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PETROGRAPHIC CHARACTERIZATION OF THE SOLID PRODUCTS OF COAL–PITCH COPROCESSING*

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ABSTRACT

Petrographic studies were conducted on four solid residues resulting from the hydrogenation process of 1) Forestburg sub-bituminous coal alone, 2) the coal with a non-coking solvent (anthracene oil), 3) pitch (Cold Lake vacuum-bottom deposits), and 4) a mixture of coal and pitch. The purpose was to determine the amounts of coal- and pitch-derived solids in the residues. All the residues were produced under identical severe conditions of liquefaction to promote the formation of solids. The coal processed with anthracene oil gives a residue consisting mainly of isotropic huminitic solids. If the coal is hydrogenated under similar conditions but without a solvent, the predominant residual solids are anisotropic semicokes displaying coarse mosaic textures, which form from vitroplast. The residual products from the hydrogenated Cold Lake vacuum-bottom deposits are also dominantly anisotropic semicokes; these display coarse mosaics and flow textures, and form by the growth and coalescence of mesophase spherules. Both coal- and pitch-derived solids are identified in a residue produced by coprocessing the Forestburg coal with the pitch from the Cold Lake vacuum-bottom deposits. It is concluded that the huminite macerals in the coal generate the fine-grained, mosaic-textured semicokes, whereas the pitch produces the coarse mosaics and flow-textured semicokes.

Keywords: sub-bituminous coal, pitch, hydrogenation, petrography, coprocessing of coal and pitch, semicokes, vitroplast.

SOMMAIRE

On a examiné, au microscope polarisant, quatre résidus solides d'un processus d'hydrogénation. Ceux-ci dépendent du matériau hydrogéné; 1) charbon sous-bitumineux de Forestburg, 2) ce même charbon avec solvent non-cokéfiant (huile d'anthracène), 3) poix (fonds de Cold Lake), seule, et 4) mélange de charbon et de poix. Notre but est de permettre la détermination des quantités de solides dérivés soit du charbon, soit de la poix dans des résidus tels que 4). Tous les résidus ont été produits dans des conditions identiques de liquéfaction conçues pour favoriser la formation de résidus solides. Le charbon hydrogéné en présence d'huile d'anthracène (2) laisse un résidu qui consiste surtout en solides huminitiques isotropes. Si le charbon est hydrogéné dans les mêmes conditions, sauf sans solvant (1), les solides résiduels prédominants sont surtout des semi-cokes à texture mosaïque grossière, formée à partir du vitroplaste. Les produits résiduels des fonds de Cold Lake hydrogénés (3) sont les mêmes qu'en (1), sauf addition de textures d'écoulement, formées par la croissance et la coalescence de sphérules de mésophases. Les solides dérivés tant du charbon que de la poix ont été identifés dans un résidu provenant de l'hydrogénation simultanée du charbon gras de Forestburg et de la poix des fonds de Cold Lake (4). En conclusion, les solides d'huminite du charbon produisent le semi-coke à grain fin et texture mosaïque, tandis que la poix produit le semi-coke à mosaïque grossière et textures d'écoulement.

(Traduit par la Rédaction)

Mots-clés: charbon sous-bitumineux, poix, hydrogénation, pétrographie, traitement simultané de charbon et de poix, semi-cokes, vitroplaste.

INTRODUCTION

In the coprocessing of coal and pitch, the hydrotreatment of pitch and the hydroliquefaction of coal are combined into one process, and the liquid products are derived either from the coal or the pitch or both. However, it is impossible to calculate the extent of conversion of either the pitch or the coal unless the amounts of insoluble coal or pitch-derived solids (or both) in the product residues are known. At present, it is assumed that all of the tetrahydrofuran-insoluble residue obtained by coal–pitch coprocessing is derived from coal. Previous studies at the Energy Research Unit (1981) have shown that if we assume that all of the residue is coal-derived, a negative value is sometimes obtained for the percentage of coal converted. In this case, not all of the THF-insoluble residue can be coal-derived; some of it must come from the pitch. Kelly (1981) showed that at a low partial pressure of hydrogen, pitch behaves differently under coprocessing conditions than when it is processed alone. He also showed that one cannot simply subtract the THF-insoluble products obtained from the hydrotreatment of pitch alone from the THF-insoluble products formed under coprocessing conditions in order to obtain a true value for coal conversion.

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Petrographic methods normally used to study minerals, *e.g.*, reflected-light microscopy, are used to determine whether coal- and pitch-derived solids can be identified and distinguished in the residues generated by coprocessing coal and pitch. Since pitch cannot be studied using oil-immersion techniques, detailed studies of the coal feedstock and residues generated by processing the coal alone, with and without a hydrogen-donor solvent, are necessary in order to determine the behavior of the coal macerals. Moreover, the effects of mineral matter, which can either be indigenous to the coal or involved in catalytic reactions in the coprocessing of coal and pitch, can be studied as part of the analysis of coal feedstocks and hydrogenation residues by optical microscopy.

