottom, cm					
1 - 2 cm	0.4	4.9	64.4	26.3	4.0
6 - 7 cm	1.0	2.2	51.5	37.2	8.1
12 - 13 cm	1.1	1.5	57.6	34.7	5.1
18 - 20 cm	1.9	1.4	58.2	32.9	5.6
Radial Section, mm					
0 - 23 mm	0.7	1.9	59.5	34.0	3.9
23 - 41 mm	1.5	2.9	55.9	32.4	7.3

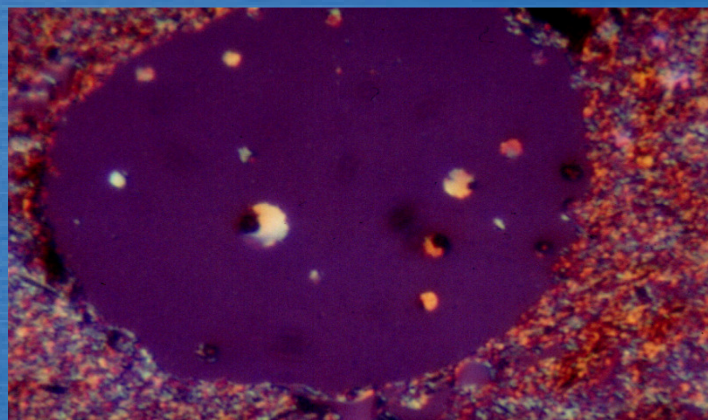
Distribution of Ash and Volatile Matter:

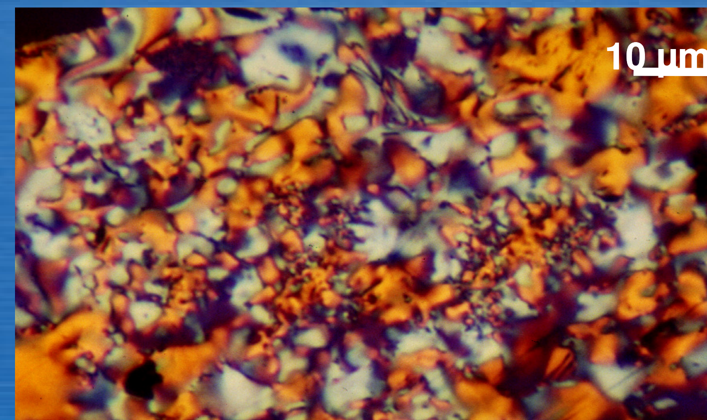
4:1 Decant Oil : Powellton (After Steam Stripping)

Location		% Ash, dry	% Volatile Matter, dry
From Bottom	Radial Section		
1 - 2, cm	0 - 20, mm	9.3	8.2
	20 - 42, mm	15.0	9.9
12 - 13, cm	0 - 20, mm	5.0	7.3
	20 - 41, mm	11.8	9.6
24 - 25, cm	0 - 18, mm	3.0	7.3
	18 - 38, mm	12.8	9.9
Composite	1408 g sample	6.6	7.2

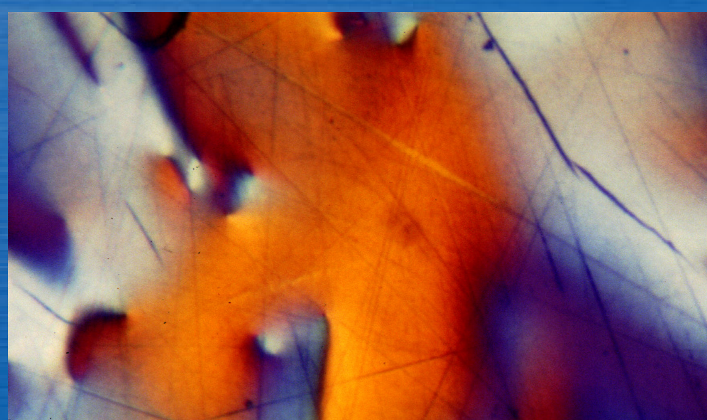
Vertical Distribution of Carbon Textures from Co-coking Pittsburgh Seam Coal

