IN SEARCH OF A HIGH-VALUE CARBON PRODUCT FROM CO-COKING

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Introduction

As applied here, co-coking involves the simultaneous thermal treatment of a bituminous coal and a petroleum product such as decant oil [1]. Investigation of co-coking at The Energy Institute (The Pennsylvania State University) has centered around two main objectives, 1) to obtain a coal-based liquid [1-5] that will improve the thermal stability of jet fuel in the pyrolytic regime and 2) to obtain a high-value carbonaceous material [6,7].

As this is a complementary paper to previous preprints, product assessment of the co-coking distillate has been reported elsewhere [8]. However, the focus of the current paper will be on the solid product. In particular, our approach has been to determine if the THF-insoluble residue from co-coking experiments could be use to generate synthetic graphite. Credit for selling such a product to the graphite industry could offset processing cost for the jet fuel. In addition, it is possible that the blend of the petroleum stream and coal could reduce the cost of graphite since coal is a less expensive feedstock.

Experimental

Samples:

The decant oil was obtained from Seadrift Coke in Texas and was selected because it is a material used to make premium coke.

A number of compatible coals with regard to thermoplastic properties, ash and sulfur values were evaluated in past investigations [1]; that work led in the selection of Powellton seam coal. This coal was mined in Boone County, West Virginia and as received by us, was mechanically cleaned at the nearby Marfork coal cleaning plant. Hereafter this coal will be called "whole clean Powellton".

Procedure:

Approximately 20 g of the mixture decant oil / coal (2:1) was added to the type of reactor bomb described previously [5,8,9]. Briefly, the reactor has three sections (bomb, transfer pipe and catchpot) and is vented to avoid excessive pressure and secondary reactions among volatile components. The reactor was assembled, purged with N_2, and then heated in a sand bath held at a constant temperature of 465°C. Experiments were conducted by varying the reaction time from 2 to 12 hours in 2 hour increments.

When the reaction was completed at each specific time interval, bombs were cooled to room temperature, the apparatus was disconnected and the solid product was Soxhlet extracted with THF and dried for 1 hour at 100°C in an oven. The THF-insoluble fraction is hereafter called "semi-coke". Each test was run in duplicate to provided sufficient material for necessary analytical procedures.

Characterization of the semi-coke was carried out by using a Zeiss Universal microscopy, proximate analyzer -LECO MAC-400, -LECO 600 CHN elemental analyzer, total sulfur in a LECO SC-132, and TGA in a Perkin Elmer TGA-7. Semi-coke was thermally graphitized under nitrogen in a Centorr Vacuum Industries series 45 furnace at 2280°C; the graphitization at 2900°C was carried out by OENL in He. Samples were evaluated by XRD analysis using SCINTAG 2-normal powder diffraction apparatus.

For microscopic analysis, about a quarter of the solid residue was split out as removed from the Soxhlet, embedded in a cold setting epoxy resin, placed under vacuum and then in a centrifuge to force a density/particle size gradient. After hardening, samples were cut in half longitudinally to expose the gradient and mounted in 25 mm diameter molds. The hardened samples were polished for reflected light microscopy using a series of grit papers (400 and 600 grit) and alumina polishing slurries (0.3 mm and 0.05 mm). The carbon material was evaluated in white light using an oil immersion objective at a total magnification of 625 X in polarized or cross-polarized light. Point count analysis was performed by traversing the sample based upon a 0.4 x 0.4 mm grid and identifying the textural elements under a crosshair held in the microscope eyepiece. A total of 1000 counts was accumulated, 500 from each of two polished mounts. The textural elements identified and shown in Table 2 have been described previously [7].

The remainders of each THF-insoluble fraction from duplicate runs were combined and crushed to pass a 60 mesh sieve (0.25mm) and then distributed for standard analyses, i.e., proximate, ultimate and sulfur. Samples to be analyzed in the Perkin Elmer TGA were first dried at 110°C for 1h prior to the run. About 10 mg of sample was placed in the pan; the run started from room temperature to 800°C in nitrogen at 10°C/min.

For the XRD, the samples were ground with a mortar to get -60 mesh; samples were pestle and then sprinkled over the surface of a quartz zero background sample holder coated with a thin layer of petroleum jelly. X-ray diffraction data were acquired using SCINTAG 2-normal powder diffraction. The scan conditions were 2-70 degrees 2-theta, continuous scan, 2 deg. per minute and power settings 30 mA, 35 kV. The standard used was graphite ICDD 41-1487.