In the present study, a series of experiments was conducted using Forestburg sub-bituminous coal and pitch obtained by vacuum distillation of Cold Lake heavy oil (Cold Lake vacuum bottoms); the coal and the pitch were hydrogenated separately under similar process conditions and then processed together. Quantitative microscopic petrography, supplemented by semiquantitative elemental analysis by scanning-electron microscopy with energy-dispersion X-ray spectroscopy, was used to characterize the coal-derived and pitch-derived solids in the residues.

TABLE 1. SAMPLE DESCRIPTIONS AND PROCESSING CONDITIONS

SAMPLE NO.	DESCRIPTION	PROCESS
SBC 1	Forestburg Subbituminous Coal	-
AC 2	Hydrogenated SBC 1	Hydrogenation in Anthracene Oil[1]
HB 3	Hydrogenated Pitch	Hydrogenation[1]
HC 4	Hydrogenated SBC 1	Hydrogenation[1]
HC/B 5	Hydrogenated SBC 1/Pitch	Hydrogenation[1]

[1] under severe conditions

TABLE 2. PREPARATION OF REFERENCE SAMPLES

SAMPLE NO.	WT. OF COAL CHARGE (g)[1]	WT. OF SOLVENT OR PITCH (g)	WT. OF THF-INSOLUBLE RESIDUE(g)[2]
AC 2	20.0	60.0	12.0
HB 3	-	80.0	20.8
HC 4	25.0	-	10.2
HC/B 5	10.0	30.0	13.3

[1] includes moisture and ash

[2] includes ash

EXPERIMENTAL

A series of batch autoclave-hydrogenation experiments using Forestburg sub-bituminous coal and pitch, obtained by the vacuum distillation of Cold Lake heavy oil (vacuum bottoms), were run under severe process-conditions to promote the formation of solids for petrographic examination. Four experiments were conducted using the same conditions. Firstly, the coal was hydrogenated with a non-coking, hydrogen-donor solvent (anthracene oil); secondly, the coal was hydrogenated without a solvent; thirdly, the pitch was hydrogenated alone; finally, a coal–pitch mixture was hydrogenated. The sample numbers of the residues analyzed and brief descriptions of the samples are given in Table 1. Table 2 gives the amounts of coal and pitch used in each experiment, together with the amounts (weight %) of THF-insoluble residue obtained. Petrographic and analytical data for both the coal and the pitch are given in Tables 3 and 4.

SAMPLE PREPARATION AND ANALYTICAL METHODS

Petrographic analysis

Polished pellets of coal and THF-insoluble residue were prepared for analysis by microscopy. Approximately 2–3 g of sample were mounted in epoxy resin, which was allowed to set in a vacuum oven, at 50°C, for eight minutes and then in air, for two to three hours. The mounted samples were ground on 600-grade carborundum paper and then polished on a rotating selvyt cloth-covered lap using 2.0 μm, 0.2 μm and 0.01 μm grades of alumina, respectively, and water.

Petrographic analyses of the coal and the residues were conducted using a Leitz Orthoplan-pol MPV II microscope photometer system. Quantitative analyses were carried out by point counting using a Swift automatic point counter and a Leitz click-stop sample holder; each analysis was based on a total of 500 points. Quantitative analysis of the residue components was facilitated by the insertion of a λ plate in the vertical illuminator; this enhanced the optical characteristics of the anisotropic components. Reflectivity was measured on eu-ulminite B in the feed coal and on the corresponding residue component, under standardized conditions (546 nm, oil immersion, *etc.*). Random reflectance ($R_{oil}m$) was measured on the coals, but maximum ($R_{oil}max$) and minimum ($R_{oil}min$) values of reflectance were measured on the residue components and $R_{oil}m$ calculated according to the method in Ting (1978).

Scanning-electron microscopy – energy-dispersion X-ray spectrometry (SEM-EDS)

Coal macerals and residue components were selected for elemental analysis by SEM–EDS from the mounted, polished samples during routine petrographic analysis. The subject areas were circumscribed using an eccentric diamond indentor, and surface maps and photomicrographs were made to facilitate the relocation of these areas in the SEM (Energy Research Unit 1981). The mapped, polished pellets were sputter-coated with gold and analyzed with a Cambridge Instruments Stereoscan 100 SEM with a Kevex 7000 EDS system. The difficulty in obtaining accurate images of polished samples was overcome by operating in the low-angle, backscattered-electron mode. Semiquantitative analyses for minor elements with an atomic number greater than 10 (Ne) were conducted using the Quantex microanalysis software system on the Kevex with MAGIC V quantitative corrections. The results (Table 7) do not give the actual concentrations of the elements, but the ratios of the elements Al, Si, S and Fe in any sample, and the changes in these ratios from sample to sample, are valid.

PETROGRAPHY OF HYDROGENATION RESIDUES

Petrographic studies of the residual solids from coal-liquefaction processes by Mitchell *et al.* (1977), Shibaoka & Ueda (1978), Shibaoka & Russell (1981), Ng (1983), MacKay *et al.* (1984) and Diessel & Guyot (1985) have contributed greatly to our understanding of the behavior of coal macerals in coal liquefaction. It is important in coal–pitch coprocessing, as in coal liquefaction, to identify unaltered coal, altered or reacted coal and intermediate products such as vitroplast, which derives from vitrinite by hydrogenation in the presence of a solvent (Mitchell *et al.* 1977), or hydroplast, analogous material that forms by hydrogenation of vitrinite in the absence of a solvent (Shibaoka & Russell 1981). These constituents are collectively referred to as *plasticoal* by Shibaoka & Russell (1981); Diessel & Guyot (1985) prefer the term *coagulant*. The International Committee for Coal Petrology (1985) deems all of these terms synonymous and recommends the use of *vitroplast*. The present authors concur with the recommendations of the ICCP, although it is appropriate in this study to retain the use of the term *hydroplast* when no solvent is used.

