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Investigation of retrogressive reactions leading to the carbonization of solvent-refined coal

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The carbonization of solvent-refined coal (SRC) samples produced by the liquefaction of an HVc bituminous coal has been studied. Carbonization conditions were 450°C, 34.4 MPa, for 1 and 5 h hold times. The original SRCs and pyridine-insoluble fractions of the carbonization products have been characterized by Fourier-transform infrared spectroscopy. Spectral changes demonstrate that the formation of larger molecules during carbonization involve the joining together of aromatic molecules that were originally present, without increasing their size significantly. This is accomplished by the elimination of methylene units and condensation of phenolic functional groups originally present on the aromatic groups in the SRCs.

Examination of materials which accumulate within coal-liquefaction reactors (so-called reactor solids) shows that they are composed of mixtures of carbonaceous and inorganic solids^{1,2}. The carbonaceous solids can be divided into two categories; unreacted (or partially reacted) macerals, and those materials which are formed by retrogressive reactions, i.e. soluble components reverting to insoluble semi-cokes. An understanding of these retrogressive reactions is of major significance because it yields information on the propensity for coke formation. Efficient operation of these types of plants will be somewhat dependent on minimizing coking phenomena. In a previous investigation¹ into a coking problem at the Wilsonville Solvent Refined Coal (SRC) pilot plant* it was found, by optical microscopy, that the coke deposits were predominantly composed of insoluble particles (e.g. quartz, calcite and a coke contaminant) surrounded by layers of an anisotropic semi-coke. The mechanism by which anisotropic semi-coke is deposited from SRC onto inert particles involves the production of an intermediate anisotropic phase which resembles a nematic liquid crystal and is referred to as 'mesophase'. The precise nature of mesophase is known to depend upon the chemical structure of the starting material and decisively affects the properties of the coke produced. Consequently, the characteristic anisotropic materials formed from various precursors have been widely investigated³⁻⁵. However, most of these studies have concentrated upon observations of the growth mode and coalescence of mesophase. Relatively little work has been reported concerning the chemistry of these retrogressive reactions. Honda and Yamada⁶ and Yamada *et al.*⁷ utilized a number of techniques, including infrared spectroscopy, to investigate the chemical structure of anisotropic spheres produced during carbonization. It was concluded that the planar molecules incorporated into the spheres consist predominantly of

alkyl-substituted aromatics. Walker⁸ mentioned that the growth of mesophase required an increasing proportion of aromatic molecules of larger size. More recently, Mochida *et al.*³ have suggested that the components of the sphere consist of relatively small condensed-ring compounds connected by methylene bridges.

In this communication we will present an analysis of the chemical changes occurring upon formation of semi-coke from SRC. As will be seen, carbonization of SRC results in both isotropic and mesophase-derived semi-cokes. It is suggested that the retrogressive reactions involved in the production of these materials are essentially the same although they result in solids of varying optical texture. The occurrence of anisotropic semi-cokes reflects the ability of component species to form well aligned structures. This phenomenon is not only a function of the 'chemistry' of the precursors but also reflects the mobility of the species involved. It is well known that SRC contains a wide distribution of species of varying molecular weight, aromaticity, and chemical functionality. Each of these species will have very different propensities to form semi-coke and mesophase. For this reason, it is important to perform also experiments on various SRC fractions if we are to understand the mechanisms involved in the formation of these materials. The fractions used in this investigation were prepared by elution from a silica-gel column using a specific sequence of solvents, as described by Farcasiu⁹. The chemical structure of these fractions has been characterized by Fourier-transform infrared spectroscopy (FTIR), as reported in the preceding paper. We have also applied this technique to the determination of the chemistry of mesophase formation. Although the infrared spectra of carbonized materials are considered amongst the most difficult to obtain¹⁰, the enhanced energy throughput and multiplexing advantages of FTIR¹¹ results in spectra markedly superior to those obtained on conventional dispersive instruments.

