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Studies of the Effect of Selected Nondonor Solvents on Coal Liquefaction Yields

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Chemical Technology Division

STUDIES OF THE EFFECT OF SELECTED NONDONOR SOLVENTS ON COAL LIQUEFACTION YIELDS

R. L. Jolley, B. R. Rodgers, B. M. Benjamin,
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ABSTRACT

The objective of this research program was to evaluate the effectiveness of selected nondonor solvents (i.e., solvents that are not generally considered to have hydrogen available for hydrogenolysis reactions) for the solubilization of coals. Principal criteria for selection of candidate solvents were that the compound should be representative of a major chemical class, should be present in reasonable concentration in coal liquid products, and should have the potential to participate in hydrogen redistribution reactions. Naphthalene, phenanthrene, pyrene, carbazole, phenanthridine, quinoline, 1-naphthol, and diphenyl ether were evaluated to determine their effect on coal liquefaction yields and were compared with phenol and two high-quality process solvents, Wilsonville SRC-I recycle solvent and Lummus ITSL heavy oil solvent.

At 427°C (800°F) and a solvent/coal ratio of 1.5, none of the selected nondonor compounds was highly effective in pure form except 1-naphthol. The relative effectiveness of the compounds, as determined in tubing-bomb tests conducted at 427°C for 10 min, was as follows: 1-naphthol, 78%; quinoline, 50%; naphthalene, 39%; phenanthridine, 37%; phenanthrene, 36%; carbazole, 36%; pyrene, 33%; and diphenyl ether, 32%. Comparable values for phenol, Wilsonville SRC-I recycle solvent, Lummus ITSL heavy oil solvent, and coal heated alone were 36, 61, 82, and 24%, respectively.

When tested at 427°C (800°F) and 10 min in the presence of a supplemental source of hydrogen (i.e., in a 30% nondonor — 70% Wilsonville SRC-I recycle solvent mixture), conversion was, in most cases, significantly greater than that predicted from the weighted average of the two components. An incremental increase (above the weighted average) in conversion of greater than 18% was observed for pyrene, phenanthridine, and carbazole. The comparable incremental increase for naphthalene and phenanthrene was greater than 10%. Incremental increases for 1-naphthol, quinoline, diphenyl ether, and phenol were 3 to 8%. When the 30% Lummus ITSL heavy oil solvent — 70% Wilsonville SRC-I recycle solvent mixture was tested, the incremental increase in conversion above the weighted average was 7%. As in the case of the pure nondonor experiments, coal conversion was highest with 1-naphthol.

The high conversion efficacy of 1-naphthol may be attributed to its condensation to binaphthol and the consequent availability of hydrogen. The effectiveness of both the nitrogen heterocycles and the polycyclic aromatic hydrocarbon (PAH) compounds may be due to their polycyclic aromatic nature (i.e., possible hydrogen shuttling or transfer agents) and their physical solvent properties. The relative effectiveness for coal conversion of the Lummus ITSL heavy oil solvent as compared with the Wilsonville SRC-I process solvent may be attributed to the much higher concentration of 3-, 4-, and 5-ring PAH and hydroaromatic constituents in Lummus solvent.

More than 100 constituents were identified by gas chromatography/ mass spectrometry (GC/MS) and quantified by GC in both the Wilsonville SRC-I process solvent and the Lummus ITSL heavy oil solvent. The major GC constituents in the Lummus solvent are PAHs, whereas the major GC constituents in the Wilsonville solvent are naphthalenes, tetralins, alkanes, phenols, and nitrogen heterocycles. An estimated 99% of the Wilsonville solvent and 46% of the Lummus solvent were volatile enough to pass through the gas chromatograph for analysis. Approximately the same amount of donor hydrogen was available in the GC constituents of each solvent.

The chemistry of coal liquefaction and the development of recycle, hydrogen donor, and nondonor solvents are reviewed. The experimental methodology for tubing-bomb tests is outlined, and experimental problem areas are discussed.

> A great part of the literature of solvent extraction resembles alchemy more than science, perhaps as a result of the complex nature of the problem.
>
> M. W. Kiebler
> The Actions of Solvents on Coal, 1945

1. INTRODUCTION

Preparation of liquid fuels from coal may provide an alternative to liquid fuels derived from petroleum. This is particularly attractive to those countries with significant coal reserves and may become even more attractive as petroleum reserves decrease in size and become more expensive. In the last seven decades, coal liquefaction has been studied and commercially utilized on a relatively small scale. The magnitude of research, development, and industrial efforts in this area appears to have been directly dependent on the economy and availability of other sources of energy. Nevertheless, a considerable literature has been accumulated and, especially within the last decade, significant progress has been made toward a more fundamental understanding of the chemical and physical processes involved in coal liquefaction.

The overall objective of our research program was to explore new reactions of coal with a view toward formulation and initial experimental laboratory evaluation of new process concepts to convert coal to liquid fuels. Research for the previous two years was related to our observation that solubilization of coals in the nondonor solvent, phenol, in the absence of hydrogen gas is accompanied by extensive redistribution of the native hydrogen in coal to give a hydrogen-enriched soluble portion and a hydrogen-depleted char.[1] The generic chemical phenomenon of hydrogen redistribution need not be limited to phenol and, in fact, phenols may not necessarily be the optimum media for maximizing it. We report here results of a broader study to explore the behavior of other nondonor solvents which might function similarly. The studies were aimed at consideration of both the underlying chemistry and the process implications of the hydrogen redistribution phenomenon.

Three principal criteria for selection of nondonor solvents for these studies were:

1. presence of the constituent in coal liquefaction products in order to permit process development using recycle streams,
2. potential for the constituent to participate in hydrogen redistribution reactions, and
3. choice of constituent representative of a major chemical class (e.g., polycyclic aromatic hydrocarbon, nitrogen-containing heterocyclic, or oxygen-containing constituent).

Based on these considerations, naphthalene, phenanthrene, pyrene, quinoline, carbazole, phenanthridine, 1-naphthol, and diphenyl ether were selected for evaluation of their effect on coal liquefaction yields. Results from use of the nondonor solvents were compared with yields obtained with phenol and two high-quality process solvents, Wilsonville SRC-I recycle solvent and Lummus ITSL heavy oil process solvent.

2. CONCLUSIONS

Donor species in coal conversion solvents have been shown to be important to the mechanism of producing pyridine-soluble products directly from coal. The conversion mechanism is believed to depend almost entirely on transfer of hydrogen from liquid organic species to coal; the liquid species are then rehydrogenated by molecular hydrogen to again become hydrogen donors. While non-hydrogen donors may not directly participate in this mechanism, the current work shows that they do play an important support role and may indeed be crucial as regards their hydrogen-shuttling and dissolution capabilities. This is seen in the form of a synergistic effect that occurs when some nondonor molecules are added to donor solvents. Additionally, a hydrogen availability difference was shown to exist between process-derived, hydrogen-donor liquids. These conclusions are supported by the specific citations of important findings from this work given below.

1. Efficient liquefaction with all nondonor compounds evaluated in this study except 1-naphthol requires a supplemental source of hydrogen (e.g., H_2 or a donor solvent).
2. Using micro-reactors, the relative effectiveness of selected pure nondonor solvents for converting Kentucky No. 9 coal (Fies mine) to pyridine-soluble products at 427°C (800°F), 10-min reaction time and 1.5 solvent/coal ratio was: 1-naphthol, quinoline, naphthalene, phenanthridine, phenanthrene, phenol, carbazole, pyrene, and diphenyl ether. The range of conversions varied from 78 to 32%.

3. Without supplemental hydrogen, among the pure nondonor compounds studied, only 1-naphthol (78% conversion) was as effective at converting coal to pyridine-soluble material as two high-quality process solvents, Wilsonville SRC-I (61%) and Lummus ITSL heavy oil solvent (82%).
4. Pure 1-naphthol appears to be highly effective for solubilizing coal; pure quinoline was moderately to highly effective; pure naphthalene, phenanthrene, pyrene, phenanthridine, carbazole, phenol, and diphenyl ether were only moderately effective.
5. The high conversion efficacy of 1-naphthol may be partially attributable to its condensation to binaphthol and the resulting availability of hydrogen, i.e., it may act as a limited hydrogen donor.
6. When tested at 427°C (800°F) and 10 min in the presence of a supplemental source of hydrogen (i.e., in a 30% nondonor — 70% Wilsonville SRC-I process solvent mixture), in most cases conversion was significantly greater than that predicted from the weighted average of the two components. An incremental increase (above the weighted average) in conversion of greater than 18% was observed for pyrene, phenanthridine, and carbazole. The comparable incremental increase for naphthalene and phenanthrene was greater than 10%. Incremental increases for 1-naphthol, quinoline, diphenyl ether, and phenol was 3 to 8%. When the 30% Lummus ITSL heavy oil solvent and 70% Wilsonville SRC-I

recycle solvent mixture was tested, the incremental increase in conversion above the weighted average was 7%. As in the case of the pure nondonor experiments, coal conversion was highest with the 1-naphthol-containing mixture.

7. The results from the current study indicate that, at least for quinoline, carbazole, and phenanthridine, the basicity of the nitrogen-containing compounds may not be the significant factor in their coal conversion mechanisms. For the pure compounds, the most basic example, quinoline, is the most effective, giving a conversion of 50% at 427°C and 10 min, whereas phenanthridine and carbazole gave 36% conversion. When mixed with supplemental hydrogen (i.e., Wilsonville solvent) then both phenanthridine (72% conversion) and carbazole (72% conversion) were significantly more effective than quinoline (66% conversion). Because their effectiveness increased significantly in the presence of a supplemental hydrogen source, their effectiveness with suplemental hydrogen may be related to their hydrogen shuttling or transfer properties.

8. Over 100 constituents were identified by GC/MS and quantified by GC in both the Wilsonville SRC-I process solvent and the Lummus ITSL heavy oil solvent. The concentration of each of the selected nondonor solvents in this study were quite low and/or not detected, except for pyrene (6.8 wt%), phenanthrene (4.4 wt%), carbazole (1.4 wt%), and naphthalene (1.2 wt%) in the Lummus solvent; and except for diphenyl ether (3.3 wt%), phenanthrene (2.0 wt%), naphthalene (1.7 wt%), and quinoline (1.0 wt%) in the Wilsonville solvent.

9. The major GC constituents in the Lummus ITSL solvent are PAHs, whereas the major GC constituents in the Wilsonville solvent are naphthalenes, tetralins, alkanes, and phenols. An estimated 99% of the Wilsonville solvent and 46% of the Lummus solvent were volatile enough to pass through the gas chromatograph and were analyzed. Approximately the same amount of donor hydrogen was available in the GC constituents of each solvent (i.e., 0.48 wt% in the Lummus solvent and 0.45 wt% in the Wilsonville solvent). Thus, assuming the same relative concentration of available hydrogen in the nonvolatile portion of the Lummus solvent, the two solvents were approximately equivalent in quantity of hydrogen.

10. The relative higher effectiveness for coal conversion of the Lummus ITSL heavy oil solvent as compared with the Wilsonville SRC-I process solvent may be attributable to the higher concentrations of 4- and 5-ring PAH and hydroaromatic constituents in the Lummus solvent, i.e., the availability of the hydrogen in the Lummus solvent appears greater.

11. The limited data base from this set of experiments tends to support the conclusion that increasing the concentration of pyrene, carbazole, phenanthridine, phenanthrene, naphthalene, quinoline, and 1-naphthol in the Wilsonville SRC-I solvent would improve coal liquefaction capability of that solvent. The experimental results also indicate that increasing the concentration of higher molecular weight PAH and hydroaromatic compounds would improve the coal conversion efficacy of the Wilsonville solvent.

12. Some mesophase coke formation was observed in tubing-bomb tests with Lummus ITSL heavy oil solvent at 460°C (860°F) and 10 min, indicating the beginning of retrograde reactions.
13. Presoaking coal in methanol for several weeks prior to microreactor tests of the methanol-soaked coal in Wilsonville solvent at 427°C (800°F) and 10 min, increased the coal conversion from 61 to 75%.

3. RECOMMENDATIONS

The experimental results in this research program indicate that at 427°C (800°F) 1-naphthol is highly effective for converting coal to a liquid product and that with supplemental hydrogen, most of the nondonor compounds evaluated synergistically increase coal conversion to liquid products. Since essentially only one reaction temperature-time regimen was used in the experimental results reported here, further research is necessary to determine for selected best-candidate solvents the optimum reaction temperature and time, as well as the optimum nondonor solvent and supplemental hydrogen concentrations. Further study using different coals, including dried and undried samples, in addition to better definition of optimum temperature-time regimens and reactant concentrations is required in order to recommend coal liquefaction process improvements. When used with supplemental hydrogen, widely different chemical types were effective solvents, thus it is apparent that different chemical processes are occurring during coal liquefaction with such solvents. Developing a fundamental understanding of these chemical reactions and mechanisms is important.

Further experimentation using deuterium and radiotracer labeled model compounds may facilitate this understanding. Solvent loss (both incorporation and degradation) is important from process and economic viewpoints. Consequently, incorporation and degradation studies with labeled model compounds are also recommended. To more clearly understand the role of the process solvent in improving the yields obtained with the nondonor compounds in this study, a series of experiments with varying sets of nondonor and donor compounds should be conducted (e.g., ternary or quaternary mixtures of compounds). In addition to micro-reactor determination of gross coal conversion yields, further characterization of the reaction products is necessary to arrive at a more fundamental understanding of the chemical processes. For example, in addition to the traditional parameters such as oils, asphaltenes, and preasphaltenes, the products should be molecularly characterized. To better understand the role of nitrogen-containing heterocycles in the coal conversion process, a series of tests should be made with labeled compounds of widely varying basicity to determine relative conversion effects and possible reaction mechanisms.

4. BACKGROUND AND HISTORICAL CONSIDERATIONS

The history, chemistry, and process developments in coal liquefaction have been detailed in several comprehensive reviews.[2-17] The reviews by Whitehurst et al.[12] and Pullen[17] summarize most recent significant research.

