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FINAL TECHNICAL REPORT

PRODUCTION AND SCREENING OF CARBON PRODUCTS PRECURSORS FROM COAL

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We have examined the effects of blending a raw coal extract (EXT) with an extracted coal-tar pitch (ECTP). Previous reports were concerned with the addition of 15 wt% EXT, or less, on the physical characteristics of the blend and on the development of optical texture following carbonization.

Two additional blends of ECTP and EXT were prepared at the 30 and 50 wt% EXT content using a procedure already described. The characteristics of the blends are presented in Table 1.

Table 1. Comparison of the properties of EXT and ECTP blends.

	30 wt% EXT	50 wt% EXT
Density, g/cm^3	1.301	1.300
Softening Point, °C	222.1	ND
Coke Yield, wt%	63.8	66.3
Ash Content, wt%	0.10	0.11

The density for these blended materials is not much different than the density for the blends reported earlier. The softening point temperature for the 30 wt% EXT increased to over 200 °C while the softening point temperature for the 50 wt% EXT blend was too high to be determined by the Mettler method. Coke yields approximately follow the law of mixtures.

Figure 1 shows the optical texture of the green cokes for the 30 and 50 wt% EXT blends. Though the optical texture of the green cokes was not significantly affected where the level of EXT is 15 wt% or less, larger proportions of EXT exert a marked reduction in anisotropy.

The co-processing of coal with petroleum residues or other heavy hydrocarbons at elevated temperature and pressure has received considerable attention in the research community as a means to upgrade simultaneously coal and byproducts (Rincon et al, 1990; Cugini et al., 1989; Curtis et al., 1987; Rincon and Angulo, 1986; Orchin et al., 1951; Orchin and Storch, 1948). Heavy hydrocarbons can function as sources of hydrogen, as well as performing as a medium for dissolution and dispersion of coal fragments. However, the focus of much of the prior research has been on developing fuels, distillable liquids, or synthetic crudes. Comparatively little effort has been deliberately directed toward the production of heavier, non-distillable materials which could perform as binder and extender pitches, impregnants, or feedstocks for cokes and other carbons.

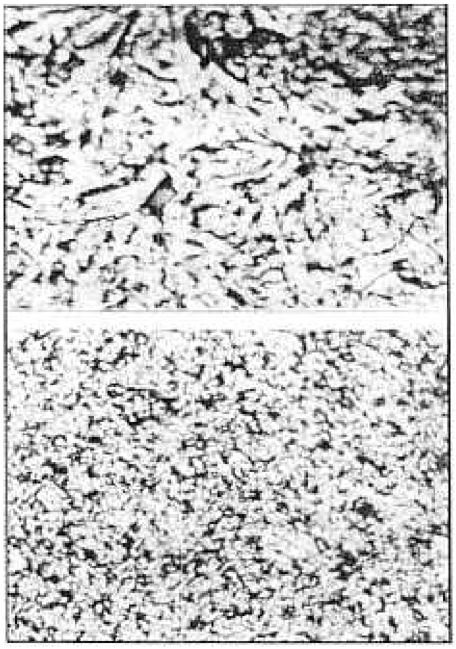

Figure 1. Photomicrographs of green cokes of EXT and ECTP blends. Top, 30 wt% EXT; Bottom, 50 wt% EXT. Scale: 1 inch = 145μm.

Two materials were selected for co-processing with coal: one coal based and the other petroleum based. The former is a heavy distillate fraction (henceforth identified as heavy oil, HO) derived as a byproduct of metallurgical coke making and was used without any modification. The latter is a tar product obtained by the thermal cracking of petroleum gas oil. The as-received petroleum-based tar contained considerable low-boiling substances, which were removed prior to use by vacuum distillation at 350 °C. This vacuum-distilled material is designated as TT. The coal used is a mv bituminous coal (WVGS 13421, <60 Taylor mesh, vacuum dried). Some properties of the co-processing additives are provided in Table 2.

Table 2. Properties of co-processing additives.