*Operated by Catalytic Inc., for Southern Company, Inc., and U.S.D.O.E. and EPRI

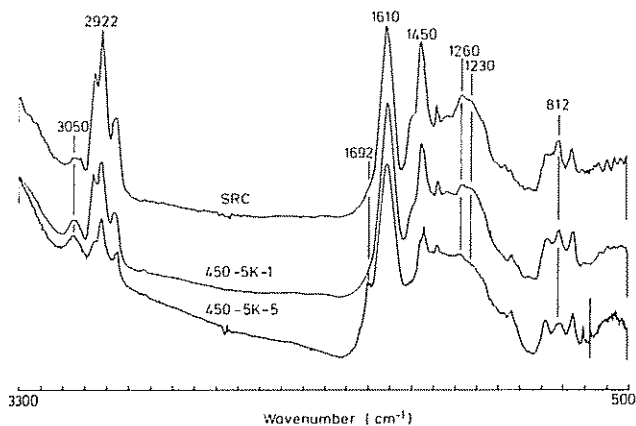


Figure 1 Top: Infrared spectrum of SRC-SC.
Middle: Spectrum of SRC carbonized at 450°C, 34.4 MPa (5000 psi) for 1 h
Bottom: Spectrum of SRC carbonized at 450°C, 34.4 MPa (5000 psi) for 5 h

EXPERIMENTAL

The SRC samples used in this work were produced from Illinois No. 6 coal (Monterey mine). A short-contact-time SRC (SRC-SC), designated 77D-13, and a long-contact-time SRC (SRC-LC), designated SN-18875, were fractionated by sequential elution through a silica-gel column with a specific sequence of solvents by Mobil Research & Development Corporation, using the method described by Farcasiu⁹.

Insoluble semi-coke were prepared from the SRC samples by the so-called 'Gold Tube' technique¹². About 250 mg of SRC is loaded into a gold tube (0.5 cm i.d. × 6 cm long) which is then evacuated and filled with nitrogen. The tube and its contents are cooled with liquid nitrogen and the open end is pinched and welded. Liquid nitrogen is used to ensure that the sample does not undergo carbonization during the welding. The sealed tube is tested for leaks by placing it in boiling water. Heat treatment of the samples is carried out in a hydrothermal pressure vessel. Pressure is applied to the gold tube by a hydraulic compressor, using demineralized water as the transmitting medium. Samples can be heated to final temperature (400 to 600°C) in about 5 to 8 min. Temperatures can be maintained to $\pm 5^\circ\text{C}$ by careful manipulation of a controller.

After a specific period of time the tube is cooled rapidly, the pressure is released, and the sample is removed for further investigation. A known weight of solid from the gold tube experiment is extracted with boiling pyridine. In initial studies to determine a standard set of operating conditions the proportion of pyridine-insoluble material was taken as a measure of the amount of semi-coke formed. This work is reported elsewhere¹³. In order to compare the amount of semi-coke formed from the different SRC fractions, standard carbonization conditions of 450°C at 34.4 MPa (5000 psi) for 1 h (designated 450-5K-1) were used. The pyridine-insolubles characterized by FTIR were also examined by optical microscopy¹³ to determine the extent of mesophase formation.

Infrared spectra were obtained by use of a Digilab 15/B FTS system. Samples were prepared as standard KBr pellets by grinding about 1 mg of material with 300 mg KBr in a Perkin-Elmer Wig-L-Bug for 8 min. In this time period there is no apparent heating of the sample. Four hundred 'scans' (interferograms) of the sample at a resolution of

2 cm^{-1} were co-added to obtain each spectrum. The frequency scale of the instrument is internally calibrated by a He-Ne laser and is accurate to 0.2 cm^{-1} .

RESULTS

The infrared spectrum of the SRC-SC is compared in Figure 1 to spectra of the same sample carbonized for 1 h and 5 h respectively at 450°C and 34.4 MPa. This treatment resulted in 43 wt % of pyridine-insolubles being formed in 1 h, 87 wt % after 5 h. An optical analysis of the carbonized material estimated that after 1 h the volume of anisotropic material present in the pyridine-insoluble fraction is only 18%, but this is increased to 100% after 5 h¹³. For the 1 h material the anisotropic areas consisted of small irregular shapes (0.5 to 1.5 μm); however, in the 5 h sample the mesophase-derived semi-coke was composed of coalesced domains (4 to 8 μm diameter) and of mosaics (0.5 to 2 μm).