Coal liquefaction involves the complex interaction of a series of physical processes and chemical reactions including (1) physical breakdown of the coal particles;[18] (2) solubilization and solvation of the particles and molecular constituents;[18-23] (3) thermally and chemically induced bond rupture of the coal structure;[18-35] (4) intracoal reactions, i.e., fluxing, autostabilization, and recombination or regressive reactions (refs. 18,26,34,36); (5) coal-solvent reactions, i.e., hydrogen shuttling or transfer reactions, solvent-induced bond ruptures, and solvent degradation, modification, or incorporation reactions (refs. 20, 24-26, 36-42); and (6) thermal degradation of solvent constituents.[43-45]

4.1 Coal Structure and Solvent Interaction

Substantial evidence indicates that the three-dimensional structure of coal, regardless of rank, consists of aromatic and polycyclic aromatic rings which are connected with each other by ether, methylene, and some ethylene, propylene, acyl, and tertiary carbon cross-links (refs. 21, 30, 37, 46-51). There appears to be a greater content of aliphatic side chains and carbonyl groups in low-rank coals as compared with high-rank coals.[52] Many units of relatively low molecular weight are known to be dispersed within the three-dimensional structure. Van Krevelen concluded that coalification is a progressive polycondensation (increasing three-dimensional cross-linkage) and that the potential solubility of coal decreases with increasing coalification; for example, lignite is almost entirely soluble in caustic solutions, whereas coal does not dissolve completely in any solvent.[53]

Because of the structure of coal, three major types of reactions are expected to be important in the conversion of coal into liquid and gaseous products: alkyl bond fission, hydrogenolysis of oxygen and sulfur groups, and aromatic ring hydrogenation. Each type of reaction consumes hydrogen.[54] In addition, other factors may be significant such as acid-base interactions, hydrogen bonding, dipole-dipole interactions, and localized charge interactions.[55]

Solvent extraction has been extensively used for studying the composition of coal. Historically, the primary aim of the solvent extraction studies was to isolate the materials from which coal derives its coking properties, and essentially all organic solvents were tried in this effort.[5] Efforts have been made to correlate the effectiveness of solvents with their chemical and physical properties.

Van Krevelen[53] analyzed (on a theoretical basis) the change of free energy when a fundamentally soluble macromolecular substance is mixed with a solvent.[56-60] From this analysis, he postulated that maximum swelling of the insoluble coal network structure and dissolution of the soluble "monomers" dispersed in the network are achieved by solvents having similar or higher solubility parameters than the coal (see also refs. 61, 62). The solubility parameter δ is defined by the following relationship:

$$\delta = \sqrt{\frac{\Delta U_{vap}}{V_M}}$$

where ΔU_{vap} is the molar heat of vaporization (or molar cohesion energy) and V_M is the molar volume. Thus, the solubility parameter deals primarily with the cohesive energy of the solvent (which relates primarily to dispersive forces). Substances such as pyridine and ethylenediamine have δ values similar to high-rank coals and are therefore suitable solvents at low temperatures. Van Krevelen cautions that electronic and hydrogen bonding which are highly significant in coal dissolution are only roughly considered in δ values. He concluded that factors of this type may explain why coal dissolution in phenanthrene and higher molecular weight polycyclic aromatics requires higher temperatures than does dissolution in pyridine, although their δ values are similar.[53]

As early as 1940, Kiebler found that for constant temperature extraction of a Pittsburgh seam coal in a variety of solvents, the effectiveness of a given solvent was directly proportional to the internal pressure of solvent, i.e., the square of the solubility parameter (δ^2).[63] Howard observed that the correlations were only moderately successful and that maximum solubility occurs when the solubility parameter of the solute and solvent are identical. That is, in a series of solvents a maximum will be encountered in the solubility-solubility parameter relation on one side of which a decrease in the solubility parameter results in a decrease in solubility and on the other side of which an increase in solubility parameter results also in a decrease in solubility.[64] This observation has been experimentally supported.[65-67] These studies indicated a relationship between the effectiveness of a solvent for dissolving coal and the solubility parameter at moderate temperatures but did not evaluate this effect at temperatures used in coal liquefaction processes nor consider complicating effects of solvent polarity.[68] Blanks and Prausnitz[69] proposed that the solubility parameter of polar compounds should involve two parts — a polar part, τ, and a nonpolar part, λ — related to the solubility parameter by the relationship

$$\delta^2 = \tau^2 + \lambda^2 \quad .$$

Angelovich and coworkers[68] concluded that for groups of solvents of similar polarity and hydrogen bonding tendencies, maximum coal solubility should occur when the nonpolar parts of the solvent and solute (coal) solubility parameters are equal. They present experimental evidence obtained at liquefaction temperatures (and hydrogenation conditions) in support of their analysis indicating that optimum values for λ of about 9.5 produced maximum liquefaction yields. They suggest that the nonpolar part of the solvent's solubility parameter should be a useful tool for screening solvents,[70] but that other factors such as thermal stability at reaction temperatures, Lewis basicity (electron pair donor) and hydrogen donor capacity must also be considered.[68]

In consideration of effects such as hydrogen bonding and dipole-dipole interactions in addition to dispersive forces, Hansen separated the solubility parameter in to three components: hydrogen bonding properties (δ_h), disperson forces (δ_d), and dipole-dipole interactions (δ_p). He quantitatively described a solvent's ability to dissolve a solute using a three-dimensional plot of these parameters.[71] According to Whitehurst et al.,[12,72] the plot was simplified to a two-dimensional, three-coordinate plot of the three parameters represented as fractions f_h, f_d, and f_p respectively. This treatment permits the prediction of liquid-liquid miscibility, polymer solubility, adsorption on surfaces, and solubility of inorganic and organic compounds (including lignin).[12,72]

The effectiveness of electron donors (e.g., basic nitrogen compounds) as coal solvents was observed by Dryden[6] and is currently receiving increased attention.[23] In a series of extraction experiments with several pyridine bases, Halleux and Tschamler[73] obtained evidence supporting Dryden's hypothesis that the interaction between some specific solvents and coal involves the availability of a free electron-pair in the solvent molecules.

In consideration of the effectiveness of Lewis bases (electron donors) as solvents, Marzec and coworkers have developed a coal extraction model to account for such effects.[74] They postulate that coal consists of a matrix of macromolecules with extractable molecular substances filling the pores and bonded to the matrix by electron donor and acceptor centers. According to Gutmann, solute-solvent (or ion-solvent) interactions are the result of nucleophilic attack of a solvent functioning as electron-pair donor at an area of low electron density of a substrate, i.e.,

$$\overset{\delta^+}{A} - \overset{\delta^-}{B} \quad ,$$

and/or by the electrophilic attack of a solvent functioning as an electron-pair acceptor at the area of high electron density. Both donor or acceptor attack shifts the negative charge from A to B:

$$\text{Donor} \rightarrow \overset{\delta^-}{A} \overset{\longrightarrow}{-} \overset{\delta^+}{B} \rightarrow \text{Acceptor}.$$

The electron shift in either or both of these ways may lead to heterolysis (ionization) of the covalent bond A - B, if the products (ions) are sufficiently stabilized by solvation.[75] Using the concept of electron donor numbers (DN) and electron acceptor numbers (AN) described by

Gutmann[75] as quantitative measures of electron donor and acceptor properties, Marzec and coworkers observed coal extract yields increase with increasing DN of the solvent and correlate with positive values for the difference DN-AN.[74] The observation of higher coal extract yields with solvents of higher DN corroborates Dryden's observation concerning solvents with unshared elecron pairs.[6]

4.2 Coal Liquefaction Considerations

In addition to simple dissolution, high yields in coal liquefaction must involve a depolymerization of the coal structure (the insoluble network) via degradative homolysis (thermal cleavage) of the cross-linkages. In most direct liquefaction processes currently under study, the initial reactions involve thermal decomposition of the coal in an appropriate solvent that is usually generated by the process itself (for economic reasons). The liquefaction is usually conducted under hydrogen pressure. The solvent has several functions: (1) a slurry vehicle for transport of the coal to the liquefaction reactor, (2) a medium for heat transfer to the coal particles, (3) a vehicle to promote hydrogenation and hydrogen transfer reactions, and (4) a medium to disperse reaction products. The chemical composition of the solvent can significantly affect the extent of coal conversion and the nature of the products.[36]

In direct liquefaction the principal objective is to stabilize the molecular fragments generated by thermal degradation of coal with hydrogen in order to maximize useable product. This requires that hydrogen be available in a form suitable to satisfy the demand. The demand for hydrogen in liquefaction reactions is apparently largely determined by the structure of the coal and the reaction temperature. Hydrogen demand may be met by transfer from a solvent donor, formation of solvent-solvent and solvent-coal adducts, dehydrogenation of the coal itself, and molecular hydrogen.[36] An effective route for hydrogen transfer is by way of the liquefaction solvent. The ideal hydrogen carrier structure is generally considered to be a partially hydrogenated PAH that can alternate between this form and the fully aromatic form through successive reversible dehydrogenation and rehydrogenation. The key reactions between the hydroaromatic solvents and the coal during the liquefaction appear to be principally free radical in nature.[76] The free radicals may also be stabilized by other competitive reactions with solvent or coal constituents.[77]

Coal liquefaction is a heterogeneous process. The solvent rapidly diffuses into the coal, dissolving in the coal "gel," and thus the initial reaction takes place within the coal particles.[20] According to Larson and coworkers, Neavel has postulated that the initial chemical reactions occurring in both coking and direct liquefaction are identical.[78] This argument is supported by Mochida and coworkers.[49]

When heated to 300-500°C, coal materials undergo thermal condensation and decomposition reactions to an extent dependent upon the coal rank. Free radicals are formed through thermal homolysis of bonds and (1) may combine with each other or larger molecular weight material (preasphaltenes) or (2) may be stabilized by hydrogen transfer from the solvent or by addition reaction of the solvent itself to form oils or asphaltenes. The properties of solvent that influenced these reactions may be dissolution ability, viscosity, and radical quenching reactivity.[49]

Mochida and coworkers postulate two possible functions for the solvent in solvolytic liquefaction of coal at temperatures below 400°C near the softening point of coal: (1) providing a high fluidity to the system and (2) providing unit reactions for liquefaction. They correlated liquefaction yields with the softening point of coal and concluded that softening point is a better index of liquefaction reactivity than carbon content. They conclude that coal liquefaction solvent should have the following properties to give high liquefaction yields:[49]

1. high boiling point,
2. stability against decomposition and carbonization,
3. high dissolution ability for the coal fragments to maintain a low viscosity in the system, and
4. reactivity for solvolytic reactions.

4.3 Donor Solvents and Hydrogen Transfer

The first commercial coal liquefaction process was developed by Pott and Broch, who used a mixture of tetralin, naphthalene, and phenol in a 2:2:1 weight ratio as a solvent for bituminous coal.[19] Early investigators understood the effectiveness of hydroaromatics and the importance of hydrogen donor solvents and hydrogen transfer in the coal liquefaction process.

4.3.1 Tetralin

For many years tetralin has been accepted as the paradigm of hydrogen donor solvents and, consequently, has been much used in experimentation. However, a wide diversity of solvents may function as hydrogen donors, and the rate of thermal decomposition of the coal may be a major factor in determining the extent of hydrogen transfer once a sufficiently reactive donor is used.[20] Most investigators have concluded that coal depolymerizes by thermal decomposition into free radicals that are stabilized by capture of a hydrogen atom from a donor molecule. If other means of stabilization are not present, aromatic fragments will polymerize into large "molecules" that are nonvolatile and insoluble.[26] Wiser observed, in hydrocarbon thermal cracking studies, that thermal decomposition reactions become appreciable at 350°C and concluded that thermal rupture of bonds in the coal structure would become extensive above that temperature. He observed that the greater portion of the stabilization process (in dissolution studies at 350-450°C using tetralin and Utah bituminous coal in a 10:1 weight ratio) was apparently accomplished by the hydrogen atoms from tetralin, and that the rate controlling process was the hydrogen transfer. Wiser postulated that interactions between solvents such as tetralin and coal may significantly reduce activation energies associated with bond rupture.[26]

Benjamin and coworkers studied the pyrolysis of tetralin using isotope labelling (nmr) and GC/MS techniques to study the pyrolysis products. When tetralin was heated at 400°C for 1 h, only a trace of it was converted to naphthalene and 1-methylindane. After 18 h at 400°C, only 1% decomposition occurred. However, at 500°C extensive decomposition was observed with only 25% of the tetralin remaining after 1 h. Naphthalene was the major product and only small amounts of 1-methylindane, indane, ethylbenzene, and toluene were formed. Benzene, o-xylene, methylethylbenzene, butylbenzene, 2-methylindane, and 1- and 2-methylnaphthalene were present, representing about 1-3% each. Traces of propylbenzene, two C_3-benzenes, 1- and 2-ethylnaphthalene, 1- and 2-ethylindane, three binaphthyls, and chrysene were detected. After 1 h pyrolysis at 500°C, the gas fraction contained 35% hydrogen, 45% methane, 31% ethane, and 13% propane. Traces of propane and butane were detected.[31] Hooper and coworkers independently came to approximately the same results for tetralin pyrolysis (350-450°C). They concluded that hydrogen produced from the cracking tetralin could be a significant source of hydrogen for hydrogenation reactions in addition to the source usually alluded to in the literature, i.e., the reaction of tetralin with free radicals formed by the thermal dissociation of coal.[43]

From tubing-bomb experiments at 427°C with tetralin and coal [Illinois No. 6 (Monterey) bituminous or Kaiparowitz subbituminous] at a 2:1 solvent/coal ratio, Franz and Camaioni concluded that the 1-methylindane observed in reactions of coal and tetralin is a product of the reverse 1,2-aryl migration of 2-tetralyl radical, an endothermic reaction with an activation energy of 22 kcal/mol. Thus, the presence of 1-methylindane in coal reactions indicates that coal-derived radicals are sufficiently nonselective to produce 1- and 2-tetralyl radicals.[34] According to Heredy and coworkers, both 1- and 2-tetralyl radicals were intermediates in the oxidation of tetralin to naphthalene.[40] The rate of scrambling of isotopic labels is enhanced by constituents in the coal (e.g., Fe^{+3}) which convert radicals (that undergo relatively inefficient bimolecular interconversion) to carbonium ions, which undergo very rapid unimolecular rearrangements. According to Franz and Camaioni, Bokrath observed that the addition of pyrite enhances the rate of isomerization of tetralin to 1-methylindane.[34]