End products, such as a *granular residue* (Mitchell *et al.* 1977) and semicokes, also occur; the latter components are particularly abundant in the residues examined by the authors because of the severe process-conditions used. Semicokes, which are characteristically anisotropic, result from the carbonization of numerous coal-derived components such as the altered coal, vitroplast or hydroplast, (Shibaoka *et al.* 1980) and accordingly display a variety of optical textures ranging from fine-grained to coarse mosaics. They resemble the products of coal carbonization described by Patrick *et al.* (1973).

Solids arising from the pitch may be present in coal–pitch coprocessing residues in addition to coal-derived ones (Energy Research Unit 1982, 1983).

TABLE 3. PETROGRAPHY OF FORESTBURG COAL

MACERAL GROUP[1]	MACERAL SUBGROUP[1]	MACERAL[1]	%
HUMINITE	Humotelinite	Ulminite	74.1
	Humodetrinite	Densinite	15.0
	Humocollinite	Gelinite	2.9
LIPTINITE		Sporinite	1.3
		Liptodetrinite	0.7
INERTINITE		Fusinite	0.7
		Semifusinite	0.8
		Inertodetrinite	1.4
MINERAL MATTER			0.7
REFLECTANCE, R_{om}[2]			0.42

[1] according to the International Committee for Coal Petrology, 1975

[2] mean random reflectance measured on eu-ulminite B

TABLE 4. ANALYTICAL DATA FOR COAL AND PITCH

	FORESTBURG COAL	COLD LAKE VACUUM BOTTOMS PITCH
Moisture[1], wt.%	19.10	-
Ash[1], wt.%	7.68	-
Volatile Matter[1], %	34.00	-
Fixed carbon[1]	39.10	-
Carbon[2], wt.%	64.04	78.60
Hydrogen[2], wt.%	3.87	9.30
Nitrogen[2], wt.%	1.65	0.60
Sulphur[2], wt.%	0.053	5.50
Ash,[2] wt.%	9.50	0.00
Oxygen[2,3]	20.41	5.90
Nickel, ppm	18.00	93
Vanadium, ppm	trace	235
Iron, ppm.	2,379.00	18
Specific gravity (at 15/15°C)	-	1.038
Conradson carbon residue, wt.%	-	17.10
Asphaltenes, wt.%	-	23.48
Preasphaltenes, wt.%	-	0.28
Aromaticity %	-	34.50
Viscosity (poise)		
at 80°C	-	249.12
at 100°C	-	39.40
at 110°C	-	21.59
Distillation[4]:		
Initial boiling point, °C	-	420
Distillate (at-525°C), wt.%	-	16.75
Residue (at 525°C), wt.%	-	83.25