Progressive changes were observed in the infrared spectra with increasing carbonization time. The aliphatic C-H stretching bands observed near 2960, 2922 and 2860 cm^{-1} are reduced in intensity after 1 h and finally appear as only weak absorptions after 5 h. The 1450 cm^{-1} band, assigned to methylene and methyl bending vibrations, shows equivalent changes. In contrast, the aromatic C-H stretching modes centred near 3050 cm^{-1} are not appreciably affected by carbonization under these conditions. The bands appearing at 870, 812 and 748 cm^{-1} can be assigned to predominantly aromatic C-H out-of-plane vibrations^{14,15}. The relative intensity of the 870 cm^{-1} to the 748 cm^{-1} band remains unaltered, but the 812 cm^{-1} is significantly weaker after 5 h. However, this is probably not due to a reduction in the amount of aromatic C-H or the pattern of substitution, since the 870 and 748 cm^{-1} bands should also be affected by such factors. More probably, there is an underlying absorption due to a methylene rocking vibration in this region of the spectrum. The intensity of such a mode would show a decrease that parallels that of the aliphatic C-H stretching and bending modes. The absorptions centred near 1260 and 1230 cm^{-1} also display a progressive decrease in intensity with increasing carbonization time. These bands can be assigned to aromatic-oxygen vibrations^{14,15}. The spectra of cast films of SRC fractions, reported in the preceding paper, demonstrate that these bands are primarily due to phenolic groups.

Consequently, these results indicate that the retrogressive reactions associated with the formation of semi-coke in SRC-SC (at 450°C and 34.4 MPa) involve predominantly the loss of alkyl and hydroxyl functional groups. Only one new band appears in the spectrum, at 1692 cm^{-1} . This absorption is characteristic of an alkyl aryl ketone^{14,15}. There is little evidence for any change in the amount of aromatic hydrogen, or for the formation of polycondensed aromatic molecules of larger size. As the number of rings in a condensed aromatic system increases, the intensity of the 1600 cm^{-1} band decreases and the out-of-plane modes below 900 cm^{-1} become the strongest in the spectrum. Subtle spectral changes associated with the formation of low concentrations of any such reaction products can often be revealed by digital subtraction techniques¹¹. Figure 2 shows the infrared spectrum of the original SRC-SC together with that of the sample carbonized for 5 h. Presented in the same Figure is a difference spectrum obtained by subtracting the spectrum of the carbonized sam-

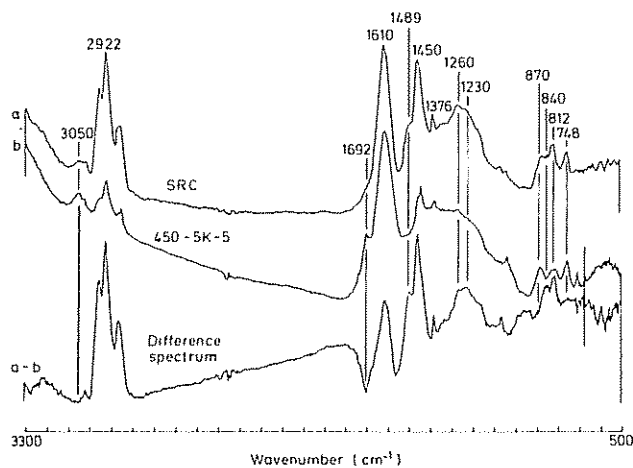


Figure 2 a: Infrared spectrum of SRC-SC.
 b: Infrared spectrum of SRC carbonized at 450°C, 34.4 MPa (5000 psi) for 5 h
 a-b. Difference spectrum, SRC minus carbonized SRC

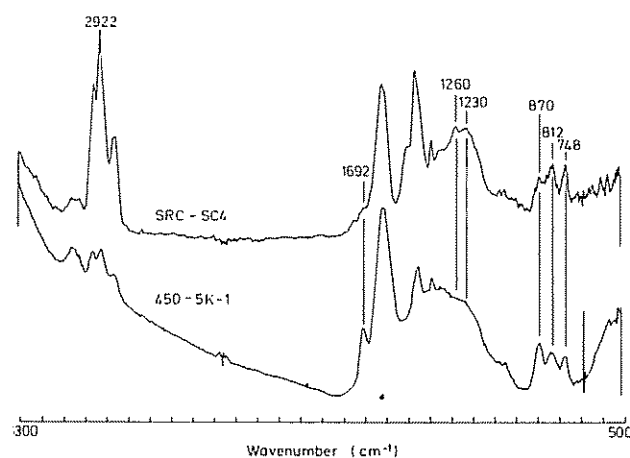


Figure 3 Top: Infrared spectrum of short-contact-time SRC, fraction 4.
 Bottom: Spectrum of carbonized sample, 450°C, 34.4 MPa (5000 psi), 1 h

ple from that of the original SRC. By multiplying the spectra by fractional constants it is possible to subtract different proportions of one spectrum from another. A fractional constant was chosen (on a trial-and-error basis) such that the aromatic C-H stretching mode near 3050 cm^{-1} was reduced to the base-line. It can be seen that the 870 and 748 cm^{-1} aromatic C-H out-of-plane modes are also completely eliminated on this basis. This again indicates that there is little change in the average size of aromatic groupings, since we would expect a change in the pattern of aromatic hydrogen substitution as the number of rings in a condensed system increases, together with a general decrease in the amount of aromatic C-H.