About 55% of the Kaiparowitz subbituminous coal dissolved at 427°C within 10 min using a 2:1 weight ratio of tetralin to coal. Because it was unlikely that the solvation process (in tetralin) would select aliphatic structures over aromatic structures, Franz concluded that during the first 10 min, introduction of deuterium occurs much more rapidly at aliphatic sites.[39] This is in agreement with Benjamin et al. who observed very rapid hydrogen exchange with methyl groups (e.g., 1-methylnaphthalene).[42] This conclusion is also supported by Wilson, and coworkers, who studied the liquefaction of an Australian bituminous coal (Liddell) in tetralin and hydrogen at 400°C and 425°C. After 2 h, tetralin conversion to naphthalene was about 10% at 400°C and 16-20% at 425°C. They concluded the major role of hydrogen at 400-425°C and >6.9 MPa hydrogen pressure was not hydrogenation of aromatic rings, but that most of the hydrogen was consumed by alkyl bond fission and hydrogenolysis reactions.[54]

4.3.2 Hydrogen transfer

Curran and coworkers[20] evaluated the kinetics of coal conversion and hydrogen transfer to coal by assuming two simultaneous first-order reactions in which two types of bonds were broken, one relatively strong and the other relatively weak. They observed that approximately one-third of the total conversion occurs rapidly and with no significant hydrogen transfer and also that the low activation energy (30 kcal/mol) for the high initial coal conversion rate was well below that of most chemical bond strengths. Thus, they concluded that the initial reactions did not involve rupture of covalent bonds but involved the breaking of hydrogen bonds. The activation energy (45 kcal/mol) of the later, slow conversion rate was somewhat low for normal covalent bonds. Therefore, they concluded that a highly resonating structure stabilized the free radicals produced by bond rupture,[20] (i.e., achievement of homolysis rates of C-C, C-O, or C-S bonds commensurate with those of coal decomposition at about 400°C appears to require aromatic resonance stabilization of the radicals produced[33]). The reaction rate, in the later stages of the reaction, was independent of the donor hydrogen concentration. This fact and the observation that hydrogen was consumed in the actual conversion process tend to support the free radical hypothesis for the conversion process.[18]

Franz[39] corroborated these conclusions in coal liquefaction/ tetralin experiments at 427°C. Using nmr techniques, he determined that hydrogen transfer during the reaction is very rapid during the first 15 min but levels off and becomes slow after 30 min. Presumably, the first phase involved low energy processes (conversion of coal to preasphaltenes) and the second phase involved slower bond-breaking processes (forming asphaltenes). However, hydrogen uptake per incremental increase in product yield was much lower in the initial 5 min of reaction time. This is consistent with autogenous hydrogen transfer from coal donor molecules to radicals[39] and the observation that vitrinite is superior to tetralin for certain hydrogen transfer reactions.[29,42]

Experiments were conducted by Heredy and coworkers to explore the roles of gas-phase and donor-solvent hydrogen on coal liquefaction. In experiments with tetralin, deuterium labeled tetralin, hydrogen gas, and deuterium labeled hydrogen gas, it was concluded that the 1-tetralyl radical had a significant role in the transfer of deuterium from the gas phase into the coal. They also concluded from the large amount of deuterium incorporated that there was apparently a direct route for incorporation of deuterium into the coal without the participation of tetralin, although the extent of isotopic exchange between the coal and the solvent is greater than it is between the hydrogen gas and the solvent. They observed a significant amount of gas-phase hydrogen exchange with naphthalene.[40]

4.4 Thermal and Chemical Splitting of Bonds

That thermal and chemical splitting of bonds (both intracoal and solvent-coal reactions) must be considered an important factor in coal liquefaction is concluded from several model compound studies. For example, vitrinite was found to be a better catalyst and hydrogen transfer agent than tetralin for the thermolysis of 1,1,2-triphenylethane and 1,1,2-triphenylethylene.[27] The cleavage of alkyl-oxygen bonds may also occur under coal liquefaction conditions as indicated by Kolling[27] and his coworkers in their studies of the action of 1,2,3,4-tetrahydroquinoline on model compounds at temperatures up to 390°C. Kessler and coworkers observed that reduction of coal vitrain using lithium-ethylenediamine increased its solubility in pyridine by (1) splitting ether linkages in the coal, (2) partially eliminating organic sulfur from the coal structure, (3) formation of lower molecular weight aromatic hydrocarbons, and (4) formation of hydroaromatic compounds.[79]

The high content of oxygen in subbituminous coal suggests that oxygen-containing functional groups are important in coal liquefaction and may function as "solvent oxidants."[22] For example, phenols are effective in reducing benzophenone but at much slower rates than those for hydroaromatic compounds.[38] If the oxygen atom is located α or β to an aromatic ring, thermolysis could generate anion radicals that would be reasonably stable and also function as hydrogen sinks in the presence of donor molecules such as octahydrophenanthrene.[22] Ruberto and coworkers, who detected free radicals in solid coal and in the coal liquids, state that the lifetime of the free radicals is very long, frequently surviving all hydrogen transfer reactions. Quinones abstract hydrogen from donor solvents (e.g., 1,4-dihydrobenzene, dihydronaphthalenes, and tetralins) in a two-stage ionic process. Although the presence of quinone structures in coal was not established by Ruberto et al., they concluded, based on e.s.r. observations and the common occurrence of phenols in coal liquefaction products, that the intermediacy of aryl-oxyl radicals is plausible and stated that this conclusion is substantiated by (1) studies of Sternberg and Donne showing the ease of generating free radical carbon and oxy-anions by electron transfer from potassium metal[80] and (2) studies by Russell and coworkers indicating that many aliphatic and aromatic oxy-anion radicals are stabilized in reducing environments as their semidione intermediates.[81] Therefore, Ruberto and coworkers concluded that one of the most important steps in coal liquefaction is the quenching of radical anions by hydrogen or small alkyl fragments before recombination can occur.[22]

Using nmr techniques, Franz determined in coal liquefaction/tetralin experiments at 427°C that reactions leading to the removal of oxygen-containing functional groups are essentially complete within 10 min. Presumably the remaining compounds were relatively stable phenols, aromatic ethers, and dibenzofuran structures. Franz observed significant isotopic scrambling between phenol and 1,1-d_2-tetralin for 1 h and 2 h at 427°C and that the presence of coal significantly enhanced deuterium incorporation in the phenol. He concluded that the introduction of deuterium into phenolic aromatic systems competes with the very rapid conversion of labile aliphatic oxygenated structures in coal to deuterated aliphatic structure. The overall hydrogen transfer process is stoichiometric and irreversible with respect to naphthalene, indicating that reduced coal constituents have low potential as a source of hydrogen. The hydrogen transfer process occurs initially and rapidly at aliphatic sites but is soon incorporated in aromatic structures. The gradual production of aromatic structure (phenolic or aryl ether) during the reaction was confirmed through nmr results.[39]

4.5 Coal Reactivity

Coal is a highly reactive material. For example, coal (Illinois No. 6 vitrain) is a better hydrogen donor, for several receptors, than tetralin.[27,32,38] Coal is apparently a good alkylating agent and also akylates readily. As reported by Larson and Kuemmerle, Kroeger concluded that alkylation of coal increases its aromaticity via condensation of alkylaromatics with loss of hydrogen.[37] Coal is dehydrogenated readily by quinone. The reaction rate compares favorably with that achieved with 1,4-dihydronaphthalene, one of the more reactive hydroaromatics. Peover observed that the addition of quinone to the coal occurs simultaneously with dehydrogenation and concluded that adducts occur with anthracene and perylene structures.[25]

Evidence of the reactive nature of coal is supplied by Gorbaty, who observed that drying subbituminous coal had a marked effect on its physical structure, resulting in decreased mass transport through the coal particles and, consequently, less conversion.[82] Other investigators have reported that oxidation reduces the amount of coal conversion to liquid products.[2, 72] For example, Neaval observed that oxidation of coal (oxygen concentration increased 3 wt% by heating at 177°C in air) dropped conversion from 62% to 35% (30-min reaction in tetralin at 400°C) and concluded that oxidation of coal is deleterious to liquefaction yields.[18] One effect of drying is probably pyrite oxidation.[83] To what extent pyrite oxidation may be related to reduction of coal conversion yields is unknown. However, recent evidence indicates that hydrogen sulfide may react as a hydrogen donor in the coal liquefaction process.[84] In coal, sulfur can exist as pyrite (FeS_2), other metallic sulfides (e.g., ZnS, PbS, FeS), sulfates [e.g., $FeSO_4$, $Fe_2(SO_4)_3$, or $CaSO_4$], organic sulfur (mainly thiols, sulfides, disulfides, and substituted thiophenes) and elemental sulfur.[83,85] The reactivity and possible involvement of these sulfur-containing compounds in liquefaction processes is receiving increased attention, as discussed below.

Further evidence of the reactivity of coal is the chemical comminution of the coal that occurs when it is exposed to certain chemicals (e.g., ammonia, methanol, acetic acid, and trifluoroacetic acid). Apparently these chemicals interact with inorganic minerals along the mineral matter boundaries.[86]

Because of this reactivity and possible variations in reactivity, it is well known that the liquefaction behavior of coals varies widely, depending upon the chemical and petrographic characteristics. With coals of higher carbon content, depolymerization is less effective and gives products of higher molecular weight presumably because of the presence of larger polycyclic aromatic units, i.e., a more graphite-like structure.[37,87] Abdel-Baset and coworkers observed that conversion tends to increase with increasing sulfur content of the coal, except for some western coals. Using regression analysis, they developed a correlation relating conversion to sulfur content, total reactive macerals, and carbon content, but they cautioned that this does not imply a causal effect. The high partial correlation coefficient for sulfur may be attributable to pyrite as a catalyst; it may occur because some organic sulfur compounds may be readily removed, generating free radicals that promote further hydrogenation; or, the sulfur content may be an index of the extent of certain processes that occurred during the coal formation that promoted production of particularly labile organic constituents.[88] Empirical support for this regression analysis has been provided in a subsequent report.[89]

Whitehurst and coworkers reported that pyrites and other catalysts catalyze hydrogen transfer, dehydrogenation, and solvent isomerization.[36,72,77]

4.6 Recycle Solvents

For economic reasons, coal liquefaction process solvents are generally developed as an integral part of the coal conversion process through recycle of selected fractions. Extensive effort has been expended on measuring solvent parameters and correlating the parameters with liquefaction yields and product quality.[44,90] It has been generally concluded that solvent quality parameters must be adjusted for efficient liquefaction of different coals. A systematic study of SRC recycle solvents was conducted by Curtis and coworkers. Based on coal conversion efficacy (in tubing-bomb experiments) they determined optimum solvent ranges for a series of parameters including hydrogen content, atomic C/H ratio, aromatic hydrogen, and aliphatic hydrogen. They concluded that there are solvent factors in addition to those studied which affect conversion efficacy.[90] Excessive hydrogenation of an initially aromatic solvent is possible and may be detrimental to coal liquefaction. That is, the relative amounts of aromatic and aliphatic proton types must be finely adjusted to provide sufficient hydrogen for hydrogen transfer as well as maintaining sufficient aromaticity for solvating action.[90] The high solvent quality of the heavy fraction [+427°C (+800°F)] produced in the direct liquefaction of coal has recently received attention. The large molecules present in this heavy solvent undergo very well the principal reactions involved in coal liquefaction:[23,36,91-93]

1. Large polycyclic aromatic compounds readily cycle between a hydroaromatic state and an aromatic state, transferring hydrogen to reactive species.
2. The large molecules are good physical solvents.
3. The large solvent molecules may contain several heteroatoms, especially nitrogen.
4. The large aromatic rings make the heteroatom electrons more available for hydrogen bond formation.

4.7 Solvent Degradation and Modification

Because of the high process temperatures and complex chemical environment, process solvents are subject to degradative and modifying reactions (e.g., transalkylation and isomerization).[45] In addition, the concentrations of reactive constituents in solvents may decrease during the liquefaction process due to their incorporation into insoluble residues. Studies with individual model compounds such as tetralin indicate that a number of side reactions occur that alter the carbon skeleton and therefore deter regenerating the original compound by rehydrogenation. Products from reactions of coal and tetralin are methylindanes after ring contraction (and indane after demethylation), butylbenzene after ring cleavage, and methylnaphthalenes after alkylation.[32,44]

Poutsma and coworkers quantified the reactions of coal and tetralin at 454°C under 13.9 MPa hydrogen pressure with an approximate 40-min residence time using simulated SRC-I conditions. They determined that under these experimental conditions, approximately half of the introduced ^{14}C-labelled tetralin was consumed with 15% of the tetralin entering into reactions more complex than hydrogen donation to form naphthalene. Approximately one-third of this diverted tetralin was converted to methylindanes, indane, and methylnaphthalenes, whereas about two-thirds was grafted to much larger molecules. Presumably the incorporation of tetralin in larger molecules involves reactions of tetralyl radicals, and the grafting reactions are not limited to specific functional groups in the coal but occur indiscriminantly. These reactions may occur for other hydroaromatics and are thus an obvious source of loss of solvent quality and quantity. Similar experiments should be conducted with naphthalene, phenanthrene, and pyrene to further explore the generality of such reactions.[76]

Solvent loss has often been associated with using basic nitrogen compounds as solvents even at comparatively low temperatures (i.e., at the solvent boiling point).[23,94] Amines during extraction of coals apparently are incorporated into or retained by both the solubles and the residues from the extractions. Such retained amines are exchangeable in the case of pyridine and ethlenediamine but are not exchangeable in the case of tetrahydroquinoline.[94]

4.8 Liquefaction Products

The liquid products resulting from direct liquefaction of coal are complex mixtures. Some investigators have operationally defined three broad classes of compounds that make up coal-derived liquids: (1) oils (i.e., pentane- or hexane-soluble fraction), (2) asphaltenes (i.e., fraction soluble in benzene or toluene but insoluble in hexane or pentane), and (3) preasphaltenes (i.e., soluble in pyridine or tetrahydrofuran but insoluble in benzene or toluene).