[1] as received

[2] dry basis

[3] by difference

[4] by spinning band method

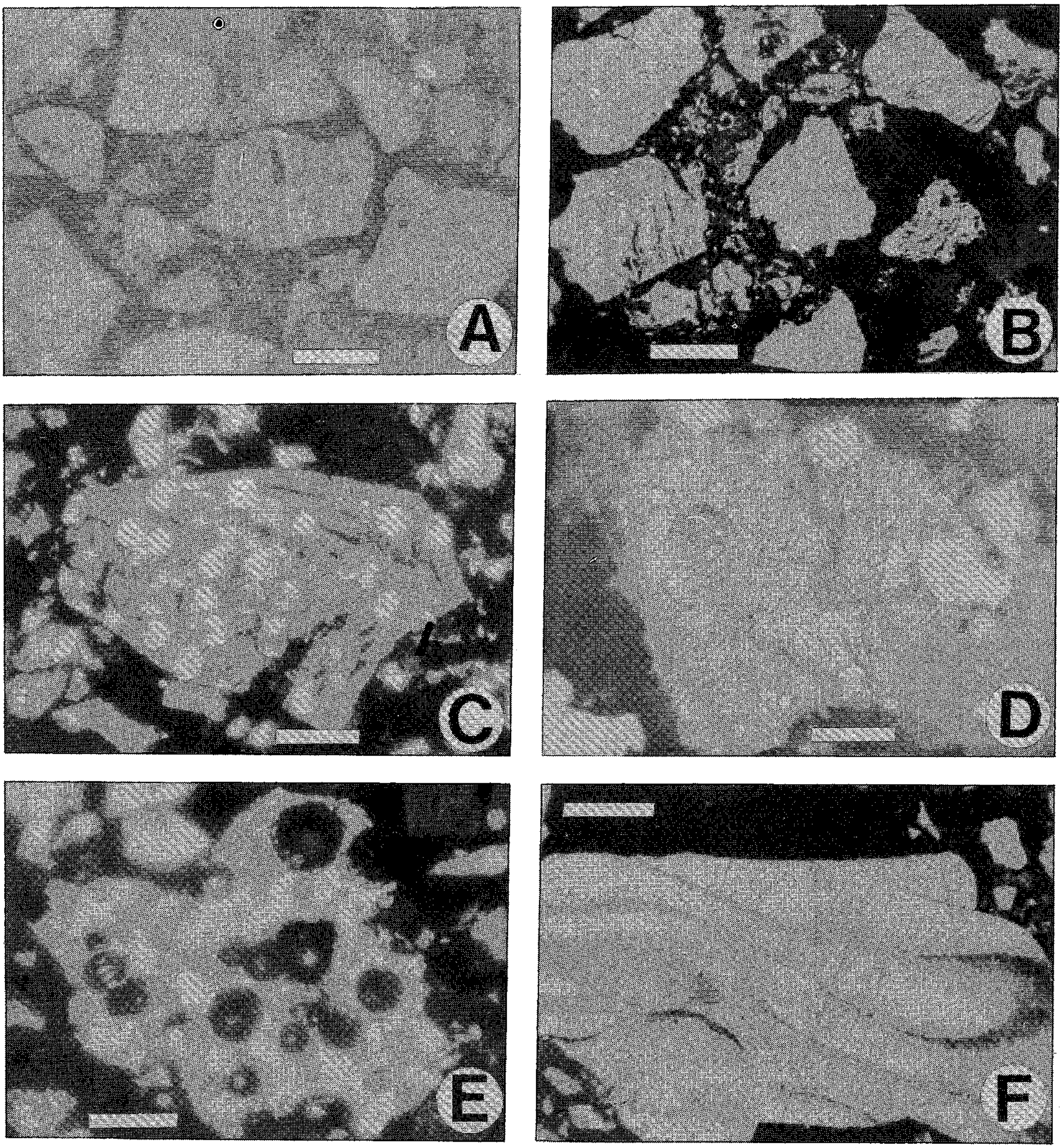

FIG. 1. A. SBC 1. Huminite-rich Forestburg coal, $R_{oil}m$ 0.42%, showing liptinite and inertodetrinite. Plane-polarized light. B. AC 1. Isotropic, vesicular huminite char, $R_{oil}m$ 1.67%, with granular isotropic residue, Forestburg coal char. Plane-polarized light. C. HB 3. Mesophase spherules forming in isotropic solids, $R_{oil}m$ 0.42%, exhibiting characteristic shrinkage. Hydrogenated pitch. D. HB 3. Anisotropic mesophase and mosaic-textured semicoke, $R_{oil}m$ 2.3%, forming from granular isotropic solids. Hydrogenated pitch. E. HB 3. Vesicular, anisotropic semicoke formed by growth and coalescence of mesophase spherules. Hydrogenated pitch. F. HB 3. Flow-textured anisotropic semicoke. Hydrogenated pitch. Bar represents 200 μm. Unless indicated, the photomicrographs were taken with partly crossed polars.

Whereas some may be isotropic, they are most likely to be anisotropic carbonized products because of the severe process-conditions used. Marsh *et al.* (1973) and Brooks & Taylor (1966) described anisotropic semicokes produced by the carbonization of coal-tar pitches and petroleum pitches, respectively, and Grint *et al.* (1979) described cokes obtained by the cocarbonization of coals with petroleum pitch, in which the addition of the pitch significantly modified the optical textures of the resultant coke from the coal. Ragan & Marsh (1981) described "intermediate" cokes with mosaic textures, formed by solution of coal in pitch, during coal–pitch cocarbonization.

RESULTS

Coal feedstock

The coal feedstock is a sample of Cretaceous coal from the Forestburg Collieries, southeastern Alberta. The petrographic and chemical characteristics are shown in Tables 3 and 4, respectively. Petrographically, the Forestburg coal is huminite-rich (total huminites, 94.4 vol.%), with small amounts of liptinite macerals (2.0 vol.%), inertinites (2.9 vol.%) and minor mineral matter (0.7 vol.%) (Fig.1a). The reflectance (R_{oil}m), measured on eu-ulminite B, is 0.42%.

THF-insoluble products of hydrogenation

The weights of coal and pitch used in each of the four experiments are shown in Table 2. The weight of the THF-insoluble residue HC/B5 is greater than the initial charge of coal, indicating that the residual solids are derived, in part, from the pitch. The petrographic characters of the THF-insoluble products of hydrogenated coal (HC4), coal–anthracene oil (AC1), pitch (HB3) and the coal–pitch mixture (HC/B5) are shown in Tables 5 (composition) and 6 (reflectance).