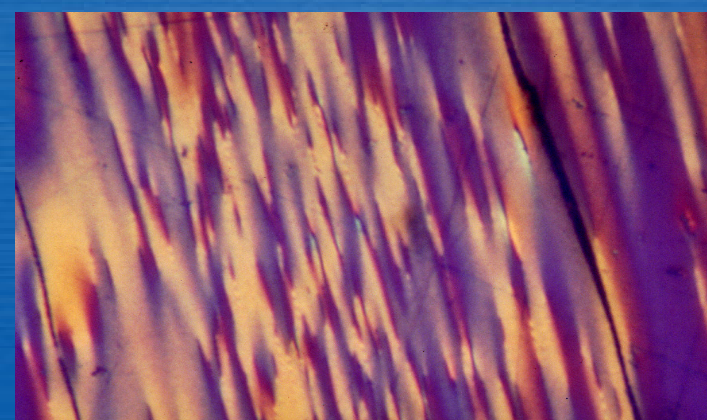
Bottom to 18 cm





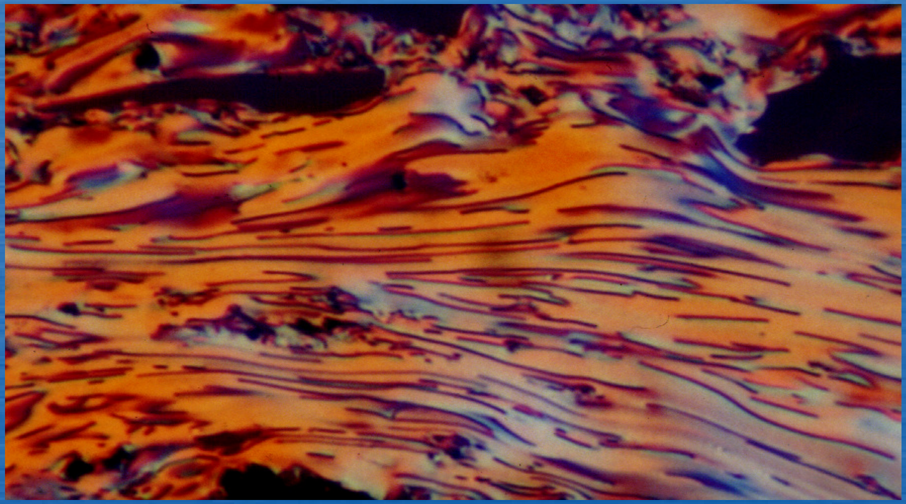
Above 18 cm





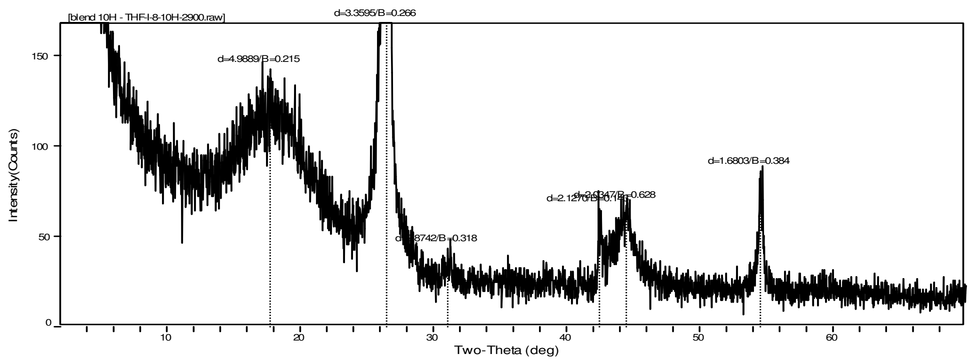
A Practical Consideration:

Is uniform incorporation of coal necessary to compete in anode / electrode markets?



Also, we should be looking into emerging markets, such as direct reduction of iron processes.

X-ray Characterization of Co-Coke Before Heat Treatment



- Co-cokes even before graphitization heat-treatment do show a distinct (*002*) peak.
- However, d_{002} = 3.3595 for this sample.

Laboratory Graphitization of Co-Coke

- Samples were heated to 2280° C in N_2 and 2900° C in helium.
- Characterization by X-ray diffraction for interlayer spacing and crystallite height.
- Degree of graphitization calculated from