A major goal of coal liquefaction research is to maximize the production of oils. In coal-derived products, oils consist not only of alkanes or aliphatic hydrocarbons but also of 1- and 2-ring aromatic constituents. The latter may predominate in some products.[95] Asphaltenes are presumed to be key intermediates in the conversion of coal to liquids.[96-100] Consequently, they may be the principal product and must be upgraded by hydrogenation.[96-98] Sternberg and coworkers report that asphaltenes consist of hydrogen-bonded complexes that can be separated into acid and base components. The oxygen in the acidic component is present as phenolic hydroxyl and the nitrogen as acidic nitrogen, as in pyrrole. The oxygen in the basic component is present as ring or ether oxygen and the nitrogen as ring nitrogen, as in pyridine. Complex formation occurs by hydrogen bonding between acidic phenol and basic nitrogen groups. The acid components contain essentially all the exchangeable protons, whereas the basic components contain essentially none. The hydrogen-bonded structure of asphaltenes is consistent with their solubility characteristics. In moderately polar solvents such as benzene, the asphaltenes are soluble because the acidic and basic components are separately solvated. Upon replacement of benzene by nonpolar solvents such as pentane, hydrogen bonding between the acidic and basic components takes place and the asphaltenes precipitate as a large insoluble complex.[99] Several investigators have studied the hydrogen bonding of model compounds (e.g., o-phenylphenol and pyridine or quinoline[100-104]), providing evidence that the acid and base components of asphaltene are essentially hydrogen donor and the basic components are essentially hydrogen acceptor.[100]

Coal-derived liquids may be hydrogenated for purposes of recycling or as preparation for fuels and chemical feedstocks.[105] Ouchi and coworkers studied the catalyzed hydrogenation of preasphaltenes and concluded that at temperatures <400°C the conversion of preasphaltene to asphaltene plus oil is a reaction involving depolymerization of the preasphaltene structure by splitting of ether linkages and the partial saturation of the aromatic rings with hydrogen, thus increasing their solubility in benzene. They also conclude that splitting of carbon-carbon bonds occurs spontaneously at >400°C (ref. 50,51). Kanda and coworkers concluded that at <400°C, hydrogenation of asphaltenes in the presence of catalysts involved the saturation of the aromatic rings with hydrogen to form naphthenic rings without changing the degree of polymerization.[106]

5. NONDONOR SOLVENTS

Several investigators observed that initial coal liquefaction reactions are rapid and that hydrogen consumption per unit yield is much lower in this initial phase than in the later reaction phases (refs. 10, 20, 39). This fact indicates facile hydrogen transfer reactions are occurring with little external hydrogen input. Furthermore, coal is a good hydrogen donor.[27,38] From these facts it can be concluded that coal contains both hydrogen donor and hydrogen acceptor molecular constituents or moieties bonded to or within the three-dimensional structure. Thus coal liquefaction reactions can occur by internal hydrogen rearrangement (i.e., intra-coal hydrogen transfer and shuttling).

This observation is substantiated by the ability of certain nondonor solvents (i.e., solvents that are not, or are not known to be, hydrogen donors) to extract coal significantly. A brief summary of successful solvents for such extractive disintegration includes polycyclic aromatics, such as naphthalene, phenanthrene, and pyrene; nitrogen-containing heterocycles such as pyridine and quinoline; and phenols such as phenol itself and naphthols (Table 1). In contrast, some superficially very similar structures such as anthracene, dibenzofuran, and o-phenylphenol were relatively ineffective.

5.1 Phenols

The amount of hydrogen in coals associated with phenolic hydroxyls is in the range of 2-8% of the total hydrogen.[25] The hydroxyl groups appear to be paired with another heteroatom and most are hydrogen bonded in the three-dimensional coal structure.[111] Phenols are commonly found in coal liquefaction products.[112,113] Several phenols have been evaluated as nondonor solvents (Table 1).

Favorable effects of phenols on donor-solvent liquefaction were recognized by Pott and Brocke who used phenol, naphthalene, and tetralin as the solvent in an early commercial coal liquefaction process.[1,19] Orchin and Storch speculate that the effectiveness of

Table 1. Coal conversion yields obtained with nondonor solvents (selected values)

Nondonor Solvent	Conversion (%)	Temperature (°C)	Time (min)	Coal	Solvent to coal ratio	Reference
Phenols						
Phenol	82[a]	482	15	Bruceton	10	1
Phenol	10[a]	460	15	Bruceton	1.5	1
Phenol	61[a]	455	10	Wyodak	10	1
Phenol	7[a]	427	5	Wyodak	5	1
Cresol	19-32[b]	400	30	Bruceton	4	19
1-Naphthol	80	288	--	Pittsburgh	--	1
2-phenylphenol	15	275	--	Pittsburgh	--	1
2-phenylphenol	20[b]	400	30	Bruceton	4	19
4-Cyclohexylphenol[c,d]	58	287	--	Pittsburgh	--	1
2-Cyclohexylphenol[c,d]	82[b]	400	30	Bruceton	4	19
Tetrahydronaphthol[c,d]	85[b]	400	30	Bruceton	4	19
Diphenylether	40[a]	460	15	Wyodak	10	78
Diphenylether	54[a]	482	15	Bruceton	10	78

Table 1. (continued)

Nondonor Solvent	Conversion (%)	Temperature (°C)	Time (min)	Coal	Solvent to coal ratio	Reference
Diphenylether/ Diphenyl	84	Eutectic	--	Dutch Creek	--	107
Diphenylether/ Diphenyl	20	Eutectic	--	Montana	--	107
N-Containing Compounds						
Ethylenediamine	22	20	--	Bituminous	--	74
Ethylenediamine	35-40	117	--	<85% C	--	108
Ethylenediamine	1-5	117	--	>85% C	--	108
Pyridine	12	20	--	Bituminous	--	74
Pyridine	30	427	60	Bituminous	4	72
Quinoline	17	150	--	Bituminous	--	2
Aliphatic Hydrocarbon						
Dodecane	20[b]	400	12	Bituminous	2	18

Table 1. (continued)

Nondonor Solvent	Conversion (%)	Temperature (°C)	Time (min)	Coal	Solvent to coal ratio	Reference
Polycyclic Aromatic Hydrocarbons						
Biphenyl	19[b]	400	30	Bruceton	4	19
Naphthalene	22[b]	400	30	Bruceton	4	19
Naphthalene	46[a]	460	15	Wyodak	10	78
Naphthalene	51[a]	482	51	Bruceton	10	78
Naphthalene	25[b]	400	5	Bituminous	2	18
Naphthalene	14[e]	400	60	Annesley	4	109
Naphthalene/ biphenyl	52	406	3	--	4	72
2-Methylnaphthalene	50	404	3	--	4	72
2-Methylnaphthalene	28[f]	400	60	Belle Ayr	3	36
Tetralin[c]	49[b]	400	30	Bruceton	4	19
Phenanthrene	90	340	360	Ireland	15	110
Phenanthrene	90-95	340	--	Bruceton	--	1

Table 1. (continued)

Nondonor Solvent	Conversion (%)	Temperature (°C)	Time (min)	Coal	Solvent to coal ratio	Reference
Phenanthrene	85	340	360	Bruceton	15	110
Phenanthrene	55[e]	400	60	Annesley	4	109
Phenanthrene	15[e]	400	60	Garw	3	109
Phenanthrene	80[e]	400	60	Bersham	3	109
Pyrene	70[f]	--	--	--	3	36
Pyrene	95[f]	400	60	Belle Ayr	3	36
Pyrene	35[f]	400	60	Monterey	3	77
Pyrene	33[f]	400	60	Belle Ayr	3	77
Pyrene	83	400	60	Annesley	4	109
Pyrene	79[e]	370	60	Miike	1	49
Pyrene	20[e]	390	60	Kentucky 14	1	49

Table 1. (continued)

Nondonor Solvent	Conversion (%)	Temperature (°C)	Time (min)	Coal	Solvent to coal ratio	Reference
Fluoranthene	85[e]	390	60	Miike	1	49
Mixed Synthetic[c,g]	50	404	3	--	4	72

[a] Extracted with pyridine.

[b] Extracted with benzene.

[c] Donor solvent.

[d] Initial reaction mixture contained 0.05 mol H_2, 40 g coal, and 160 g solvent.

[e] Extracted with quinoline.

[f] Extracted with THF.

[g] Mixture: 2% 4-methylpyridine; 17% 4-cresol; 38% tetralin; 43% 2-methylnaphthalene.

the hydroxyl group is probably related to its hydrogen bonding properties and that one of the forces holding together the reactive, unsaturated fragments of the coal structure is the associative force resulting from hydrogen bonding.[19] More recently, several investigators have attributed the phenol effect (i.e., improvement in coal conversion yields) to accelerated scission of ether linkages.[51,114] Further studies by Orchin and Storch revealed rather specific structural effects on the ability of phenols to extract coal [e.g., the effectiveness of 1-naphthol (Table 1)].[1]

Recent information by Poutsma and Dyer[115] indicates the effectiveness of 1-naphthol may be related to dimerization of 1-naphthol and formation of hydrogen that may be available for reduction of other organic species (i.e., 1-naphthol may be a limited donor solvent). Poutsma and Dyer observed that after 5 min at 400°C, the major thermolysis products of 1-naphthol (2.9% conversion) were: dinaphthofuran (33%), binaphthol (27%), 1-tetralone (24%), 5,6,7,8-tetrahydro-1-naphthol (4%), naphthalene (0.8%), tetralin (0.5%), 1-tetralol (1.2%), bis(1-naphthyl)ether (1.3%), 1,1'-binaphthalene-4,4'-diol (3.8%), and naphthylnaphthols (2.9%). They concluded that binaphthols were the dominant precursors of the dinaphthofurans. The equivalent of hydrogen made available by this conversion of two molecules of naphthol to a binaphthol is not released as molecular hydrogen but is transferred somehow to a third molecule of naphthol to effect reduction. Addition of benzophenone accelerated condensation to the furans and eliminated the reduction of naphthol in favor of almost exclusive formation of diphenylmethane. This has considerable implication for coal conversion processes, as will be discussed later.[115]

Experimental data from Oak Ridge National Laboratory[1,78,116] identified the importance of internal hydrogen redistribution in addition to simple solubilization. In this experimentation using phenol as a nondonor solvent, a hydrogen-enriched soluble portion along with a hydrogen-depleted char was produced in the absence of hydrogen gas. However, significant loss of phenolics occurred during coal liquefaction. This loss may be related to the formation of dibenzofurans and alkyldibenzofurans that are detected in many solvent-refined coal liquids.[38,115]

5.2 Polycyclic Aromatic Hydrocarbons

Several polycyclic aromatic hydrocarbons have been evaluated as nondonor solvents (Table 1). Their solvent action mechanism may be purely physical and/or through chemical interactions (e.g., hydrogen shuttling). Furthermore, they may participate as intermediates in the transmission of hydrogen from the gas phase to coal by formation of active hydrogen donors.[18,36,110] Hydrogen exchange has been demonstrated between naphthalene, phenanthrene, pyrene, and coal.[26-34,36-42] For example, after 10 h at 400°C, 21.9% of the deuterium in the α and β positions of naphthalene-d_8 was exchanged with the hydrogen in coal. The α position was the most active position for exchange.[117] Ruberto and coworkers concluded that phenanthrene functioned as an intermediate hydrogen transfer agent. They concluded that hydrophenanthrenes are good coal solvents because they are both donors and transfer agents and because they have the same structural features as completely depolymerized coal. When hydrogenating Big Horn subbituminous coal at 313°C, they achieved 72–89% conversion with phenanthrene to coal ratios ranging from 2 to 1 to 5 to 1 (ref. 22). Kamiya and coworkers observed that 3-ring aromatic hydrocarbons are more effective solvents than 2-ring aromatic hydrocarbons for brown coals.[118]

Coal conversions up to 90% have been reported with pyrene as a nondonor solvent.[36] Mochida et al. report that fluoranthene is somewhat more effective than pyrene.[49] According to Derbyshire and Whitehurst, the benefits of adding higher molecular weight PAHs (in the form of high boiling reaction products) to the solvent recycle stream are higher coal conversion, more effective hydrogen gas utilization, higher liquid yields, improved product selectivity, and reduced reaction severity.[92,93] They also postulate that in coal dissolution in pyrene, hydrogen transfer to the dissolving coal is enhanced through the formation in situ of hydropyrenes which are active hydrogen donors.[36,92,93]

The quality of polycyclic aromatic hydrocarbon solvents may be altered during processing in current coal liquefaction processes. For example, both hydrogenation and alkylation of pyrene occurs during coal conversion irrespective of the atmosphere, although alkylation decreases in the presence of hydrogen gas and with increasing carbon content (coalification) of the coal.[36] During coal liquefaction with phenanthrene at 350°C, a small amount of phenanthrene is chemically bonded to the coal as a side reaction.[110] Neavel observed that continued reaction in nondonor solvents such as pyrene decreased the liquefaction yield (benzene solubles), probably because of the formation of high molecular weight substances. From his data he concluded that prolonged reaction time in a hydrogen-deficient system is likely to be deleterious to overall yields.[18]

Several investigators[20,36,39] observed that there appears to be two regimes of reactivity in coal liquefaction. The first regime consists of the liquefaction of easily dissolved coal components. This occurs rapidly and requires little hydrogen consumption. The second regime involves the cleavage of a larger number of stronger chemical bonds, proceeds at a slower rate, and requires considerably more hydrogen. Derbyshire and Whitehurst conclude that conversion obtained with a nondonor solvent in an inert atmosphere (e.g., argon) represents conversion in the first regime and that higher conversions require the introduction of hydrogen gas.[36]