TABLE 5. PETROGRAPHY OF THF-INSOLUBLE PRODUCTS OF HYDROGENATION

SAMPLE NO.	AC 2	HB 3	HC 4	HC/B 5
	%	%	%	%
Altered coal				
(i) isotropic:				
huminitic solids	86.6	-	-	41.6
granular residue	9.8	-	-	-
vitroplast[1]/hydroplast[2]	0.2	-	1.0	-
inertinite	0.4	-	-	0.4
(ii) anisotropic semicokes:				
fine-grained mosaics	2.8	-	59.2[3]	31.2
medium-grained mosaics	-	-	13.6[3]	1.0[3]
coarse mosaics	-	-	25.2[3]	-
coarse-flow textures	-	-	1.0[3]	-
(iii) mineral matter	0.2	-	-	-
Altered pitch				
(i) isotropic solids	-	6.6	-	0.6
(ii) anisotropic semicokes:				
mesophase spheres	-	1.2	-	0.8
coarse mosaics	-	32.4	-	11.8
coarse-flow textured	-	26.2	-	9.8
flow textured	-	3.4	-	-
fine-grained mosaics	-	0.2	-	-
fines	-	30.0	-	2.8
	100%	100%	100%	100%

[1] after Mitchell et al. (1977)
[2] after Shibaoka & Russell (1981)
[3] from vitroplast/hydroplast

TABLE 6. REFLECTANCE[1] OF THF-INSOLUBLE COMPONENTS OF LIQUEFACTION RESIDUES (%)

SAMPLE NO.	AC 2	HB 3	HC 4	HC/B 5
Altered Coal				
huminitic solids	1.67		0.7	1.6
vitroplast/hydroplast	-	-	0.4	-
semicoke (coarse mosaic)				
$R_o$max	-	-	2.5	-
$R_o$min	-	-	1.5	-
R_om	-	-	2.3[3]	2.3[2]
Pitch				
isotropic residue	-	0.42	-	2.4
semicoke (coarse mosaics)				
$R_o$max	-	2.3	-	2.4
$R_o$min	-	1.4	-	1.4

[1] unless specified, refers to % random (mean) reflectance, R_om.
[2] measured
[3] calculated according to Ting (1978)

Coal hydrogenated with anthracene oil (AC2)

The THF-insoluble products of coal (SB1) hydrogenated in anthracene oil are predominantly isotropic solids. The bulk of the altered coal (86.6%) consists of isotropic huminitic solids (Fig. 1B) having a reflectance R_{oil}m of 1.67% (Table 6) and a granular residue (9.8%), also shown in Figure 1B. Very small amounts of vitroplast (0.2%) are present, and small quantities of the granular residue (2.8%) are anisotropic and consist of fine-grained mosaic-textured semicoke.

Hydrogenated pitch (HB3)

The THF-insoluble products of the hydrogenated pitch are principally anisotropic semicokes (R_{oil}max 2.3%, R_{oil}min 1.4%). Small quantities of isotropic solids are present (R_{oil}m 0.42%), and commonly anisotropic mesophase spherules are observed forming in the isotropic matrix (Fig. 1C). Ultimately, this leads to shrinkage of the matrix (Fig. 1D) and the formation of coarse mosaic-textured semicokes by growth and coalescence of the mesophase spherules (Fig. 1E). The textures of the semicokes range from coarse mosaics to flow types (Fig. 1F).

Hydrogenated coal (HC4)

The THF-insoluble products of hydrogenation of the coal (SBC1) without solvent are very different from those of the coal hydrogenated with solvent (AC2). The coal-derived solids are almost entirely (99%) composed of anisotropic semicokes derived from hydroplast (Fig. 2A), altered huminitic solids (Fig. 2B) and coal-derived liquids (Fig. 2C). The isotropic hydroplast (1%) is weakly reflective (R_{oil}m 0.43%), with a range of reflectivity similar to that