	Coal-Derived Solvent [HO]	Petroleum-Derived Solvent [TT]
Density, g/cm^3	1.130	1.203
Softening Point, °C	Pasty at Room Temperature	214.2
Coke Yield, wt%	4.0	67.5
Ash Content, wt%	<0.01	<0.1
THF-Insolubles, wt%	0.0	<0.1
Distillation, wt%		
0-270 °C	0.5	--
0-300 °C	5.0	--
0-355 °C	25-35	--
Residue	65-75	>90

The additives are low in ash content, highly soluble in tetrahydrofuran (THF), and exhibit high boiling points. The coke yield for HO is dramatically lower than for TT, and the optical structures of the green cokes for both materials are highly anisotropic.

Co-processing experiments were conducted in duplicate employing 25 cm^3 stainless steel tubing bomb reactors. In all of the experiments, the mass charged to the reactor was held constant at 10 grams. After placing the appropriate proportion of material into the reactor, the reactor was sealed and purged three times with dry nitrogen. The nitrogen pressure within the reactor prior to heating and at room temperature was 1 atmosphere. The reactors were mounted on a shaker mechanism and agitated vertically at 600 rpm through a displacement of 1.75 inches while immersed in a pre-heated fluidized sandbath heater. After reaction, the tubing bomb reactor was quenched by cool water to room temperature.

Each reactor was then opened slowly to vent gas and the product washed out with THF into a tared porous ceramic thimble. The thimble was placed inside a Soxhlet apparatus and extracted for 24 hours with THF. The soluble product was recovered from the THF by rotary evaporation and then vacuum dried along with the thimble containing the insoluble residue overnight at 170 °C.

Conversion was calculated on a dry-ash-free basis (daf) based on the amount of THF-insoluble residue as follows:

$$\text{Conversion} = \frac{[\,(\text{mass charged to reactor}) - (\text{mass of residue})\,]}{[\ \text{daf mass charged to reactor}\ ]} \times 100$$

Mass balances were typically 93 to 96 wt%, the mass loss attributed to product gases, light distillates, and material not recovered during work-up.

The pitch-like, THF-soluble products were characterized by Mettler softening point temperature, helium pycnometry, and coke yield. Samples were also converted to green coke and mounted in epoxy and polished for examination using optical microscopy. The THF-insoluble residue was also mounted in epoxy, polished, and inspected by optical microscopy. Table 3 shows the percent conversion for the co-processing of coal with HO, coal with HO and TT, and HO and TT without coal.

Table 3. Conversion (daf) to THF-soluble products following co-processing. (400 °C, 1 Hour, 1 atmosphere nitrogen gas, initial cold)

Mass Proportion	Coal:HO 1:3	Coal:HO:TT 1:1.5:1.5	HO:TT 1:3
Conversion	86.5	73.7	96.6

The conversion to THF-soluble products for the Coal:HO case demonstrates that HO was only slightly effective in dissolving or dispersing the coal under the reaction conditions used. Assuming that none of the coal was converted and the HO remained unaltered, the yield of soluble product would be about 75 wt%. The Coal:HO:TT mixture was less conducive to providing an environment for coal dissolution with a conversion of about 74 wt%. On the other hand, the mixture of HO:TT alone remained essentially completely soluble after reaction. Examination of the insoluble residues by optical microscopy revealed the presence of elliptical or spherical anisotropic bodies, i.e. mesophase, for all three mixtures. Mesophase in the residue indicates that polymerization and condensation occurred and that the system probably was not able to provide enough hydrogen to prevent retrogressive reactions. For example, Figure 2 shows, in addition to unconverted coal remnants and an insoluble isotropic background, several small bodies of mesophase for the case of the Coal:HO combination.