5.3 Nitrogen-Containing Compounds

Dryden hypothesized that nucleophilic attack by basic nitrogen solvents is important in dissolving coal molecules. He speculated that the unpaired electrons of nitrogen or oxygen in some solvents form complexes with coal molecules.[6] It is well known that pyridine, alkylated pyridines, and quinoline are effective solvents for coal (refs. 23,73,108). Burchill and coworkers extensively analyzed the nitrogen-containing compounds in a coal extract (in a recycle solvent) and in a light-ends distillation product. Of the total nitrogen (4050 mg/L) in the coal extract, 84% was basic and 16% neutral. Eighty-six basic nitrogen-containing compounds were identified by

GC/MS in the coal extract. The basic compounds were principally alkyl-substituted quinolines, tetrahydroquinolines, benzoquinolines, diphenylamines, carbazoles, and azafluoranthenes or pyrenes. A similar fraction (total nitrogen, 1200 mg/L) of the basic nitrogen-containing compounds was present in the light-ends distillate. The basic compounds were principally alkyl-substituted pyridines, anilines, and tetrahydroquinolines.[119] There has been much recent interest in tetrahydroquinoline as a coal liquefaction solvent.[23] Tetrahydroquinoline is known to be a better hydrogen donor than tetralin.[120]

Atherton and Kulik state that the effectiveness of basic nitrogen solvents may be attributable to two properties: (1) catalysis of tautomerization processes and subsequent cleaving of ether linkages and (2) carbonyl reduction. As an example of the efficacy of nitrogen-containing compounds, they cited an experimental run using 4-hydroxydiphenyl ether, tetrahydroquinoline, and tetralin (5/10/85, wt%) at 400°C (750°F) and 15-min reaction time in which the ether was completely decomposed to phenol. The decomposition rate was 200 times that measured in tetralin solutions. Atherton and Kulik also conclude that the improved solvent efficacy when heavy material (+427°C) is recycled may be attributable to nitrogen-containing heterocycles and amines.[23]

One investigator has observed that there is good correlation between the solvent power of ethylene diamine for coals and the phenolic hydroxyl content of the coal. This tends to corroborate the observation that hydrogen bonding between solvent and coal molecules may be an important factor in coal dissolution.[24]

5.4 Preparation or Isolation of Nondonor Solvents

Ideally, optimum concentrations of nondonor compounds in the recycle process solvent would be achieved by recycle of the appropriate boiling point cuts containing the desired constituents. Each of the nondonors studied in this research have been identified in coal liquefaction products and, theoretically, the concentrations of the nondonors could be increased in liquefaction solvents by suitable recycle. However, in most cases their concentrations are very low. Increasing the concentrations of the desired nondonor in the process solvent to optimum process concentrations may require addition of the constituent. This addition may necessitate obtaining the constituent from a separate industrial source or developing a specific process component for preparation and isolation of the desired nondonor.

Most of the nondonors selected for evaluation have been prepared commercially from coal tar distillation, or similar processes. In processing coke-oven tar, the common commercial objective is to concentrate naphthalene in the naphthalene oil (primary fraction distilling in the range 200-250°C) and anthracene in the anthracene oil (primary fraction distilling in the range 300-350°C). Naphthalene and crude anthracene (12-25% anthracene, 20-35% phenanthrene, and 7-15% carbazole) are separated from the respective oils on cooling or further processing.[121] Historically, solvents such as depleted anthracene oil have been used to start up coal liquefaction processes. The composition of this anthracene-poor oil is quite complex (for example, see ref. 44). Careful control and a high degree of fractionation in coal tar distillation can produce highly concentrated fractions of naphthalene, fluorene and acenaphthene, anthracene and phenanthrene, and carbazole, such as the Rutgerswerke Castrop-Rauxel plant that in 1969 produced almost all the worldwide supply of the pure PAH compounds (except naphthalene).[121]

Phenolic constituents are separated from coal tar distillate fractions (particularly those boiling at <250°C) by extraction with 10% aqueous sodium hydroxide and recovered by neutralization of the extract and subsequent distillation. Because phenol is one of the most widely used chemicals, the amount of phenol separated from coal tar is not adequate; consequently, most of the phenol used by industry is synthesized from benzene (petrochemical product). Most of the cresols and xylenols used in industry are derived from coal tar. Although present in coal tar, 1-naphthol is commercially produced by hydrolyzing 1-chloronaphthalene or 1-bromonaphthalene with sodium hydroxide (methanol solution) at 300°C or by fusion of 1-naphthalenesulfonic acid with sodium hydroxide.[121]

Diphenyl ether is present in some coal liquefaction products, but it is obtained commercially as a byproduct in the production of phenol by reacting aqueous sodium hydroxide with chlorobenzene at 375-400°C (ref. 122).

Pyridine bases are recovered from coal tar distillate fractions (150-200°C) by first washing the distillate with 10% aqueous sodium hydroxide to remove phenolics, then extracting the pyridine bases with 25-35% sulfuric acid. The pyridine bases are recovered from the pyridine sulfate extract by neutralization and subsequent distillation.[3] Quinoline is isolated from the coal tar distillate (boiling in the range 235-240°C) by extraction with dilute sulfuric acid, neutralization, and subsequent steam distillation and fractional distillation.[3,123] Carbazole is found in the crude anthracene fraction of coal tar and has been separated by fusion of the anthracene fraction with potash, separation of the alkali melt, and subsequent hydrolysis of the melt to produce carbazole.[3] Phenanthridine has not been considered of commercial significance; therefore, large-scale production processes have not been developed for it.

Naphthalene is the most abundant constituent in coke-oven tar, of which it comprises an average 9%. It is obtained in a variety of ways from naphthalene oil (bp 200-250°C), usually involving crystallization and subsequent separation and purification of the crystals. In coal tar distillation, phenanthrene is isolated with the anthracene fraction (anthracene oil, bp 300-350°C). Among the constituents usually associated with coal tar phenanthrene are anthracene, carbazole, diphenyl ether, and fluorene. Fractional distillation will concentrate the phenanthrene, from which anthracene can be substantially removed by extraction with pyridine bases, reaction with maleic anhydride, or selective hydrogenation. Carbazole is removed by hydrogenation, caustic fusion, or formation of carbazole sulfate. Fluorene and diphenyl ether have been removed by reaction with metallic sodium. Pyrene is found in coal tar fractions boiling above 360°C and can be separated by vacuum fractional distillation of the crude material. Further treatment by recrystallization of the picrates permits separation of fluoranthene and pyrene picrates.[3,121,124,125]

6. METHODS AND MATERIALS

The common physical properties of these nondonor compounds are given in Table 2. Detailed properties are presented in several references.[126,127] All chemicals were of high quality and were used as obtained from the supplier. The coal and process solvents were selected to be representative of their generic type.

6.1 Chemicals

Carbazole (mp 244-246°C), diphenyl ether (mp 26-28°C), phenanthrene (mp 98-100°C), and quinoline (98%) were obtained from Matheson Coleman and Bell Manufacturing Chemists, Norwood, Ohio. Naphthalene (fluorescence: excitation, 285 nm; emission, 300 nm), and 1-naphthol (mp 94-95°C) were obtained from Fisher Scientific Co., Fairlawn, New Jersey. Phenanthridine (98%, mp 105-107°C) and pyrene (99.9% pure as determined by GC analysis) was obtained from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin. Phenol (fp 40.5°C) was obtained from Mallinckrodt, Inc., Paris, Kentucky. Pyridine (bp 115-116°C) was obtained from Burdick and Jackson Laboratories, Muskegan, Michigan.

6.2 Kentucky No. 9 Coal

The Kentucky No. 9 coal (from the Fies Mine) used throughout this research program was a representative sample taken from a 55-gal drum of coal (sealed in the plastic bag liner within the drum) prepared by the Empire Coke Co., Tuscaloosa, Alabama, for use at the Wilsonville SRC pilot plant. The coal is ground in a closed system while being dried with hot air (80°C). During the grinding and

Table 2. Selected physical properties of the nondonor solvents used in tubing-bomb experiments [a,b]

	Molecular weight	Melting point (°C)	Boiling point (°C)	Critical temperature (°C)	Critical pressure (atm)
Phenol	94.114	40.9	181.8	419.2	60.5
Naphthalene	128.174	80.3	218.0	475	39.2
Quinoline	129.163	-14.9	237.1	527	57
Diphenylether	170.21	27.0-28.0	258.1-259.0		
1-Naphthol	144.174	95.8-96.0	288.0		
Phenanthrene	178.234	99.2	338.4	609.4	31.3
Phenanthridine	179.22	106	349		
Carbazole	167.21	245	354.8		
Pyrene	202.256	150.6	393	621.7	25.7

[a] Nondonor solvents are ranked according to boiling point.

[b] Data from refs. 126, 127.

drying operation the moisture content decreases from 7-8% to 3%. After grinding, the coal is loaded into bins previously filled and sparged with nitrogen. The sealed bins (3500 lb) are shipped to Wilsonville for use in the coal conversion plant.[128]

Analytical data for the coal used for this research program are presented in Table 3. Samples for laboratory use were stored under nitrogen atmosphere in sealed plastic bags within 5-gal tin containers.

Table 3. Analytical data for Kentucky No. 9 (Fies) coal used in ORNL experimental program

Sieve analysis[a]	Wt% passing through	Chemical parameter	Concentration (%)
200	95.2	Volatile matter	37.2
50	100	Moisture	3.0[b]
		Ash	8.9[c]
		Carbon	74.2[c]
		Hydrogen	5.6[c]
		Nitrogen	1.3[c]
		Sulfur	2.7[c]
		Oxygen (by difference)	7.3[c]

[a] Ref. 129.

[b] Moisture content of coal as received from the supplier.

[c] On a dry coal basis.

6.3 Lummus ITSL Solvent

The Lummus integrated two-stage liquefaction (ITSL) solvent used in this research was a representative sample taken from a 55-gal drum of 3LCF7-92 heavy oil product. The 3LCF7-92HO sample was obtained from the heavy oil product stream of the LC-Fining PDU Run 7-92 (ref. 130). To obtain a representative sample, the viscous oil was heated at 70°C for 48 h, rotated thoroughly, and sampled. Samples for laboratory use were stored under nitrogen atmosphere in 1-gal tin containers. Analytical data for the ITSL solvent are given in Table 4.

Table 4. Analytical data for Lummus ITSL solvent (3LCF7-92HO) used in ORNL experimental program

Chemical parameter	Concentration (%)
Carbon	88
Hydrogen	8.1
Sulfur	0.5
Nitrogen	0.8
Ash	1.4
Oxygen (by difference)	1.2

6.4 Wilsonville Solvent

The Wilsonville solvent used in this experimental program was representative of the typical SRC-I process solvent currently in use.

Solvent 131A was the designation used for process solvent taken from vessel 131A during the period 1978 to 1982. It consisted of the 230-450°C (450-850°F) boiling fraction taken from trays 3 and 8 of the distillation column and stored in vessel 131A. Four 55-gal drums of solvent 131A were collected on August 5, 1981, and designated Sample Number (SN)-71754. These drums were shipped to ORNL for use in the ORNL Coal Liquids Flow System (CLFS) and for basic research studies. Representative samples of the Wilsonville solvent SN-71754 for laboratory use were stored under nitrogen atmosphere in 1-gal tin containers. The solvent was mixed thoroughly by stirring prior to taking aliquots for tubing-bomb experiments, and the remaining solvent was resealed under nitrogen atmosphere for storage.

6.5 Tubing-Bomb Test Apparatus

The 19.5-mL SS316 tubing bombs or microautoclaves (High Pressure Equipment, Erie, Pennsylvania) are schematically shown in Fig. 1. The bombs are rated to greater than 10,000 psig. Essentially leak-free operation was obtained by tightening the large (1.5-in. diam) end caps to 95 to 100 ft-lb torque. During routine operation the end plugs were not removed from the caps. Two 0.64-cm diam SS balls were added with the coal slurry to assist mixing. To prevent sand bath sand from getting into the pipe threads during operation and perhaps ultimately into gravimeteric measurements, the bottom weep hole (in the bomb as supplied by manufacturer) was welded closed and the top weep hole was covered with 200-mesh screen by tack welding around the edges.

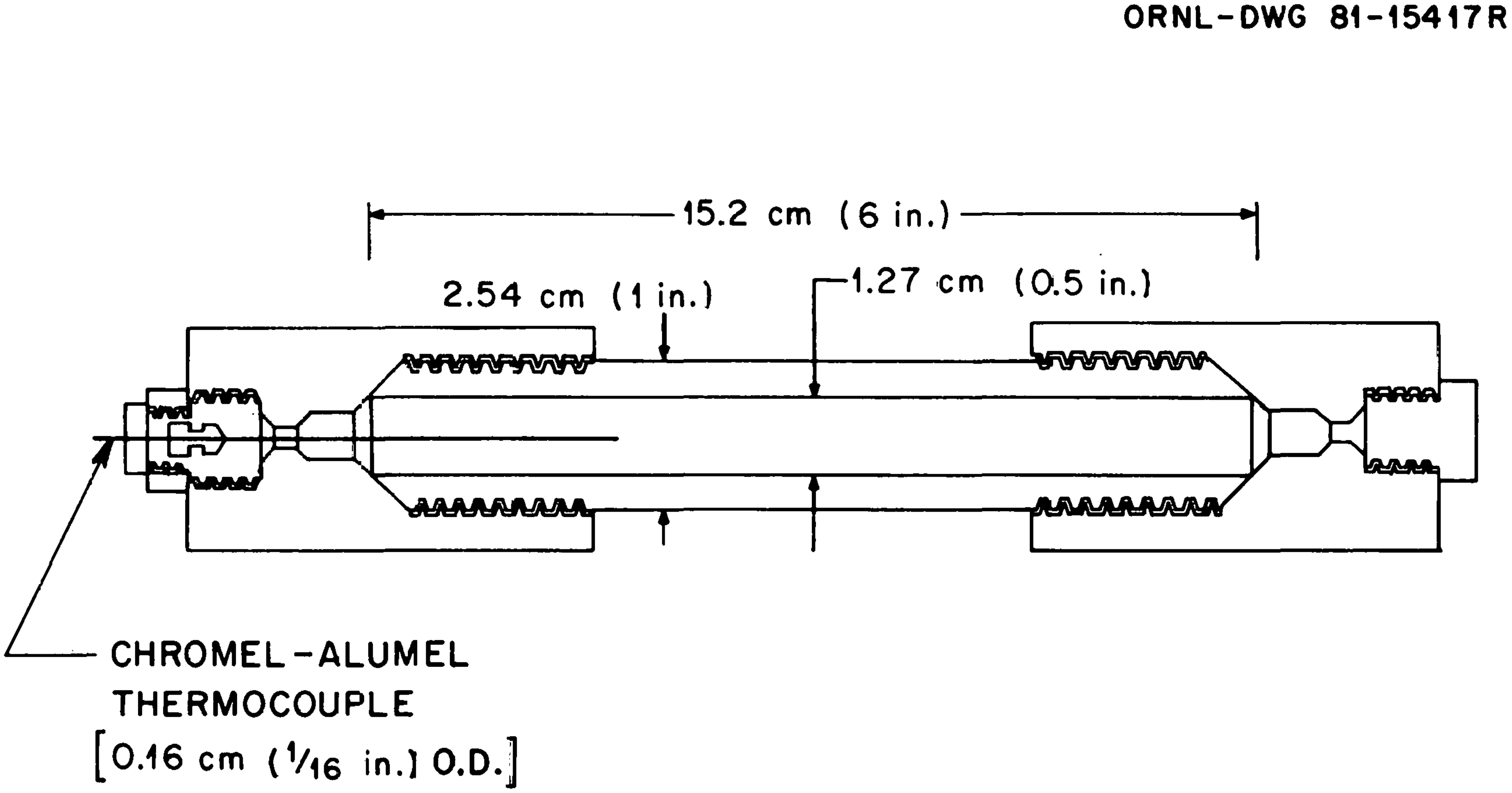

Fig. 1. Schematic of modified tubing-bomb reactor.