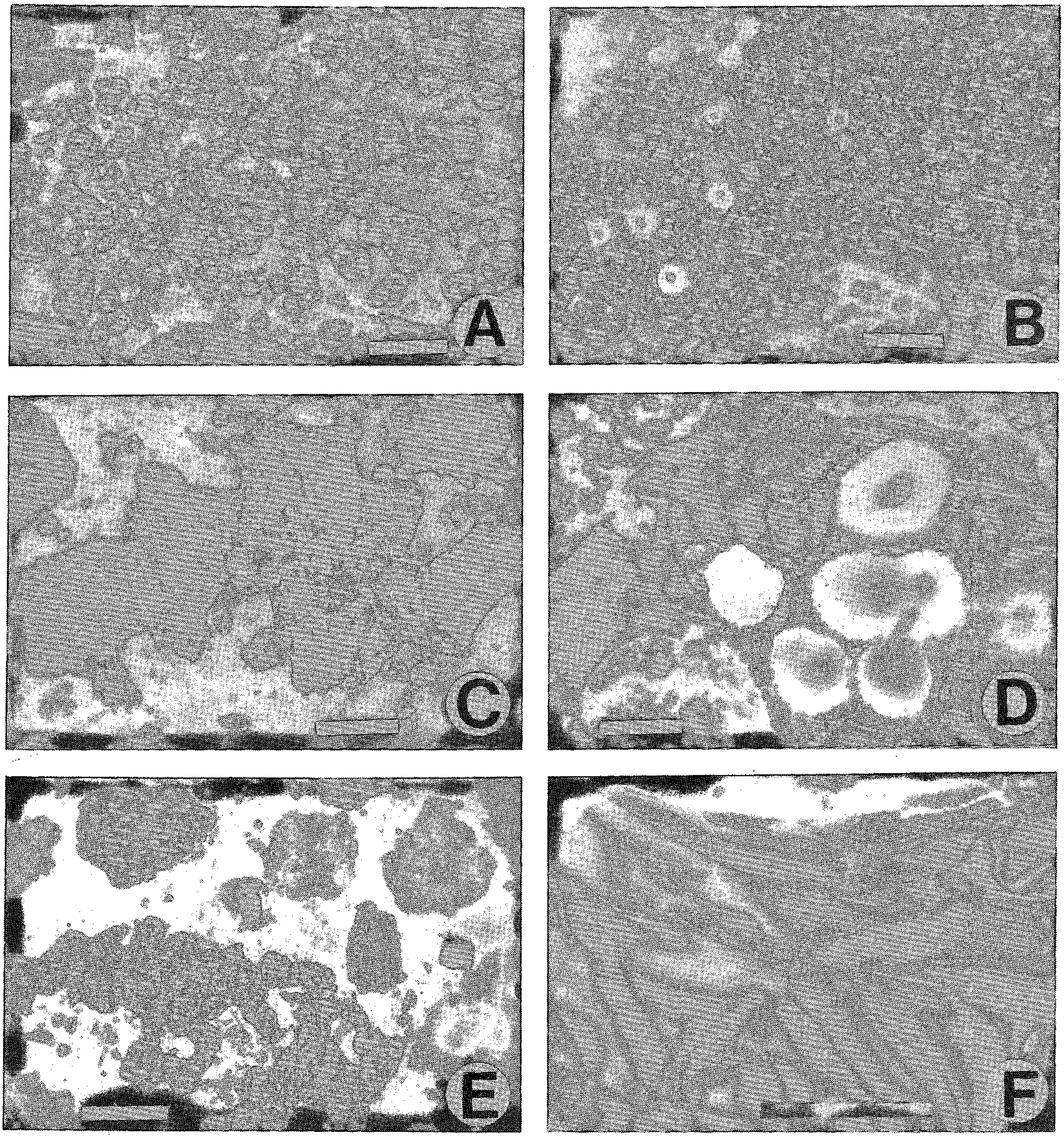

FIG. 2. A. HC 4. Hydroplast showing fine-grained mosaic texture. Anisotropic semicoke from hydrogenated Forestburg coal. B. HC 4. Fine- to medium-grained mosaic-textured anisotropic semicoke from hydroplast. Hydrogenated Forestburg coal. C. HC/B 5. Isotropic huminite-derived coal char, $R_{oil}m$ 1.6%, and anisotropic medium grained mosaic-textured semicoke from coal-derived liquid. Hydrogenated Forestburg coal/pitch. D. HC 4. Coarse mosaic-textured, vesicular semicoke. Hydrogenated Forestburg coal. E. HC/B 5. Very fine-grained, anisotroipic mosaic-textured semicoke derived from vitroplast/huminite. Hydrogenated Forestburg coal/pitch. F. HC/B 5. Flow-textured anisotropic semicoke derived from pitch . Hydrogenated Forestburg coal/pitch. Bar represents 200 μm. All photomicrographs were taken with partly crossed polars.

of the isotropic matrix in the hydrogenated pitch, HB3 (Table 6).

Hydrogenated coal-pitch (HC/B5)

The THF-insoluble residue is derived from both coal (74.2%) and pitch (25.8%); 57.4% of the residue consists of anisotropic semicokes, and the remainder is isotropic. The optical characters of the pitch-derived solids closely resemble those of HB3, and the dominant components occur in similar proportions. In contrast, the coal-derived solids are more reminiscent of AC2, *i.e.*, the products of the hydrogenation of coal with a hydrogen-donor solvent.

More than half of the coal-derived solids are isotropic, altered huminitic solids (Fig. 2C). The anisotropic solids range from very fine to fine granular mosaic-textured semicokes, which form by carbonization of huminites, to interparticulate medium-grained mosaics (Fig. 2C), which are probably carbonized vitroplast or coal-derived liquids. Some of the vitroplast exhibits fine- to medium-grained mosaics (Fig. 2E). The reflectance of the isotropic huminitic solids (R_{oil}m 1.6%) is the same as in AC2, and for the anisotropic, coal-derived semicokes, the measured reflectance (R_{oil}m 2.3%) is the same as the calculated R_{oil}m value obtained for semicokes in HC4 (Table 6).

The pitch-derived components consist of anisotropic semicokes that exhibit coarse mosaic, coarse-flow and flow-type anisotropy (Fig. 2F). The reflectance values obtained on the coarse mosaic semicokes are approximately the same as those of HB3 (R_{oil}max 2.4%, R_{oil}min 1.4%), but they are also similar to the values obtained from the coarse mosaic-textured semicokes that form from the hydroplast, in HC4.

Elemental analysis by SEM-EDS

The results of semiquantitative elemental analysis of the feed-coal macerals and hydrogenation-residue components are shown in Table 7. In the coal macerals and coal-derived residues AC2 and HC4, the elements aluminum, silicon, sulfur and iron are present in most components. The sulfur is undoubtedly organic in origin since pyritic sulfur was not identified by petrographic analysis; the aluminum, silicon and iron probably represent finely dispersed clay minerals too small to be identified by petrographic analysis, but inherent in the coal feedstock and subsequently inherited by the residue components when the coal is processed. Furthermore, the proportions of Al, Si and S in the coal-derived residual solids in AC2 and HC4, in particular the anisotropic fine- and medium-grained mosaic-textured semicokes, are consistent with those shown by the huminites and the mineral constituents in the coal feedstock (SB1), although the mineral constituents identified in the coal feedstock contain slightly more silicon than the huminites, and the coal-derived semicokes appear to lack iron. In the coarse mosaic-textured semicoke in HC4, which, on the basis of the petrographic analysis, forms either from hydroplast or coal-derived liquid, Al, Si and S are present in proportions similar to those in the huminite macerals.