Results and Discussion

Volatile Matter and TGA. Table 1 compares the elemental analysis and volatile matter (VM) of the semi-coke from the blend (co-coking) at different reaction times and from the decant oil (at 6 hours) to establish a comparison. Volatile matter of the 6h semi-coke from the decant oil is higher than the one from the blend at the same reaction time. In addition, volatile matter decreases in the blend as the reaction time increases. Furthermore, it is likely that those semi-cokes with higher nitrogen or oxygen (by difference) values and lower carbon content may have a slightly higher concentration of the chemical remnants of coal. Although this could reflect differential reaction between components of the blends, it could also suggest a sampling

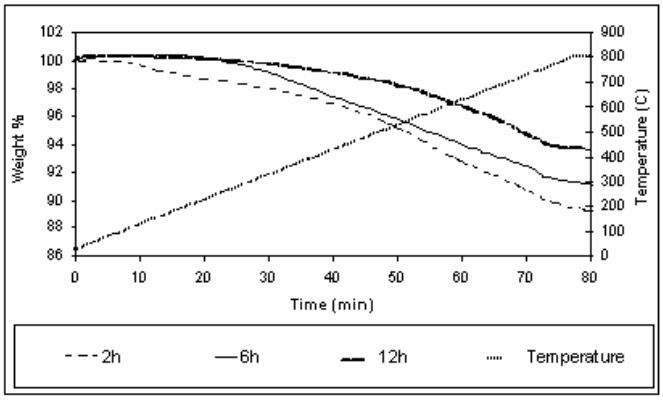
Table 1: Elemental analysis and volatile matter, dry basis

Reaction time (h)	C	H	N	S	O (diff)	VM
Blend						
2	90.57	3.30	0.93	0.63	0.00	13.23
4	89.45	3.14	1.10	0.66	1.44	11.09
6	90.18	3.34	1.12	0.68	0.73	10.19
8	89.15	3.02	1.06	0.70	1.43	10.00
10	90.27	2.78	1.18	0.70	1.04	9.26
12	90.72	3.01	1.25	0.71	0.51	9.59
Decant oil						
6	94.77	3.68	0.39	0.71	0.00	15.00
Coal Raw	85.78	5.06	1.49	0.80	5.14	29.22

problem. As coal remnants are not uniformly mixed with remnants of the decant oil in these semi-cokes.

Figure 1 shows the thermogram obtained by heating three semi-coke samples in N_2 atmosphere to 800°C at 10°C/min. These results are comparable with those found in Table 1 for volatile matter (VM) in that, as reaction time increases, the volatile matter decreases. In the TGA, as reaction time increases, the weight loss in lower for the semi-coke at 12h than that for the semi-coke at 2h. The reason for this is thought to be that as reaction time increases in the reactor, more condensation reactions occur, leading to larger compounds that do not evolve at 800°C (for TGA) or 950°C (for proximate analysis).

Figure 1: Thermograms of semi-cokes (blend) at different reaction time. Weight %



Optical microscopy provides some insight into the interactions between coal particles and the decant oil.

As seen in Figure 2, a typical region of semi-coke derived from coking the whole Powellton coal alone in the reactor bomb stands in contrast to the left half of Figure 3, which shows the type of optical texture derived from decant oil. If there were no interactions between the components of the blend, it would be relatively easy to determine the concentration of each. However, the right half of Figure 3 shows how the texture derived from the vitrinite of this coal can become enlarged or enhanced during co-coking. The fact that these types of textures were not seen in the semi-coke from either coal or decant oil and that small, angular regions of coal-derived inertinite (i) reside in the right half of Figure 3, demonstrates that these regions are remnants of coal particles that have been greatly influenced by co-coking. Nearly 98% of the vitrinite-derived carbon forms observed in the co-coking blends have isochromatic areas enlarged from 1-2 microns to 3-6 microns in diameter.

Based on the volumetric distribution of carbon textures shown in Table 2, a number of important observations can be made regarding the influence of reaction time. As time increases, the carbon textures derived from the vitrinite portion of coal becomes more fully enhanced by interaction with the decant oil; the amount of isotropic carbon derived from the decant oil decreases; and there is a steady decrease in the overall size of the isochromatic areas derived from the decant oil, i.e. mosaic and small domain concentration increases at the expense of domain and flow domain textures.

It is curious to note that after 6h of reaction, the decant oil-derived semi-coke had a significant amount of the isotropic carbon remaining, whereas no isotropic carbon derived from the decant oil was observed in the 6h co-coking run. Also, it is interesting to note that the carbon derived from the decant oil was devoid of flow domain texture. However, this could have been a function of friability as a fairly high concentration of small particles (<20μm) was observed in the sample and could represent broken fragments of the flow domain.