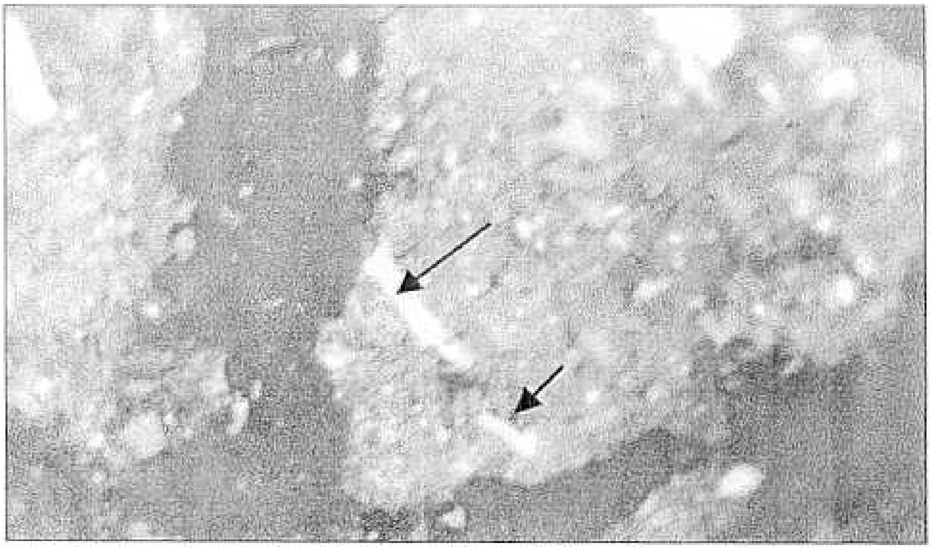

Figure 2. Photomicrograph showing the presence of mesophase in the THF-insoluble residue for the Coal:HO mixture. Arrows point to mesophase. Scale: 1 inch = 41 μm.

Table 4 provides some of the properties for the THF-soluble products. The products from the Coal:HO and Coal:HO:TT blends are pasty materials at room temperature and thus not amenable to the Mettler or helium pycnometry determination. However, the HO:TT mixture produced a product within the specification of some commercial pitches.

Table 4. Characterization of THF-soluble products from co-processing reactions. (400 °C, 1 Hour, 1 atmosphere nitrogen gas, initial cold)

Mass Proportion	Coal:HO 1:3	Coal:HO:TT 1:1.5:1.5	HO:TT 1:3
Density, c/cm^3	--	--	1.231
Softening Point, °C	--	--	118.5
Coke Yield, wt%	15.5	34.2	50.4
Ash Content, wt%	<0.1	<0.1	<0.1

Table 5 compares the effects of hydrogen pressure on conversion and some of the properties of the THF-soluble products after co-processing coal with HO. Figure 3 shows the development of optical texture of the green cokes.

Table 5. Effects of hydrogen pressure on properties of THF-soluble pitches. [400°C, 1 Hour Reaction, 1:3 wt:wt Coal:HO]

Pressure, MPa	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%	Ash Content, wt%
0.1 Nitrogen	86.5	Tacky Solid	----	15.5	<0.1
3.4 Hydrogen	91.7	Tacky Solid	----	13.7	<0.1

The products under these reaction conditions are tacky at room temperature and, thus, not amenable to Mettler softening point temperature or helium pycnometry determination. The coke yields are rather low and there appears to be a slight increase in conversion in the case of hydrogen pressure. With or without hydrogen pressure, coke structures are relatively anisotropic.

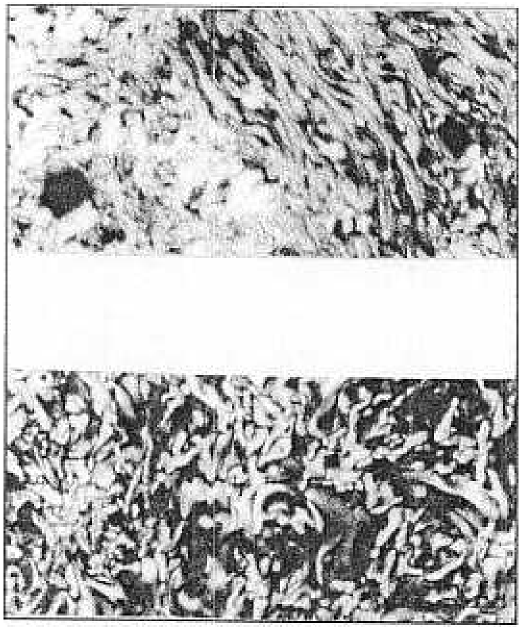

Figure 3. Effects of hydrogen pressure on green coke structure after co-processing coal with HO [400°C, 1 Hour Reaction, 1:3 wt:wt Coal:HO]. Top, 0.1 MPa N_2; Bottom, 3.4 MPa H_2. Scale: 1 inch = 145 μm.

Table 6 shows the results of hydrogen pressure after co-processing coal with HO and TT. There is a dramatic increase to THF-soluble material with hydrogen compared to the case with nitrogen pressure. The hydrogen-derived product is solid at room temperature with a softening point of 79 °C and a density of 1.221 g/cm^3. Coke yields are higher than in the case of coal and HO co-processed alone. Figure 4 indicates that the soluble materials form fairly anisotropic cokes.