The fluidized-bed sandbath (TECAM™ Fluidized Bath SBL-2D, Techne Limited, Cambridge, England) for heating tubing bombs (Fig. 2) contains approximately 19 L aluminum oxide sand (120 mesh) (Techne Inc., Princeton, New Jersey) that is fluidized with 1.5 scfm air and heated with 4000-W heating elements. Fluidization at 1.5 scfm flowrate ensured a uniform temperature in the top 14 in. of the reactor sandbath. The air-driven motor (Model No. 8AM-NRV-5B, Gast Manufacturing Corp., Benton Harbor, Michigan) and eccentric cam shaft for oscillating the tubing bombs up and down was capable of variation from 180 to 600 cpm. The magnitude of the tubing-bomb oscillation was 3.8 cm. The temperature of the sandbath and autoclave were measured using chromel-alumel thermocouples and recorded on a 10-mv strip chart recorder (Linear Instruments Corp., Model 261). The temperature readings were calibrated against a potentiometer by comparison with a cold junction (0°C).

6.6 Experimental Procedures

6.6.1 Coal liquefaction experiments

6.6.1.1 Tubing-bomb test procedure. Tubing-bomb or microautoclave experiments have been a basic tool for laboratory study of coal liquefaction research conducted at elevated temperatures and pressures. Historically, problems of experimental variability and reproducibility have been encountered. Although intralaboratory data is often acceptable, comparisons between laboratories have been particularly poor. Therefore, rigid adherence to a standard operating procedure and great attention to experimental details are necessary to ensure statistically satisfactory data.

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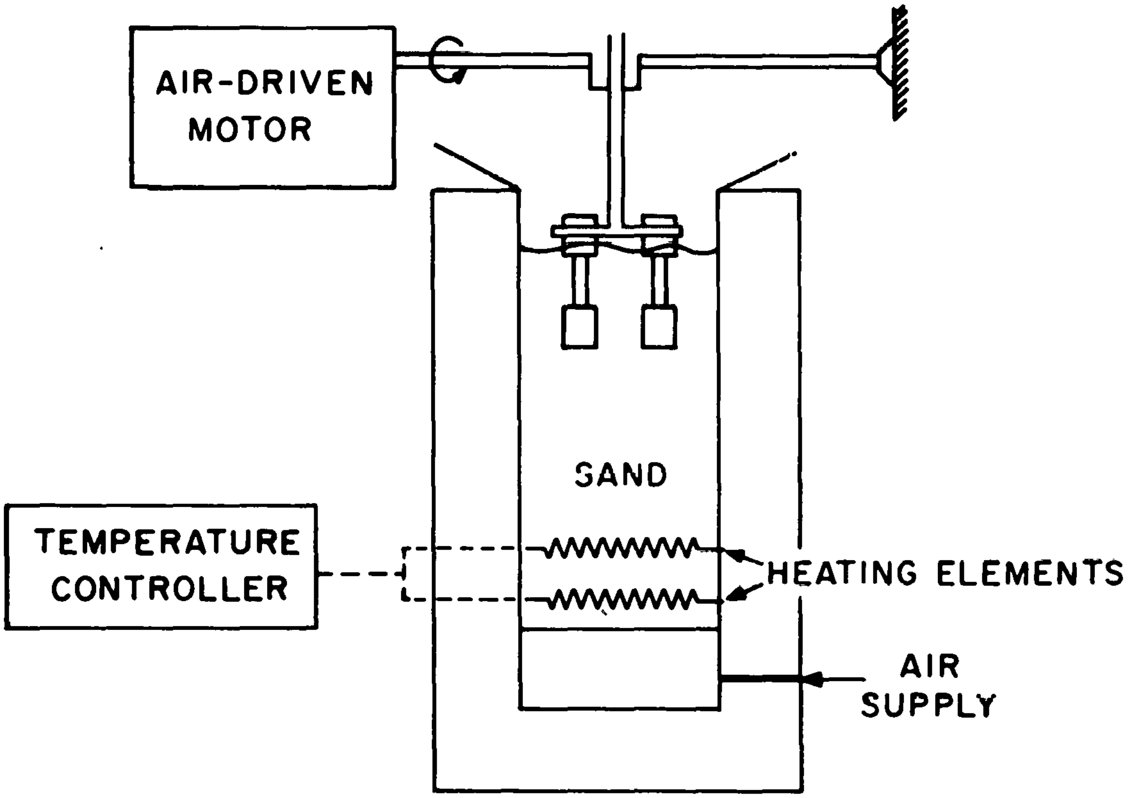

Fig. 2. Schematic of fluidized-bed sandbath for heating tubing-bomb reactors.

Tubing-bomb tests were used to determine the coal liquefaction efficacy of the nondonor solvents selected for evaluation in this research program. All tubing bomb tests were made using 12.5 g coal slurry composed of 5.0 g Kentucky No. 9 (Fies) coal and 7.5 g of a nondonor solvent or solvent mixture (composed of 30 wt% nondonor solvent and 70 wt% coal process solvent). Prior to weighing, the coal samples were dried in an inert atmosphere for 1 h at 100°C and 28-in. vacuum and placed in a dessicator (silica gel dessicant) for 15 min, then weighed immediately upon removal from the dessicator. Using these drying conditions, the coal sample lost 3.1% weight (presumably moisture). The tubing bombs were sparged with nitrogen, filled with the weighed amount of coal-solvent slurry, sparged again with a slow flow of nitrogen to remove the air from the bomb, and sealed immediately to 95 to 100 ft-lb torque.

Tubing-bomb tests were customarily run in duplicate. The sandbath was equilibrated to a temperature ~22°C (40°F) higher than the desired reaction temperature [e.g., 450°C (840°F) for a 427°C (800°F) tubing-bomb test], the two tubing bombs were attached by thumb screws to the eccentric cam of the horizontal agitator shaft, and the agitator air motor was started and adjusted to 180 cpm. The heat input to the sandbath was adjusted by the operator to achieve the desired temperature within 4-6 min. Reaction time was considered to start when the temperature reached 5.5°C (10°F) of the final temperature. After the desired reaction time (standardized at 10 min for this experimental program), the agitator was stopped, and the bombs were immediately removed from the sandbath and quenched with a spray of cold water and air. The temperature quenching was stopped when the temperature of the bombs dropped to 90°C (200°F) (accomplished within 2 min). After air cooling overnight, the bomb contents were removed by physical means (e.g., spatula, hand drill and pyridine washing). The contents were placed in tared Soxhlet extraction thimbles and extracted at 115°C under nitrogen atmosphere until the pyridine extract was colorless. The hot pyridine solution from each extraction was subsequently filtered by nitrogen pressure through two tared Whatman No. 42 filter papers. The purpose of this filtration was to determine the presence of pyridine insolubles that may have passed through the Soxhlet extraction thimble, i.e., in the size range of 0.5 to 25 μm. The Soxhlet thimbles and filter papers were dried overnight at 110°C under 28-in. vacuum, placed in a dessicator for 15 min, then weighed to determine the pyridine insolubles. The percent conversion was calculated by (1) dividing the weight of the residue by the weight of the dried coal (corrected for ash content) initially placed in the tubing bomb and subtracting from one and (2) multiplying the remainder by 100 [i.e., $(1 - W_r/W_{maf})100$].

6.6.1.2 Developmental problems. During the initial experimentation, several tubing-bomb tests were made, principally with a Wilsonville 131-A (SN/1/54) SRC-I process solvent, in order to develop experimental procedures. Careful attention to experimental details and standard operating procedures as developed during this initial experimental phase resulted in acceptable experimental reproducibility in tubing-bomb test runs during the subsequent comparative evaluation of nondonor and process solvents. In this first experimental phase, several problems were encountered that were solved by modification of equipment and procedure. Tubing-bomb leaks during high-temperature operation were eliminated by remachining the conical seating surfaces of the bomb nipples and standardizing the torque (95 to 100 ft-lb) used to seat the 1.5-in. bomb caps on the nipples. With careful attention to seating torque and visual examination of seating surfaces for possible scratches, leak-free operation was achieved through a series of over 50 runs. To prevent sand (aluminum oxide) in the sand bath from getting into the bomb pipe threads and, consequently, possibly into the test reaction mixture, the weep hole in the bottom end cap was sealed (spot welded), and the weep hole in the top cap was covered by 200-mesh screen. To ensure accurate temperature measurement, the temperature recorder was standardized against a null point potentiometer using a cold junction (0°C) prior to and during each run. To reduce experimental variability due to exposure of samples to air, all coal and solvent samples were stored and processed under nitrogen atmosphere. It was concluded that some low conversion yields in the early stages of experimentation were due to polymerization of pyridine solubles during extraction of the reaction residues without an inert atmosphere. Thereafter, all extractions and filtrations were accomplished under inert nitrogen atmosphere.

6.6.2 Gas chromatography

High-resolution gas chromatography of the coal process solvents was accomplished using a Hewlett Packard 5880A Series Gas Chromatograph equipped with a 12-m glass capillary OV-101 column and a flame ionization detector. Generally, a 1-μL aliquot of a 15% process solvent—85% acetone solution was injected onto the column using the split mode with the following operational parameters: injector temperature, 300°C; initial column temperature, 40°C; temperature program rate, 5°C/min; final temperature, 270°C; final time, 25 min; flame ionization detector temperature, 300°C; helium flow rate through column, 1.2 mL/min. Peak number and areas of peaks relative to the total flame ionization signal were determined by computer.

6.6.3 Gas chromatography/mass spectrometry

Mass spectra of gas chromatographic constituents in the process solvents were obtained on a quadrupole mass spectrometer (Hewlett Packard 5995A GC/MS System) using an ionization energy of 70 eV. Gas chromatographic separation conditions were essentially identical with those used for the high-resolution gas chromatography (see Sect. 6.6.2) to facilitate comparison. The GC/MS system is a fully computerized system with the capability of scanning from 50 to 400 amu at a rate of 690 amu/s. For identification, mass spectra were manually compared with the EPA/NIH mass spectral data base.[131]

7. RESULTS

The major objectives of the new liquefaction techniques research program were: (1) to perform comparative liquefaction studies on each of the eight selected nondonor solvents, and (2) to compare the nondonor solvents with well characterized process solvents and phenol. The experimental results for the comparative tubing-bomb liquefaction studies and characterization of two process solvents are presented here.

7.1 Comparative Liquefaction Studies

The comparative liquefaction studies using tubing-bomb tests were accomplished essentially in three phases: an initial ranking of nondonor solvents, an evaluation of nondonor solvent efficacy in 30% nondonor—70% process solvent mixtures, and a more accurate evaluation of the coal liquefaction efficacy of the most promising nondonor solvents. In addition, several "scouting" tubing-bomb tests were made to preliminarily examine other factors (e.g., replacement of moisture in coal by methanol and adsorption of quinoline from aqueous solutions). The standard experimental procedure is given in detail in Sect. 6. Table 5 presents the tubing-bomb experimental conditions and test results.

7.2 Characterization of Process Solvents

Two widely different process solvents were used in the comparative tubing-bomb tests, namely the Wilsonville SRC-I process solvent (V-131-A SN71754, sampled on 8/5/81) and the Lummus integrated two-stage liquefaction process (ITSL) solvent (3LCF7-92HO). One-microliter aliquots of acetone solutions (0.15 mL solvent, 1.0 mL acetone) of the solvents were subjected to high-resolution GC and GC/MS. (Experimental methodology was presented in Sect. 6.) Gas chromatographable constituents in the Wilsonville solvent (V-131-A) and the Lummus solvent (ITSL) as detected by flame ionization are shown in Figs. 3 and 4 respectively. An estimated 99% of the Wilsonville solvent (SN71754) and 46% of the Lummus ITSL solvent were volatile enough to pass through the gas chromatograph and were analyzed (see Appendix A).

Table 5. Experimental conditions and results for tubing-bomb runs
[All experiments made with Kentucky No. 9 (Fies) coal with a solvent/coal ratio of 1.5:1.]