Figure 2: Semi-coke from the coking of coal at 6h

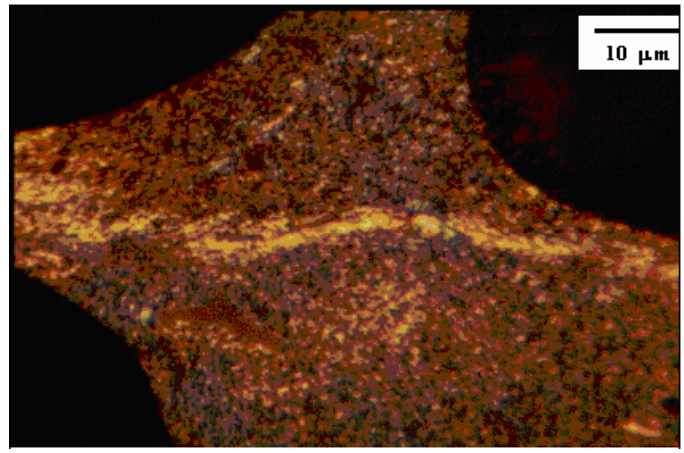
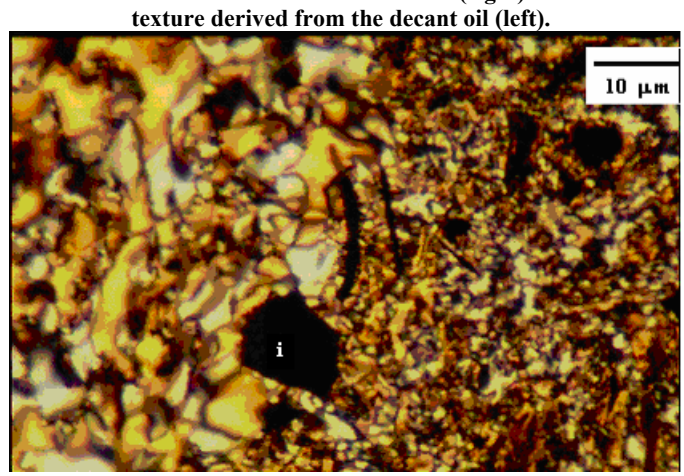


Figure 3: Semi-coke from the co-coking at 6h. Indistinct interface between enhanced coal-derived (right) and mosaic texture derived from the decant oil (left).



The mosaic texture from the blend which is decant oil-derived also is different. As shown in Table 2, the isochromatic units decrease: *small domain* (10-60 μm) is greater in the blend than in decant oil whereas *domain* (>60μm) and *flow domain* is less in the blend than in the decant oil. There is no doubt about the decant oil and coal interaction. However, the question remains what this apparent change in optical order will have on the graphitizability of the carbon product.

The three blend samples (THF-insoluble fractions from the blend at 6, 10 and 12h), in addition to one from the decant oil at 6h and one from coal at 6h were graphitized and examined by X-ray diffraction. Hereafter, these samples are going to be named as THF-I-G-B-6h, THF-I-G-B-10h and THF-I-G-B-12h for the blend samples, THF-I-G-DO-6h for the decant oil and THF-I-G-C-6h for the coal. All three samples appear to contain graphite matching the graphite standard ICDD 41-1487. There is also evidence of an amorphous phase in each sample.

Table 2: Proportion of textures derived from coal and decant oil compared with the normalized concentration of decant oil textures, Vol. %

	Origin of textures		Normalized concentration of decant oil-derived textures				
Ident. (h)	% Coal-Derived	% Petroleum-Derived	% Isotropic	% Mosaic	% Small Domain	% Domain	% Flow Domain
Decant oil							
6	1.6	98.4	16.0	15.4	36.3	32.3	0.0
12	0.0	100	3.8	7.2	42.2	45.7	1.1
Blend							
2	39.4	60.6	6.3	13.7	60.9	16.0	3.1
4	37.8	62.2	1.0	20.1	60.8	16.2	1.9
6	35.9	64.1	0.0	24.3	64.1	10.6	1.0
8	41.9	58.1	0.0	20.0	64.0	12.0	4.0
10	35.3	64.7	0.0	19.8	66.3	13.3	0.6
12	31.4	68.6	0.0	20.4	66.5	12.2	0.9

Tables 3 to 5 show the results of the XRD analysis. The interlayer spacing d_{002}, the degree of graphitization, **g,** from the equation of Seehra and Pavlovic and the probability of random disorientation between any two neighboring layers, **p,** was calculated [10]

EQ 1: $\mathbf{g} = (3.440-d_{002}) / (3.440-3.354)$
Where 3.354 Å is the interlayer spacing in graphite and 3.440, the value for a carbon with no graphitic order. The probability of random disorientation between any two neighboring layers, **p**, is given by
EQ 2: $d_{002} = 3.354 + 0.086\mathbf{p}$

The crystalline height, **Lc** was calculated by following by following the Scherrer formula
EQ 3: $t= 0.9\lambda / B\cos \eta_B$, where t corresponds to Lc
These calculations are explained in detail elsewhere [11,12].