Table 6. Effects of hydrogen pressure on properties of THF-soluble pitches. [400°C, 1 Hour Reaction, 2:3:3 wt:wt:wt Coal:HO:TT]

Pressure, MPa	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%	Ash Content, wt%
0.1 Nitrogen	73.7	Tacky Solid	----	34.2	<0.1
3.4 Hydrogen	91.1	79.0	1.221	39.6	<0.1

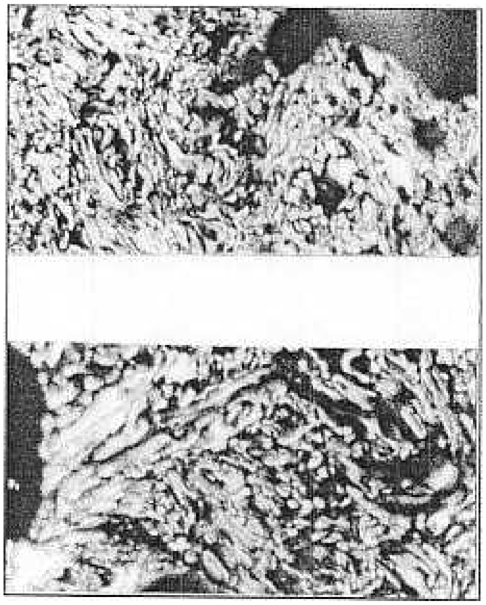

Figure 4. Effects of hydrogen pressure on green coke structure after co-processing coal with HO and TT. [400°C, 1 Hour Reaction, 2:3:3 wt:wt:wt Coal:HO:TT]. Top, 0.1 MPa N_2; Bottom, 3.4 MPa H_2. Scale: 1 inch = 145 μm.

Table 7 and Figure 5 show the effects of co-processing HO and TT in the absence of coal. In this instance, hydrogen pressure appeared to have little influence on conversion in that both of the reaction products remained highly soluble in THF. While the differences between the nitrogen and hydrogen pressures on product properties are small, hydrogen pressure did produce a pitch-like material with lower softening point temperature, density, and coke yield.

Table 7. Effects of Hydrogen Pressure on Properties of THF-Soluble Pitches [400°C, 1 Hour Reaction, 1:3 wt:wt HO:TT]

Pressure, MPa	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%	Ash Content, wt%
0.1 Nitrogen	96.6	118.5	1.231	50.4	<0.1
3.4 Hydrogen	98.1	106.1	1.222	47.8	<0.1

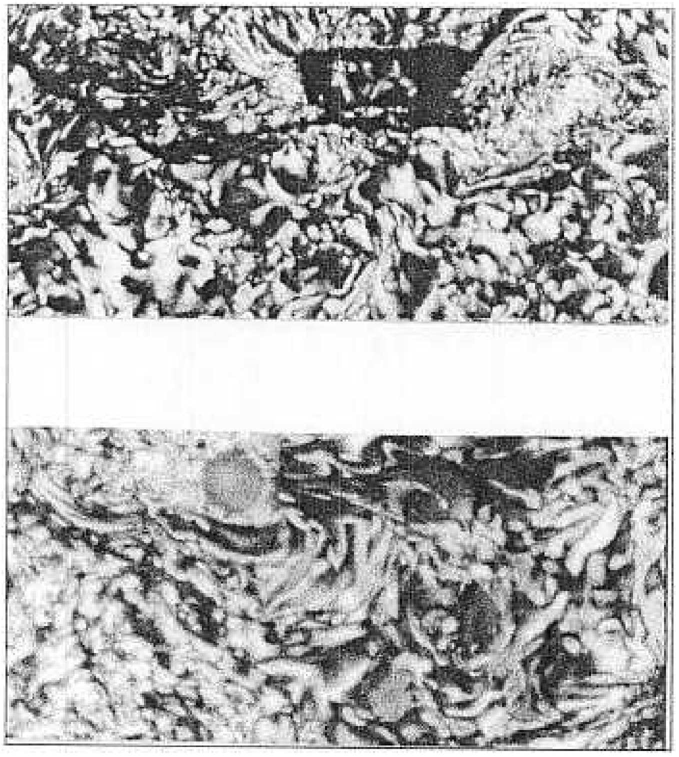

Figure 5. Effects of hydrogen pressure on green coke structure after co-processing HO with TT. [400°C, 1 Hour Reaction, 1:3 wt:wt HO:TT]. Top, 0.1 MPa N_2; Bottom, 3.4 MPa H_2. Scale: 1 inch = 145 μm.