Positive bands in the difference spectrum can generally be associated with functional groups that decrease upon reaction, while the negative band at 1692 cm^{-1} in the difference spectrum reflects the only functional group formed that we could detect. The aromatic rings mode near 1600 cm^{-1} remains as a positive difference band. This does not necessarily reflect a decrease in the aromaticity of the SRC-SC upon carbonization, but more probably

change in the intensity of this band upon removal of phenolic oxygen groups (see preceding paper). Nevertheless, the fact that this difference band is slightly positive

is a further indication that there is little or no increase in the size of aromatic molecules upon carbonization under these conditions. Consequently, the large planar molecules that constitute the anisotropic phase are probably formed by the joining together of aromatic functional groups. The positive difference bands near 2920, 1450 and 840 cm^{-1} , assigned to methylene stretching, bending and rocking modes respectively, clearly demonstrate that the elimination of aliphatic groupings is involved. The difference bands near 1260 and 1230 cm^{-1} indicate a corresponding involvement of phenolic functional groups.

In order to obtain further information on the mechanism of formation of semi-coke, fractions 3-5 and 7-9 of both short- and long-contact-time SRC were studied under standard conditions (450-5K-1). Fractions 4, 7, 8 and 9 gave appreciable amounts of pyridine-insolubles, while fractions 3 and 5 did not. Of the pyridine-solubles, fractions 4, 7 and 8 of both short- and long-contact-time SRC have also been examined under the optical microscope¹³ and consist of practically 100% (by volume) of anisotropic carbon. The spectra of the pyridine-insoluble portion of all these fractions carbonized for 1 h appear practically identical with that of the whole SRC carbonized for 5 h. We found this result initially surprising because the spectra of the original materials show differences in the type and concentration of functional groups. For example, in Figure 3 the infrared spectrum of fraction 4 of SRC-SC is compared to the spectrum of the pyridine-insoluble portion of the same sample after carbonization (450-5K-1), while Figure 4 compares the corresponding spectra of fraction 8 of the SRC-LC. Fraction 4 has a high concentration of phenolic groups (1260, 1230 cm^{-1} bands) and alkyl-substituted aromatics (methyl and methylene bands near 2920 and 1450 cm^{-1}). In contrast, fraction 8 has a lower concentration of these functional groups but aromatic esters and aryl alkyl ketone carbonyl groups are present (1760, 1690 bands). A complete discussion of band assignments is given in the preceding paper. Nevertheless, despite these differences, the spectra of both carbonized samples are remarkably similar.

DISCUSSION

The results presented above strongly suggest that under the chosen carbonization conditions chemical condensation involves primarily the alkyl and phenolic functional groups.

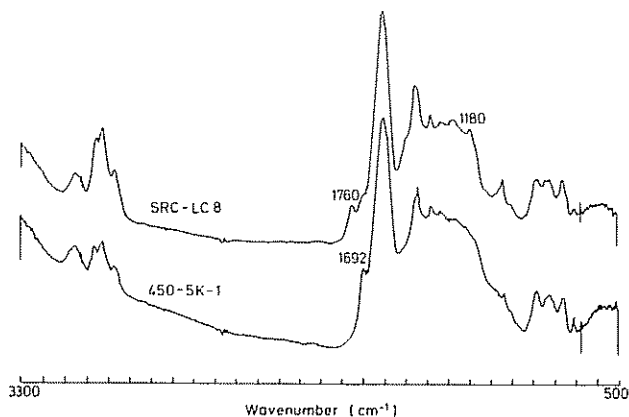


Figure 4 Top: Infrared spectrum of long-contact-time SRC, fraction 8.
 Bottom: Spectrum of carbonized sample; 450°C, 34.4 MPa (5000 psi), 1 h