$$g = (3.440 - d_{002}) / (3.440 - 3.354)$$

- Probability of random disorientation

$$d_{002} = 3.354 + 0.086p$$

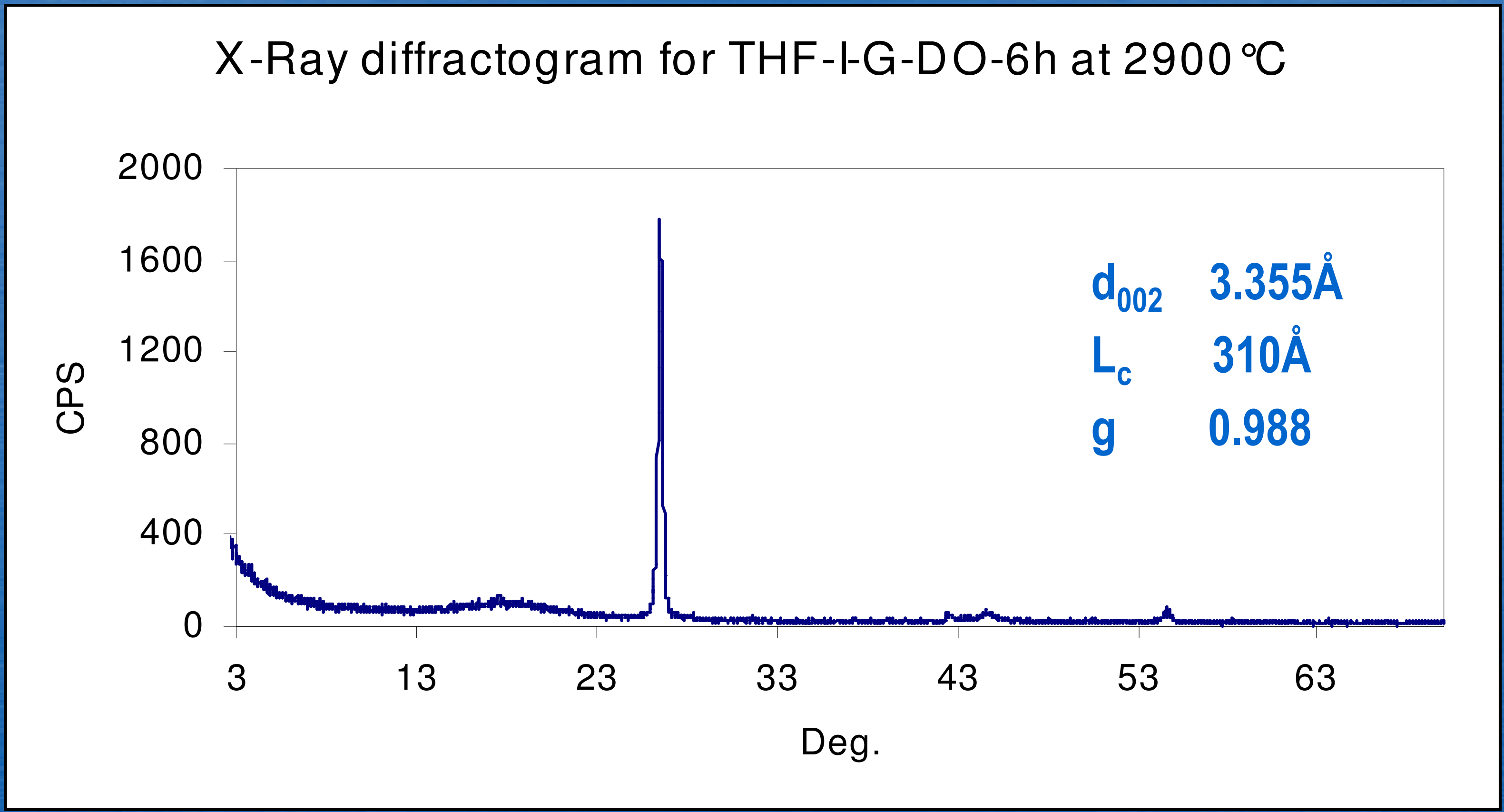
Calculation of Crystallite Height

•The crystalline height, **Lc** was calculated from the Scherrer equation

L_c = 0.9λ / B*cos θ

where L_c = crystallite height in Å
λ= 1.54056
B=FWHM (full width at half maximum)

X-Ray Diffractogram of Co-coke After Graphitization at 2900˚



X-ray Parameters of Graphites from Co-Coke

	Temp.	d_{002}	L_c	p	g
Co-coke	2280	3.360	382	0.07	0.93
Needle coke (control)	2280	3.370	250	0.19	0.81
Co-coke	2900	3.355	319	0.01	0.99
Synthetic graphites (typical)	2700-3000	3.354-3.360	100-500	0-0.07	1.00-0.93

Acknowledgements

- US Department of Energy and US Air Force Office of Scientific Research for funding.
- Maria Escallón, Parvana Aksoy, Leslie Rudnick, Gary Mitchell, Ronnie Wasco and Glenn Decker for doing the work.
- United Refining Company (Bob Ennis) for the decant oil.
- Oak Ridge National Laboratory (Peter Pappano) for graphitization at 2900˚ .