The products insoluble in THF were examined by optical microscopy under polarized light. In all of the experiments, whether nitrogen or hydrogen gas was employed, the presence of anisotropic structures (mesophase) was prevalent as shown by the example in Figure 6. The observation of mesophase in the insoluble residues indicates that polymerization has occurred and that the reaction conditions used may not have been optimal for the production of liquid products.

Figure 6. Photomicrographs showing the presence of mesophase in THF-insoluble residues [400 °C, 1 hour, 3.4 MPa hydrogen initial cold]. Top, Coal:HO:TT blend; Bottom, HO:TT blend. Scale: 1 inch = 62 µm.

The effects of temperature following the co-processing coal with HO are presented in Table 8 and Figure 7.

Table 8. Effects of temperature on properties of THF-soluble pitches. [3.4 MPa H_2, 1 Hour Reaction, 1:3 wt:wt Coal:HO]

Temperature °C	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%	Ash Content, wt%
400	91.7	Tacky Solid	----	13.7	<0.1
425	92.5	Tacky Solid	----	6.5	<0.1

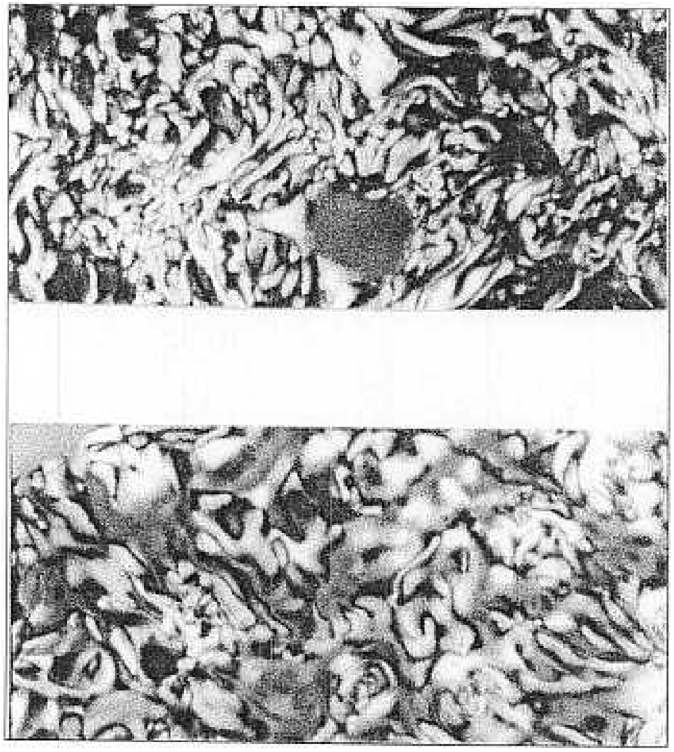

Figure 7. Effects of temperature on green coke structure after co-processing coal with HO. [3.4 MPa H_2, 1 Hour Reaction, 1:3 wt:wt Coal:HO]. Top, 400°C; Bottom, 425°C. Scale: 1 inch = 145 μm.

Similar to the other experiments involving coal and HO, these products tend to be tacky solids at room temperature which preclude the determination of their Mettler softening point temperature and density measurement. Coke yields are very low though the optical textures are typically anisotropic.

Table 9 and Figure 8 provide information following the co-processing of coal with both HO and TT. The yield of soluble material from the 400 °C reaction is over 90 wt% with the product exhibiting a softening point of 79 °C and a density of about 1.22 g/cm^3. Increasing the reaction temperature to 425 °C dramatically decreased overall conversion to THF-solubles while producing a tacky, room temperature solid. Coke yields of the products derived at both reaction temperatures are similar, around 40 wt%. Observation of the optical texture of the green cokes indicates that the lower reaction temperature for this system produced a more anisotropic carbon.