Silicon and sulfur are also present in the coarse-mosaic and flow-type semicokes formed by the hydrogenation of the pitch in HB3. They also occur, with Al, in the components identified by petrographic analysis as pitch-derived solids, in the hydrogenated coal–pitch residue, HC/B5. The con-

TABLE 7. SEMIQUANTITATIVE ELEMENTAL ANALYSIS OF COAL AND COAL-PITCH COPROCESSING RESIDUE COMPONENTS

		Relative proportions (%) of minor elements ±0.4				
Sample No.	Component	Al	Si	S	Cl[4]	Fe
	FEED COAL:					
SBC 1	Huminite[1]	7.7	7.2	25.4	4.7	1.4
SBC 1	Humotelinite[1]	8.4	7.1	24.9	5.4	1.1
SBC 1	Inertinite[1]	7.9	6.8	25.4	6.0	0.9
SBC 1	Mineral matter[1]	9.1	11.9	19.6	5.5	2.3
	Mineral matter[1]	6.0	11.3	23.3	5.0	0.9
	Mineral matter[1]	5.3	17.7	20.5	-	0.5
	ALTERED COAL:					
HC 4	Altered huminite[1]	8.6	9.9	20.0	12.8	-
AC 2	Altered humotelinite[1]	6.2	8.0	25.7	5.7	1.0
	Altered humodetrinite[1]	7.0	8.4	24.9	5.4	1.0
	Inertinite[1]	8.4	7.3	24.9	6.5	-
	Inertinite[1]	7.9	6.8	25.9	5.6	0.3
HC 4	Mesophase[2]	9.5	8.9	20.1	12.8	-
HB 3	Mesophase + isotropic solids[3]	4.4	5.3	29.5	6.8	-
AC 1	Mineral matter[1,5]	7.4	4.9	14.1	1.2	14.3
	Mineral matter[1] (large area scan)	7.4	7.4	26.0	4.9	0.2
	Mineral matter[1]	7.5	9.7	25.9	0.3	-
HC/B5	Altered huminite[1]	9.0	6.2	26.5	-	2.9
	ANISOTROPIC SEMICOKES:					
HC 4	Fine-grained mosaics[1]	9.8	8.4	21.2	10.6	-
	Fine-grained mosaics[1]	8.9	9.8	19.8	12.3	-
	Medium-grained mosaics[1]	9.5	8.9	20.3	12.0	0.3
	Medium-grained mosaics[1]	8.9	9.1	20.6	12.2	-
	Coarse-grained mosaics[2]	8.8	8.6	21.2	12.0	-
HB 3	Coarse-grained mosaics[3]	-	5.5	32.1	7.9	-
	Coarse-flow type[3]	-	5.2	32.0	8.8	-
HC/B5	Fine-grained mosaics[1]	9.1	8.4	21.5	11.4	-
	Fine-grained mosaics[1]	8.5	9.1	25.9	-	-
	Fine-grained mosaics[1]	11.5	-	31.4	-	-
HC/B5	Coarse-mosaics[3]	4.5	2.7	34.4	-	-
	Coarse-flow type[3]	5.6	3.4	32.9	-	-
	Coarse-flow type[3]	7.1	-	34.7	-	-
	Coarse-mosaics[3]	7.1	-	34.7	-	-

[1] Source: coal macerals [2] source: vitroplast/coal liquids
[3] Source: pitch [4] Cl from mounting medium [5] Ca: 16.7%

centrations of Al and Si observed in the pitch-derived solids in HC/B5 are lower than those of the coal-derived components; Fe is absent, and S is considerably more abundant. The pitch-derived solids probably accreted around coal-derived mineral matter, which would account for the Al and Si. The high S content is characteristic of degraded oils (Tissot & Welte 1978).

Aluminum, silicon, sulfur and iron are characteristic of the coal-derived residues. Similar signatures are obtained from pitch-derived solids; Si is present in significant amounts, but S is relatively more abundant than in the coal-derived residue components, and there is little or no Al. Petrographic analysis shows that optically similar materials, *i.e.*, coarse-flow and coarse-mosaic-textured semicokes, are major components in the products of coal hydrogenation (HC4), pitch hydrogenation (HB3), and they form 20% of the coal–pitch product, HC/B5 (Table 5). Not only do the semicokes exhibit identical textures in all three residues, but they have almost identical reflectance characteristics (Table 6). It is important to determine the origin of such material in the coal–pitch coprocessing residue.