Run	Run Date (1982)	Process Solvent	Nondonor Solvent	Nominal Reaction Temp. (°C)	Average Reaction Temp. (°C)[a]	Heat-up Time (min)	Reaction Time (min)	Cooling Time (min)[b]	Pyridine Solubility (%) (Soxhlet Extraction) Bomb 1	Bomb 2	Average	Pyridine Solubility (%) (Soxhlet + Filtration) Bomb 1	Bomb 2	Average	Filtration Difficulty[c]
18	3/9	V-131-A	--	427	421	8	10	2	46.0	54.0	50.0	44.0	51.0	47.5	E
19	4/23	ITSL[d]	--	427	430	5.5	10	2.5	73.0	76.9	75.0	29.2	24.0	26.6	E
20	4/29	---	Pyrene	427	431	6	10	3.5	39.5	[e]		30.0			E
21	5/5	---	Diphenylether	427	425	7	10	2	32.1	[e]		31.9			E
22	5/10	---	Quinoline	427	428	5.5	10	2	42.2	[e]		38.1			E
23	5/12	---	Naphthalene	427	420	7.5	10	2	37.4	[e]		37.4			E
24	5/20	---	1-Naphthol	427	423	6	10	2	55.6	[e]		55.5			E
25	5/24	---	Phenanthrene	427	426	6.5	10	2	41.0	[e]		38.4			E
26	5/26	---	Carbazole	427	425	6	10	2	37.0	[e]		34.5			E
27	6/1	---	Phenanthridine	427	424	8	10	3.5	37.0	[e]		35.2			E
28	6/3	---	Phenol	427	423	7	10	2	36.0	[e]		35.6			E
29	6/9	[f]	[f]	427	430	6.5	10	2	24.1	[e]					
30	6/9	---	1-Naphthol	427	427	6	10	2	42.8	49.1	46.0				
31	6/10	---	Quinoline	427	430	6.5	10	2	35.3	33.6	34.5				
32	6/11	---	Phenanthrene	427	430	5.5	10	2	35.8	36.1	36.0				
33	6/18	ITSL	--	460	459	6.5	10	2.5	30.4	31.2	30.8				
34	6/21	---	1-Naphthol	460	459	5.8	10	2	26.5	33.0	29.8				
35	6/22	---	Phenanthrene	460	462	6	10	2	30.4	30.8	30.6				
36	6/30	---	Phenol	460	457	7	10	1.5	35.0	34.0	34.5				
37[g]	7/6	ITSL	--	460	457	7.5	10	3	61.1	62.7	61.9	36.7	38.8	37.8	E

Table 5. (Continued)

Run	Run Date (1982)	Process Solvent	Nondonor Solvent	Nominal Reaction Temp. (°C)	Average Reaction Temp. (°C)[a]	Heat-up Time (min)	Reaction Time (min)	Cooling Time (min)[b]	Pyridine Solubility (%) (Soxhlet Extraction)			Pyridine Solubility (%) (Soxhlet + Filtration)			Filtration Difficulty[c]
									Bomb 1	Bomb 2	Average	Bomb 1	Bomb 2	Average	
38[g]	10/28	V-131-A, 100%[h]	Methanol[i]	427	430	5.5	10	3	77.3	77.6	77.5	73.0			VD
39[g]	8/17	ITSL	--	427	427	6.5	10	2.5	88.2	88.7	88.5	82.8	80.1	81.5	E
40[g]	8/31	V-131-A, 70%	1-Naphthol,30%	427	427	5.5	10	3	75.5	77.6	76.6	72.6			VD
41[g]	9/7	V-131-A, 70%	Quinoline,30%	427	430	6.5	10	2	65.5	67.0	66.3	65.0	66.7	65.9	D
42[g]	9/10	V-131-A, 70%	Phenanthrene,30%	427	431	7	10	3	64.9	67.7	66.3	64.7	67.5	66.1	E
43[g]	9/14	V-131-A, 70%	Pyrene,30%	427	427	6.5	10	3	73.6	73.6	73.6	73.1	72.8	73.0	D
44[g]	9/15	V-131-A, 70%	Naphthalene,30%	427	431	6.5	10	2.5	64.9	65.3	65.1	64.8	65.1	65.0	E
45[g]	9/20	V-131-A, 70%	Carbazole,30%	427	427	6	10	2	70.6	72.6	71.6	70.6	72.5	71.6	D
46[g]	9/22	V-131-A, 70%	Phenanthridine, 30%	427	427	6	10	3	71.6	72.3	72.0	70.8	71.7	71.3	D
47[g]	9/23	V-131-A, 70%	Phenol,30%	427	427	6	10	1.5	58.8	59.6	59.2	58.8	59.6	59.2	E
48[g]	9/24	V-131-A, 70%	Diphenylether, 30%	427	430	6	10	2	53.3	57.0	55.2	53.1	56.9	55.0	E
49[g]	9/27	V-131-A	--	427	428	6.5	10	2.5	60.3	61.5	60.9	60.1	61.2	60.7	E
50[g]	9/28	V-131-A, 70%	ITSL,30%	427	429	6	10	3	73.8	73.8	73.8	72.8	73.2	73.0	E

Table 5. (Continued)

Run	Run Date (1982)	Process Solvent	Nondonor Solvent	Nominal Reaction Temp. (°C)	Average Reaction Temp. (°C)[a]	Heat-up Time (min)	Reaction Time (min)	Cooling Time (min)[b]	Pyridine Solubility (%) (Soxhlet Extraction)			Pyridine Solubility (%) (Soxhlet + Filtration)			Filtration Difficulty[c]
									Bomb 1	Bomb 2	Average	Bomb 1	Bomb 2	Average	
51[g]	10/1		1-Naphthol	427	425	5	10	2	77.3	79.2	78.3	77.1	78.4	77.8	E
52[g]	10/5		Pyrene	427	423	5.5	10	2	49.5	41.2	45.4	34.5	31.7	33.1	VD
53[g]	10/26		Phenanthridine	427	424	5	10	2	40.2	36.4	38.3	38.6	35.3	37.0	D
54[g]	10/29	V-131-A, 100%	Quinoline/Water	427	424	5	10	2	64.0[j]	62.6[k]		63.8[j]	62.6[k]		E
55[g]	11/10		1-Naphthol	427	424	4.5	10	1.5	80.6	82.3	81.5	76.3	80.1	78.2	VD
56[g]	11/15		Carbazole	427	429	5.5	10	1	38.0	33.6	35.8	37.7	33.6	35.7	E
57[g]	11/19		Naphthalene	427	424	4.5	10	1	37.9	39.4	38.7	37.9	39.4	38.7	E
58[g]	1/18/83		Phenanthrene	427	427	3.8	10	1.5	38.0	37.2	37.6	36.5	36.3	36.4	E
59[g]	1/21/83		Quinoline	427	428	5.5	10	1.5	53.6	51.0	52.3	50.2	50.6	50.4	E

[a] Reaction temperature averaged over reaction time.

[b] Time required to cool reactor to 100°C (200°F).

[c] Relative difficulty in filtering the pyridine solution through two Whatman No. 42 filters after Soxhlet extraction: E, easy; D, difficult; VD, very difficult.

[d] ITSL, Lummus Integrated Two-Stage Liquefaction Solvent (3LCF7-92HO).

[e] Second bomb saved for chemical analysis.

[f] No solvent was used with the coal in the tubing-bomb test.

[g] Soxhlet extraction and filtration made under inert atmosphere.

[h] V-131-A, Wilsonville SRC-I process solvent (V-131-A, SN71754).

[i] Coal soaked in methanol prior to tubing-bomb test.

[j] Coal soaked in aqueous solution of quinoline prior to tubing-bomb test.

[k] Coal soaked in water (only) prior to tubing-bomb test.

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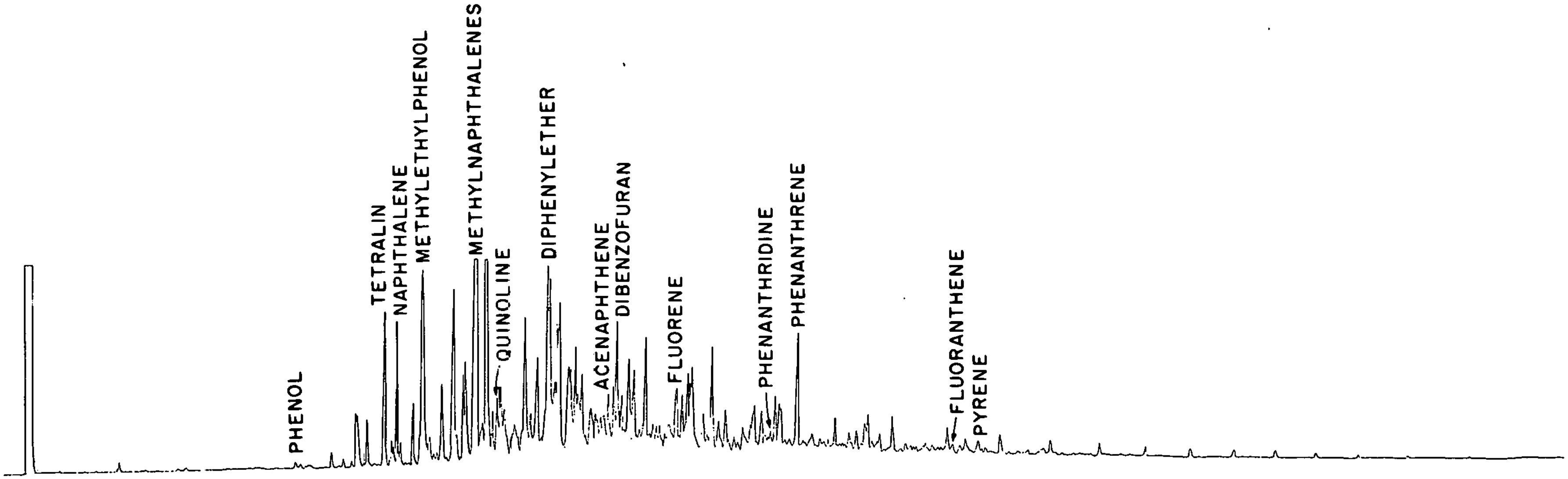

Fig. 3. Gas chromatogram of Wilsonville SRC-I process solvent (SN71754). Only selected major components are labelled in this figure; Table 6 provides a complete list of identified compounds.

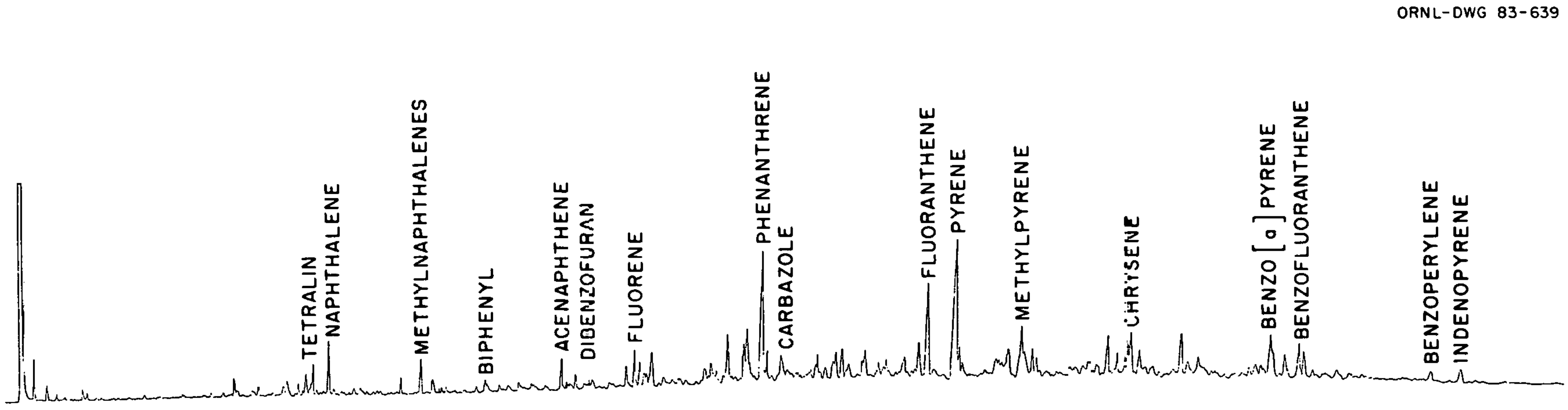

Fig. 4. Gas chromatogram of Lummus ITSL solvent (3LCF7-92HO). Only selected major components are labelled in this figure; Table 6 provides a complete list of identified compounds.

Over 100 constituents were identified in each solvent by comparison of mass spectra with spectra in the EPA/NIH Mass Spectral Data Base.[131] The identified constituents and approximate relative concentration of the gas chromatographable constituents are given in Table 6. The relative volatility of the two process solvents was determined by simple vacuum distillation and weighing the residue after distillation (Table 7).