Table 9. Effects of temperature on properties of THF-soluble pitches. [3.4 MPa H_2, 1 Hour Reaction, 2:3:3 wt: wt:wt Coal:HO:TT]

Temperature °C	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%	Ash Content, wt%
400	91.1	79.0	1.221	39.6	<0.1
425	64.6	Tacky Solid	----	40.1	<0.1

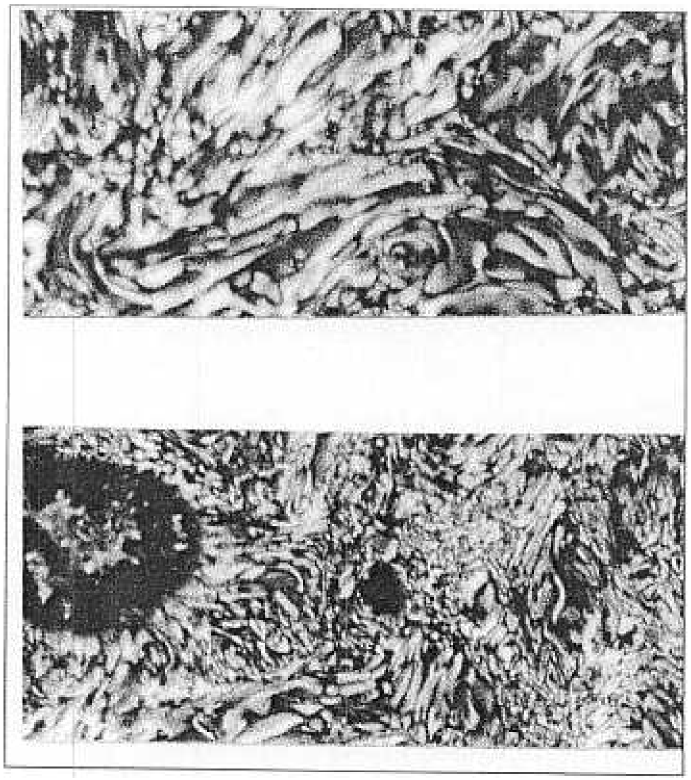

Figure 8. Effects of temperature on green coke structure after co-processing coal with HO and TT. [3.4 MPa H_2, 1 Hour Reaction, 2:3:3 wt:wt:wt Coal:HO:TT]. Top, 400°C; Bottom, 425°C. Scale: 1 inch = 145 μm.

The results of co-processing HO and TT at 400 and 425 °C in the absence of coal are shown in Table 10 and Figure 9. The products following co-processing remain highly soluble in THF for both reaction temperatures, exhibit low softening points, and produce moderately high coke yields. The coke structures are also relatively anisotropic.

Table 10. Effects of temperature on properties of THF-soluble pitches. [3.4 MPa H_2, 1 Hour Reaction, 1:3 wt:wt HO:TT]

Temperature °C	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%	Ash Content, wt%
400	98.1	106.1	1.222	47.8	<0.1
425	93.6	101.8	1.234	47.4	<0.1

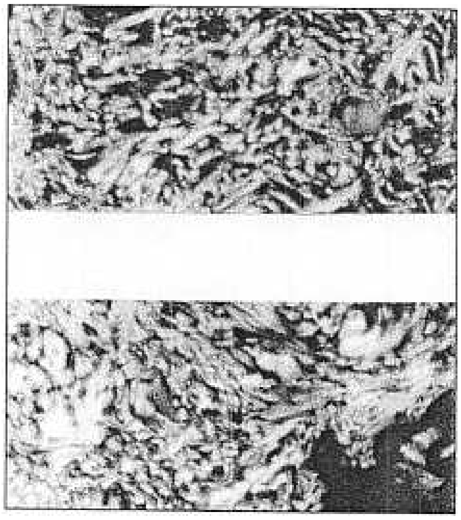

Figure 9. Effects of temperature on green coke structure after co-processing HO with TT. [3.4 MPa H_2, 1 Hour Reaction, 1:3 wt:wt HO:TT]. Top, 400°C; Bottom, 425°C. Scale: 1 inch = 145 μm.

The THF-insoluble residues were examined by optical microscopy under polarized light to detect the presence of anisotropic structures, i. e., mesophase. Mesophase is formed as the result of polymerization reactions and its presence can be used to monitor the progress of co-processing. All of the residues for the reactions reported this month contained mesophase, as shown by the example for one of the experiments in Figure 10. This observation suggests that not enough available hydrogen was present during co-processing.