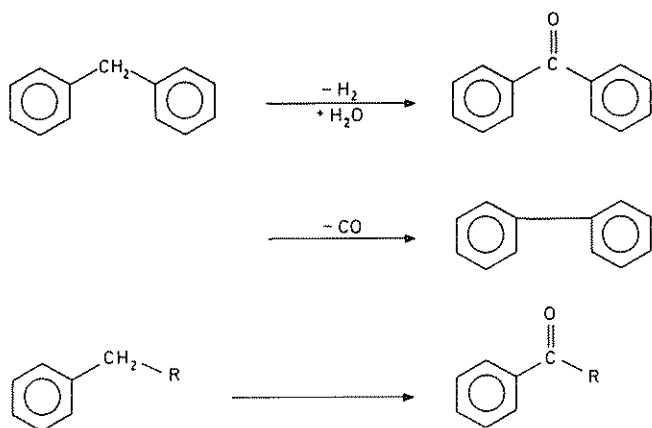
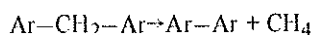


Figure 5

There is no evidence for direct ring condensation and synthesis of polycyclic aromatics as found, for example, in the carbonization of anthracene¹⁶. However, even though both fractions 3 and 4 contain a fairly high proportion of methylene and methyl groups, only fraction 4 gives substantial amounts of pyridine-insoluble material (at 450–5K-1). Fraction 3 of the SRC-SC has a very low phenolic content and the presence of both functional groups might be essential for the formation of anisotropic material. In addition, previous work on the pyrolysis of alkyl aromatics suggests that the type of aliphatic grouping present is also significant¹⁶. Isolated alkyl substituents can be split off forming gaseous products such as methane and ethane. Carbonization subsequently proceeds by synthesis reactions similar to those found in unsubstituted aromatics. The formation of pyridine-insolubles would then require higher temperatures or longer time periods than those chosen for this study. Conversely, aromatic groups bridged by methylene units can undergo elimination reactions of the following type:



Ouchi¹⁷, in a study of the pyrolysis of a phenol-formaldehyde resin, suggested elimination reactions involving ketonic intermediates, as illustrated in Figure 5 (for convenience we have used only simple benzene rings to represent the aromatic units present in SRC). The water molecules involved in this mechanism are derived from condensation reactions between phenolic groups to form diphenyl ether type linkages, as shown in Figure 6.

The spectra presented in this communication demonstrate that mechanisms of this type are also involved in the carbonization of SRC. Phenolic aromatic-oxygen stretching modes near 1250 cm^{-1} decrease in intensity, but a weak broad band centred near this frequency remains and can be assigned to the presence of some aromatic ethers. There is a large decrease in the intensity of bands assigned to methylene groups, and at the same time a band characteristic of aryl ketones appears at about 1690 cm^{-1} . This band is probably due to aryl-alkyl ketones, since the more highly conjugated diphenyl ketones have carbonyl bands¹⁷ near 1660 cm^{-1} . In fraction 8 of both short- and long-contact-time samples, decarboxylation of the original ester and alkyl ketone groups occurs, in addition to condensation reactions involving the phenolic and alkyl functional groups.

It has recently been suggested³ that the anisotropic

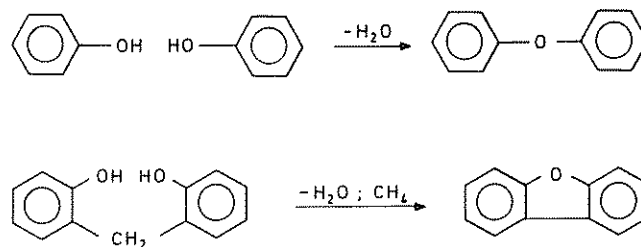


Figure 6

spheres obtained from heat-treated pitches consist of relatively small condensed-ring compounds linked by methylene bridges. SRC fractions carbonized at 450-5K-1 are probably similar, but with the small ring-systems present in the original material becoming condensed through direct carbon-carbon bridges and ether linkages. In view of the great decrease in intensity of methylene group vibrational modes observed in this study, we suggest that the more severe conditions (400–600°C for 2–46.5 h) used by Mochida *et al.*³ would result in a similar elimination of a large proportion of any methylene groups originally present.

In view of the heterogeneity of the SRC samples, even the column-separated fractions, it is not possible to be more specific about the mechanism of retrogressive reactions in SRC leading eventually to the formation of anisotropic and isotropic coke. A more complete understanding requires the careful study of the carbonization of materials of known structure. We are presently engaged in such model-compounds work and will report our results in the near future. However, the normal operational temperatures of the SRC pilot plant (400–450°C) are certainly sufficient for semi-coke and mesophase formation, particularly in the event of temperature excursions. The formation of coke is then a result of initial condensation reactions among that portion of the SRC that has a significant proportion of certain alkyl aromatic and phenolic functional groups.

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