As shown in Table 3, even at intermediate reaction time (6h) and low graphitization temperature (2280ºC), XRD results suggest a similar structural change in the THF-insoluble fraction of the decant oil (THF-I-G-DO-6h) and blend (THF-I-G-B-6h) far exceeding that of the coal-derived semi-coke (THF-I-G-C-6h). The observations made during optical microscopy of the THF-insoluble fraction of the blend in Figure 3 hinted that some improvement may be realized.

Table 3: Effect of graphitization on three different materials at 2280°C

	Interlayer spacing, $\mathbf{d_{002}}$, **Å**	Stacking height, $\mathbf{L_c}$, **Å**	Random dis-orientation, **p**	Degree of graphitization **g**
THF-I-G-B-6h				
2280°C	3.365	313	0.128	0.872
THF-I-G-DO-6h				
2280°C	3.363	338	0.105	0.895
THF-I-G-C-6h				
2280°C	3.392	136	0.442	0.558

Comparing the degree of graphitization, THF-insoluble from the blend is equivalent to that of the decant oil; the difference between them is only 2.5%; however, the blend is very far from the coal's THF-insoluble whose degree of graphitization is very low (0.558). The random disorientation of the blend is higher than that from the decant oil. This can be explained by the presence of inertinite and mineral matter which has not evolved at 2280°C. It is expected that at higher graphitization temperature (2900°C), the random disorientation will be lower for the blend compared to that at 2280°C.

Table 4 shows the difference in the random disorientation and degree of graphitization with the graphitization temperature at 2280 and 2900°C for the blend and for the decant oil. It is seen that the random disorientation decreases nearly twice as much for the blend at 6h with increasing graphitization temperature. The degree of graphitization is about 5% higher for the graphitized decant compared to the blend. This difference could stem from the presence of inertinite in the coal which may not graphitize.

Table 4: Comparison of the principal XRD characteristics of the graphitized THF-insoluble fraction for the blend and decant oil at two different graphitization temperatures

	Interlayer spacing, $\mathbf{d_{002}}$, **Å**	Stacking height, $\mathbf{L_c}$, **Å**	Random dis-orientation, **p**	Degree of graphitization **g**
THF-I-G-B-6h				
2280°C	3.365	313	0.128	0.872
2900°C	3.359	246	0.058	0.942
THF-I-G-DO-6h				
2280°C	3.363	338	0.105	0.895
2900°C	3.355	310	0.012	0.988

Since the degree of graphitization increases and random disorientation decreases as graphitization temperature increases, the influence of reaction time on the graphitized semi-coke can be assessed. Table 5 comparisons of the principal XRD characteristics for the blend at 2900°C varying the reaction time. As seen that the graphitized semi-coke at 12h has the higher degree of graphitization compared to those at 6 and 10h. Therefore, the higher reaction time generates a higher the degree of graphitization that is comparable to the value derived from graphitized decant oil at 6h.

Table 5: Comparison of the principal XRD characteristics of the graphitized THF-insoluble fraction for the blend at 2900°C graphitization temperature varying semi-coke reaction time

	Interlayer spacing, $\mathbf{d_{002}}$, **Å**	Stacking height, $\mathbf{L_c}$, **Å**	Random dis-orientation, **p**	Degree of graphitization **g**
THF-I-G-B-6h				
2900°C	3.359	246	0.058	0.942
THF-I-G-B-10h				
2900°C	3.360	310	0.070	0.930
THF-I-G-B-12h				
2900°C	3.355	271	0.012	0.988

Conclusions

Optical microscopy shows that the interaction between decant oil and coal is gives rise to a new structure which does not correspond to the structure of the decant oil and coal coked alone. In addition, the anisotropy is higher in the blend than in the decant oil.

Graphite is formed by the further heating of the semi-coke. The carbon materials obtained in the co-coking process show a potential use in the graphite manufacture since the deviation between the data

of the blend and decant oil is below 5% at 2900°C and 2.5% at 2280°C.

The higher reaction time in the blend leads in a higher value of degree of graphitization. The blend at 12h has identical values compared to the decant oil at 6h at 2900°C.

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