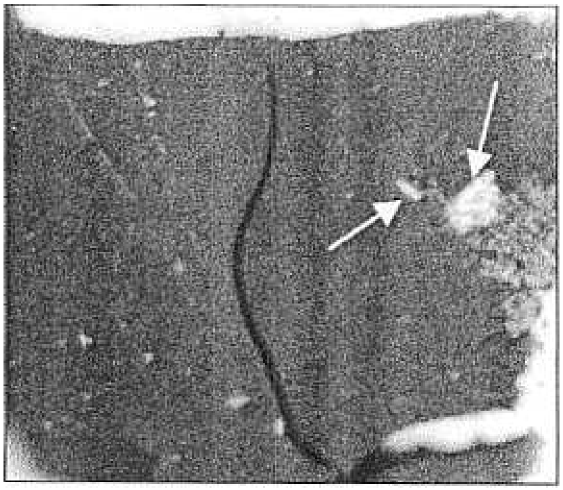

Figure 10. Photomicrograph indicating the presence of mesophase in the THF-insoluble residue. Coal:HO:TT, 400 °C, 3.4 MPa H_2, 1 Hour. Scale: 1 inch = 62 μm.

The effects of the amount of tetralin added to the coal:HO system are presented in Table 11. At the 0 wt% tetralin addition, the THF-soluble product is a tacky solid at room temperature while the coke yield from this material is very low, a little over 6 wt%. Increasing the amount of tetralin to 11 wt% slightly increased conversion from 92.5 to 94.1 wt%, but resulted in nearly tripled the coke yield from 6.5 to 17.6 wt%. Increasing the amount of tetralin further to 33 wt% produced a pitch-like substance with a softening point about 118 °C and a coke yield approaching 47 wt%. The reduction in overall conversion at the 33 wt% tetralin level appears anomalous and the experiments may have to be repeated.

Table 11. Effects of tetralin addition on properties of THF-soluble pitches. [3.4 MPa H_2, 425°C, 1 Hour Reaction, 1:3 wt:wt Coal:HO]

Tetralin, wt%	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%		Ash Content, wt%
0	92.5	Tacky Solid	----	6.5		<0.1
11	94.1	Tacky Solid	----	17.6		<0.1
33	84.6	117.9	1.254	46.2		<0.1

All of the green cokes are relatively anisotropic, as shown in Figure 11. However, the pitch product obtained by reacting coal:HO with 33 wt% tetralin produced after carbonization a coke with extensive flow anisotropy.

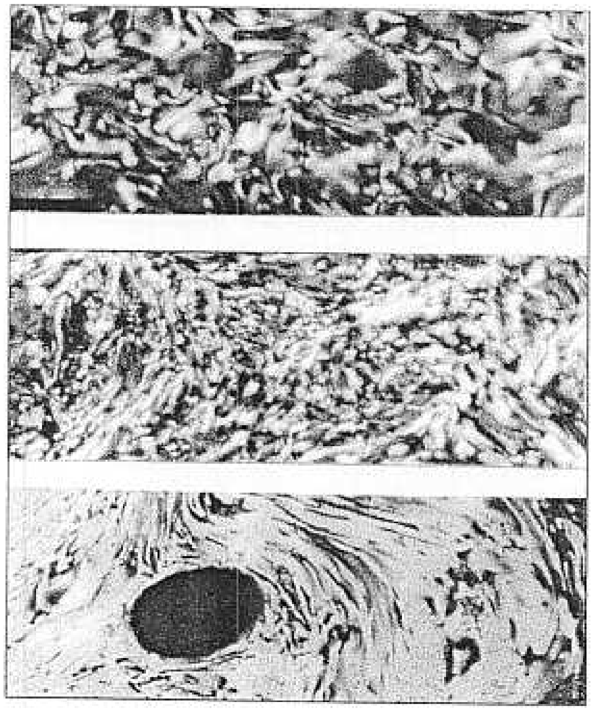

Figure 11. Effects of tetralin content on green coke structure after co-processing coal with HO. [3.4 MPa H_2, 425°C, 1 Hour Reaction, 1:3 wt:wt Coal:HO]. Top, 0 wt%; Middle, 11 wt%; Bottom, 33 wt%. Scale: 1 inch = 145 µm.