In the petrographic analysis of the coal–pitch coprocessing residue (HC/B5), the coarse-flow and coarse-mosaic-textured semicokes are tentatively interpreted as derivatives of the pitch, because the coal does not respond as well to hydrogenation in the presence of the pitch under the experimental conditions used, and it does not generate vitroplast or hydroplast, from which the coarse-mosaic-textured semicokes are derived in HC4. The elemental analyses indicate that the coarse-flow and coarse-mosaic-textured semicokes in the coal–pitch coprocessing residue, HC/B5, have high S contents, comparable to those of the pitch-derived semicokes in HB3. This supports the petrographic evidence suggesting that the coarse-flow and coarse-mosaic-textured semicokes are derived from the pitch.

DISCUSSION

The formation of mesophase and, subsequently, anisotropic semicokes by growth and coalescence of mesophase spherules produces anisotropic carbon, which is inert to further hydrogenation (Mitchell *et al.* 1977). The formation of anisotropic semicokes in the solid products of coal hydrogenation not only reduces the yields of liquids but causes reactor fouling and flow-line plugging; it is not uncommon for experiments to be aborted as a result of excessive 'coking'. In order to maximize the yields of coal liquids, it is therefore important, in coal liquefaction, to identify the conditions that affect the formation of anisotropic solids. This is just as important in coal–pitch coprocessing, but in addition, it is necessary to determine whether the semicoke forms from the coal, the coprocessing agent or from intermediate products, so that one can determine the efficiency of the process of coal (or pitch) conversion.

Severe process-conditions, such as those used in this study, promote the formation of anisotropic semicokes in the products of coal–pitch coprocessing. Such conditions are necessary to ensure that the solids produced are dominantly semicokes. Even under severe process-conditions, very little anisotropic semicoke forms as a result of the hydrogenation of sub-bituminous coal with a non-coking solvent such as anthracene oil. The solid product AC2 contains only 2.8% anisotropic semicoke, which forms directly by carbonization of huminite. Almost 10% is a granular residue that contains a large amount of inorganic minerals and is considered to be an end product of the liquefaction of the huminitic and liptinitic components of coal. The bulk of the residue consists of isotropic altered huminitic solids. Although, technically, the use of solvents such as anthracene oil in coal liquefaction reduces the formation of anisotropic semicokes, it is not economically feasible to use because of the high cost of the oil.

In contrast, sub-bituminous coal hydrogenated without a solvent undergoes extensive transformation to hydroplast, and possibly also coal liquids, which subsequently gives rise to large quantities of semicoke. Ninety-nine percent of the hydrogenated product (HC4) consists of anisotropic semicokes. A quarter of these display coarse mosaics, suggesting that the anisotropic units form easily from very plastic or liquid materials (Shibaoka & Ueda 1978).

All but 7% of the hydrogenated pitch (HB3) consists of semicokes that exhibit coarse mosaics, coarse-flow and flow-type anisotropy, indicating that the pitch generates semicoke readily under severe process-conditions. The coarse mosaics are optically similar to the semicokes produced from coal liquids in HC4, so that to distinguish between pitch-derived semicokes and those derived from coal liquids is problematical; elemental analyses of the coarse mosaic-textured semicokes from pitch and coal, by SEM–EDS, indicate that they are different. The pitch-derived semicokes are identified by their relatively high S content. It is therefore not possible to use elemental analyses alone to identify residue components, but elemental analyses can be very useful when used together with petrographic analysis to study residues from coal–pitch coprocessing.

The THF-insoluble products obtained by coprocessing sub-bituminous coal and pitch originate mostly from the coal, and they are not simple composites of the products of the independently processed coal and pitch. The optical characters of the coal-derived semicokes are strongly modified as a result of coprocessing the coal with pitch, which greatly facilitates the identification of coal- and pitch-derived components by petrographic analysis. The coal-derived solids are predominantly isotropic huminitic solids that are extensively carbonized, producing fine-grained and ultrafine-grained mosaic-textured, anisotropic semicokes. The absence of isotropic and anisotropic vitroplast in the residues from coal–pitch coprocessing, together with the smaller grain-size of the mosaics exhibited by the anisotropic coal-derived solids, suggests that coprocessing of the coal with pitch restricts the development of optical anisotropy in the huminitic residue and retards the formation of intermediate components, such as vitroplast, which are susceptible to form anisotropic semicoke. Given that this is the case, it is unlikely that the coarse mosaic-textured semicokes in the coal–pitch coprocessing residue should be derived from vitroplast.

In contrast to the coal-derived solids, the pitch-derived components of the coal–pitch coprocessing residue do not show any textural or optical modifications; they are identical to those obtained by hydrogenation of the pitch alone and display coarse mosaics and coarse-flow anisotropy. Grint *et al.* (1979) observed similar effects when they cocarbonized Ashland A200 petroleum pitch with vitrains; the pitch coke does not change, but the optical characters of the vitrains are variously modified.

CONCLUSIONS

Petrographic analysis, supplemented by elemental analysis using SEM–EDS, can be used successfully to identify and quantify residual solids derived from coal and solids derived from pitch in residues generated by coal–pitch coprocessing. It is therefore possible to calculate realistic values for coal (or pitch) conversion under coprocessing conditions. Studies of the components of residues generated by hydrogenation of the coal, with and without solvents, and the pitch alone, in addition to the solids obtained by coprocessing the pitch and the coal, show that the coal responds quite differently when processed with pitch compared to when it is processed with a solvent such as anthracene oil.

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