Data on the effects of tetralin on the character of products from co-processing coal with HO and TT are presented in Table 12. The yield of soluble material without tetralin is about 65 wt% and corresponds roughly to the proportion of HO and TT, i.e., very little coal was solubilized under these conditions. Conversion increased nearly 30 wt% after the addition of 11 wt% tetralin, producing a solid material with a softening point of 78 °C. Further increases in tetralin during the co-processing reaction appear to decrease conversion somewhat. Nevertheless, as the proportion of tetralin increases, there is an increase in softening point temperature, density, and coke yield.

Figure 12 shows the development of coke structure. Similar to the results using coal and HO, the material processed with 33 wt% tetralin produced a coke with the highest extent of anisotropy.

Table 12. Effects of tetralin addition on properties of THF-soluble pitches. [3.4 MPa H_2, 425°C, 1 Hour Reaction, 2:3:3 wt:wt:wt Coal:HO:TT]

Tetralin, wt%	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%	Ash Content, wt%
0	64.6	Tacky Solid	----	40.1	<0.1
11	92.5	78.0	1.230	41.3	<0.1
33	87.2	107.8	1.235	47.6	<0.1

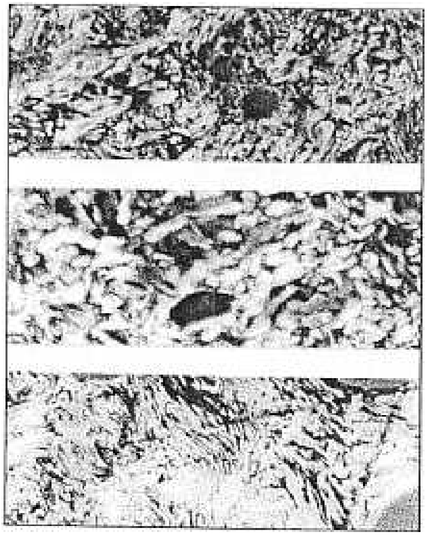

Figure 12. Effects of tetralin on green coke structure after co-processing coal with HO and TT. [3.4 MPa H_2, 425°C, 1 Hour Reaction, 2:3:3 wt:wt:wt Coal:HO:TT]. Top, 0 wt%; Middle, 11 wt%; Bottom, 33 wt%. Scale: inch = 145 μm.

The results of co-processing HO and TT with tetralin and in the absence of coal are shown in Table 13. Total conversion for this system is over 90 wt% without tetralin, though conversion increases as the proportion of tetralin increases. Softening point varies, but the density of the product systematically decreases as the amount of tetralin in the reaction mixture increases. Coke yields are all similar at about 50 wt%. All of the coke structures are anisotropic, as shown in Figure 13.

Table 13. Effects of tetralin addition on properties of THF-soluble pitches. [3.4 MPa H_2, 425°C, 1 Hour Reaction, 1:3 wt:wt HO:TT]

Tetralin, wt%	Yield THF-Soluble, daf	Mettler Softening Point, °C	Density, g/cm^3	Coke Yield, wt%	Ash Content, wt%
0	93.6	101.8	1.234	47.4	<0.1
11	97.1	96.4	1.228	50.9	<0.1
33	99.0	116.8	1.217	49.5	<0.1

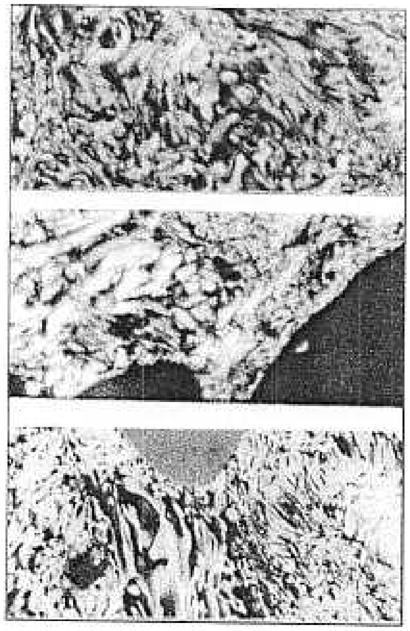

Figure 13. Effects of tetralin content on green coke structure after co-processing HO with TT. [3.4 MPa H_2, 425°C, 1 Hour Reaction, 1:3 wt:wt HO:TT]. Top, 0 wt%; Middle, 11 wt%; Bottom, 33 wt%. Scale: 1 inch = 145 μm.