8. DISCUSSION

The observation that nondonor solvent constituents facilitate conversion of coal to liquid products in high yield without molecular hydrogen addition and at short contact times could open the possibility for potential new liquefaction concepts that might be more economic than existing ones because of more efficient use of the hydrogen inherent in coal. However, a small but significant amount of solvent is generally incorporated into the product, indicating the need for makeup solvent in any process using this concept. Thus, such nondonor solvents should ideally be produced in the liquefaction process and be present in reasonable concentrations in process streams of the coal liquefaction processes per se. The nondonors should also have the potential to act as hydrogen redistribution agents and possess process characteristics relatively easy to manage in present plant systems. Although various mechanisms for hydrogen shuttling between various parts of the coal structure have been suggested, none has been firmly demonstrated. In fact, more than one chemical pathway may well contribute. A catalog of mechanistic possibilities provides

Table 6. Quantitative comparison of gas chromatographic peaks for constituents in two coal conversion process solvents

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
Methylcyclohexane	0.182	
Toluene	0.061	0.016[c]
Ethylcyclohexane	0.110	
Xylene	0.100	0.058[c]
Xylene	0.047	
Trimethylhexene	0.027	0.013[c]
Propylcyclohexane	0.062	0.035[c]
Octahydroindane	0.033	
2,4-Nonadiene	0.073	
_m_-Menthane	0.042	0.006[c]
Ethylmethylbenzene	0.034	0.003[c]
2-Methyl-4,5-nonadiene	0.034	
Indane	0.078	
Phenol		0.061
Dimethylpyridine		0.048
Ethylpyridine		0.003
Decahydronaphthalene	0.355	
Methylisopropylbenzene	0.116	
1-Methyl-4-(1-isopropyl)-benzene	0.186	
1-Ethyl-2,4-dimethylbenze	0.178	
Methylethylpyridine		0.019

Table 6. (continued)

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
2-Methylphenol		0.141
Decahydronaphthalene	0.302	
Ethyltrimethylbenzene	0.354	
4-Methylphenol		0.438
4-Methylindan		0.863
Ethyldimethylbenzene	0.238	
2-Methylindan	0.409	0.544
Tetralin	0.617	2.044
Ethylphenol		0.313
Ethylphenol		0.243
Naphthalene[d]	1.165	1.698
Dimethylindan	0.096	
Dimethylindan	0.096	0.777
Ethylphenol		4.471
2-Methyltetralin	0.158	0.396
Methyltetralin	0.190	
$C_{12}H_{26}$-Hydrocarbon	0.056	0.185
Ethylindan	0.080	0.163
Ethyltrimethylbenzene	0.066	
Dimethylindan		0.329
Ethylphenol		0.988
Dimethyltetralin		0.077
Methyltetralin	0.055	2.843

Table 6. (continued)

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
Methyltetralin	0.341	
Ethyltetralin		1.625
1-Methylnaphthalene	0.767	8.852
Methyltetrahydroquinoline		0.822
2-Methylnaphthalene	0.317	5.731
Bicyclohexyl	0.125	
$C_{13}H_{28}$-Hydrocarbon		0.390
2-C-Tetralin	0.123	0.128
Quinoline[d]		1.023
2-C Tetralin	0.037	
1,1'-Methylene-biscyclohexane	0.037	
Diethylbenzene		1.004
Ethyltetralin		0.224
Methylquinoline		0.684
2-C Tetralin	0.149	0.160
Trimethyltetralin		2.725
Biphenyl	0.305	
Methylindole	0.181	
Decahydrofluorene	trace	
Diphenylether		3.297
Dimethyltetralin		2.520
Dimethylnaphthalene	0.188	3.588
Dimethylnaphthalene	0.210	1.583

Table 6. (continued)

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
Dimethylnaphthalene	0.206	1.154
$C_{14}H_{30}$-Hydrocarbon	0.173	1.532
Dimethylnaphthalene		0.972
Dimethylethyltetralin	0.166	
3-C Tetralin		0.723
3-C Tetralin		0.396
Dihydrotrimethylnaphthalene		0.224
Acenaphthene	0.808	0.640
Tetradecahydrophenanthrene	0.231	
Pyroindole	0.272	
Dihydronaphthopyran		0.256
[1,1'-Biphenyl]-2-ol		0.256
5-C Benzene		0.256
Hydrocarbon		1.343
Tetradecahydroanthracene	0.350	
Dibenzofuran	0.572	0.147
Cyclohexylethylbenzene	0.172	
Tetramethyltetralin	0.172	
Trimethylnaphthalene		1.340
Trimethylnaphthalene		0.812
$C_{15}H_{32}$-Hydrocarbon	0.195	1.369
Trimethyldihydronaphthalene	0.109	
Trimethylnaphthalene		0.093

Table 6. (continued)

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
Butylnaphthalene		0.233
Trimethylnaphthalene		0.240
Trimethylnaphthalene		0.265
C_4-Tetralin	0.781	
Fluorene	0.973	1.071
Propenylnaphthalene	0.609	0.713
Octahydrophenanthrene	0.190	
$C_{16}H_{34}$(Branched-Chain Hydrocarbon)		1.062
Methylbiphenyl	0.190	
Octahydrophenanthrene	0.151	
Methylbiphenyl	0.151	
Methylfluorene		0.710
Butylnaphthalene	1.367	1.218
Ethylbiphenyl		0.620
Dimethyl-biphenyl	0.342	
4-Methyldibenzofuran	0.086	
$C_{16}H_{34}$-Hydrocarbon	0.271	1.625
Ethylbiphenyl	0.189	0.716
Methylisopropylnaphthalene		0.611
Dimethyl-biphenyl		0.211
9,10-Dihydrophenanthrene	0.646	0.138
Dihydrophenanthrene		0.192
Hydrocarbon (C_{17} Branched Chain)		0.192

Table 6. (continued)

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
Octahydrophenanthrene	0.560	
9H-9-Methylfluorene	0.227	
Dimethyl-biphenyl	0.342	
Hexadecahydrofluoranthene	0.171	
Octahydrophenanthrene	1.570	0.281
2-Methoxy-9H-fluorene	1.387	0.141
Ethylbiphenyl		0.937
Dimethyl-biphenyl	0.501	0.662
Ethenonaphthalene	0.501	
Hexylthiocyclohexane	0.501	
Phenanthridine[d]		0.278
$C_{17}H_{36}$-Hydrocarbon		0.739
Butylnaphthalene		0.736
C_5-Naphthalene		0.448
Phenanthrene[d]	4.429	1.986
Decahydropyrene	0.465	
Hexahydropyrene	0.465	
$C_{17}H_{34}$-Hydrocarbon		0.201
Phenanthrenol		0.144
Benzoquinoline or acridine		0.080
1,2-Dimethyl-4-(phenylmethyl)benzene		0.096
$C_{18}H_{38}$-hydrocarbon		0.345
Carbazole[d]	1.453	0.217

Table 6. (continued)

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
C_{19} (Branched-Chain Hydrocarbon)	0.340	
Decahydro-4-a-phenyl-trans-naphthalene	0.545	
Hexahydropyrene	0.749	
Dimethyl(phenylmethyl)benzene		0.265
Methylphenanthrene	0.518	0.425
Methylphenanthrene		0.508
Dihydro-1-methyl-3-phenylindane		0.179
Methylcarbazole		0.077
Octadecahydrochrysene	0.610	
Hexadecahydropyrene	0.610	
Tetrahydrofluoranthene	0.396	
Phenylnaphthalene	0.548	
$C_{19}H_{40}$-Hydrocarbon		0.467
Hexahydropyrene	0.781	
Methylcarbazole		0.090
Phenylnaphthalene		0.077
Ethylphenanthrene		0.090
$C_{19}H_{38}$-Hydrocarbon		0.118
Methylbenzophenanthrene	1.159	
Dimethylphenanthrene		0.147
Dimethylphenanthrene		0.090
Hexamethyl-biphenyl		0.048

Table 6. (continued)

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
Methoxyphenanthrene		0.048
Dihydropyrene	1.314	
$C_{20}H_{42}$-Hydrocarbon		0.387
Fluoranthene	3.285	0.170
Pyrene[d]	6.787	0.224
$C_{21}H_{44}$-Hydrocarbon		0.227
Trimethylphenanthrene		0.054
Methylpyrene	1.689	0.083
Methylpyrene	2.227	
Phenylmethylnaphthalene		0.070
$C_{22}H_{46}$-Hydrocarbon		0.237
Phenylmethylnaphthalene		0.026
Butylphenanthrene	0.227	
Terphenyl (probable)	0.130	
$C_{23}H_{48}$-Hydrocarbon	0.614	0.198
Benzofluoranthene	0.552	
Ethyldihydropyrene	1.225	
Ethyldihydropyrene	0.720	
$C_{24}H_{50}$-Hydrocarbon	1.095	0.128
Chrysene	1.455	
4-Ring PAH	0.950	
$C_{25}H_{52}$-Hydrocarbon		0.106
Tetrahydrobinaphthalene	1.482	

Table 6. (continued)

Constituent[a]	Area percent[b]	
	Lummus ITSL	Wilsonville 131A
Binaphthalene	0.947	
Dimethylbenzanthracene	0.160	
$C_{26}H_{54}$-Hydrocarbon		0.096
Perylene	0.746	
$C_{27}H_{56}$-Hydrocarbon		0.090
Benzo[a]pyrene	2.384	
Benzofluoranthene	1.297	
$C_{28}H_{58}$-Hydrocarbon		0.064
3,6-Dimethoxy-9,10-dimethylphenanthrene	0.245	
$C_{29}H_{58}$-Hydrocarbon	0.245	0.052
Dibenzacridine	0.132	
Hydrocarbon	0.132	
Benzo[ghi]perylene	0.308	
$C_{31}H_{64}$-Hydrocarbon	0.154	
Indenopyrene	0.592	
Total fraction of FID signal identified[b]	67.3%	86.6%

[a] Most probable structure from MS data.

[b] GC peak area expressed as percent of total flame ionization detector (FID) signal for GC run; therefore, area percent approximates weight percent.

[c] Identified by GC retention time only.

[d] Nondonor solvent selected for evaluation in this research program.

Table 7. Volatility of solvents

	Wilsonville SN 71754 (%)	Lummus ITSL (%)
0.02 mm/200°C/1 h	99	46
0.02 mm/200°C/6 h	--	65

a useful method for choosing candidate solvents, in addition to the historical input described above. Our thinking includes three major possibilities:

1. Free-radical pathways where the solvent R-H cycles between R-H and R•; phenol may function in this manner.
2. Free-radical pathways where the solvent R' cycles between R' and R'H•; polycyclic aromatics might function by such a pathway.
3. Non-radical pathways where the solvent R" cycles between R" and R"H$_2$.

Based on the criteria that nondonor solvents should have the potential to act as hydrogen redistribution agents and also be present in reasonable concentrations in coal liquefaction process streams, the following eight nondonor solvents representing three chemical types (i.e., polycylic aromatic hydrocarbons, nitrogen-heterocyclic compounds, and oxygen-containing compounds) were selected for evaluation in coal liquefaction studies: naphthalene, phenanthrene, pyrene, quinoline, carbazole, phenathridine, naphthol, and diphenyl ether. Because of the number of solvents to be tested and the consequent large number of experiments required to determine the effects of reaction time, temperature, and solvent/coal ratio for each, the pragmatic decision was made to evaluate the solvents at only one temperature, 427°C (800°F), for a reaction period of 10 min at a solvent/coal ratio of 1.5:1. For comparative purposes, several tests were also made at 460°C (860°F). Details of the test protocol are given in Sect. 6.

The comparative tubing-bomb test experimentation was conducted chronologically in three phases:

1. Procedure development. An initial ranking of the relative effectiveness of the nondonor solvents with one coal of process interest (Kentucky No. 9, Fies) was accomplished during the development of experimental procedures.
2. Nondonor with supplemental hydrogen. The effectiveness of the nondonors was evaluated in combination with a conventional process solvent (Wilsonville V-131-A).
3. Pure nondonor. The relative effectiveness of the pure nondonors was evaluated for coal liquefaction.

For purposes of logical presentation in this report, the experimental results and conclusions of the three phases will be discussed in reverse order. Results of two special experiments with quinoline and methanol are presented in Appendixes B and C.

8.1 Relative Effectiveness of Pure Nondonor Solvents and Process Solvents

After development of experimental methodology that yielded meaningful and reproducible data, the nondonor solvents were evaluated. The relative effectiveness of the pure nondonor solvents for converting Kentucky No. 9 coal (Fies mine) to pyridine-soluble products at 427°C (800°F), 10-min reaction time, and 1.5 solvent/coal ratio was: 1-naphthol, quinoline, naphthalene, phenanthridine, phenanthrene, phenol, carbazole, pyrene, and diphenyl ether (Table 8). The range of conversion varied from 78% to 32%. Only 1-naphthol (78% conversion) was as effective as the two high-quality process solvents — Wilsonville

Table 8. Relative effectiveness of pure nondonor and process solvents without supplemental hydrogen (all values-except those designated-an average of two runs[a])

	Pyridine solubility as determined by		
Solvent[b]	Soxhlet extraction[c] (% maf)	Soxhlet extraction and filtration[d] (% maf)	Pyridine insolubles: 0.5–25 µm particles (%)
Lummus ITSL (run 39)	88	82	6
1-Naphthol (runs 51 and 55)	80[e]	78[e]	2
Wilsonville V-131-A (run 49)	61	61	0
Quinoline (run 59)	52	50	2
Naphthalene (run 57)	39	39	0
Phenanthridine (run 53)	38	37	1
Phenanthrene (run 58)	38	36	2
Phenol (run 28)	36[f]	36[f]	0
Carbazole (run 56)	36	36	0
Pyrene (run 52)	45	33	12
Diphenyl ether (run 21)	32[f]	32[f]	0
Coal only (run 29)	24[f]	--	--

[a] Test conditions: 19.5 mL tubing bombs; 5.0 g Kentucky No. 9 (Fies) coal (dried at 110°C and 28 in. vacuum for 1 h); 7.5 g solvent; 10-min reaction time; 427°C (800°F); mixing at 180 cpm (1.5-in. stroke) using two 0.64-cm diameter SS balls.

[b] See Table 4 for run details.

[c] Pyridine solubility by Soxhlet extraction under N_2.

[d] Pyridine solubility by Soxhlet extraction under N_2 followed by filtration through Whatman No. 42 filter paper under N_2.

[e] Average of four runs.

[f] Single run value.

SRC-I (61%) and Lummus ITSL heavy oil solvent (82%). For comparison, the thermal conversion of coal without a solvent was 24%. In this test series the determination of pyridine solubility was made in an inert atmosphere, thus the experimental results should represent an accurate assessment of the relative efficacy of the nondonor and process solvents. For the pyrene experiment, note the large amount of pyridine-insoluble particulates in the 0.5- to 25-μm range (Table 8). Note too the relatively large amount of insoluble particles (0.5 to 25 μm) in the Lummus ITSL experiment which may also be a consequence of the high concentration of pyrene and other 4- and 5-ring PAH compounds in the Lummus solvent (see Sect. 8.3). It is important to determine the nature of the 0.2- to 25-μm pyridine insolubles. Does this size range of insolubles represent carbonized material which cannot be further converted to liquid products, or does it represent useable material that can be recycled? If this fraction represents material useable on recycle or further processing, then pyrene would be almost as effective as quinoline (i.e., moderately to highly effective).

In the above effectiveness ranking (Table 8), there appear to be three major groupings: highly effective (e.g., 1-naphthol), moderately to highly effective (e.g., quinoline), and moderately effective (e.g., naphthalene, phenthridine, phenanthrene, phenol, carbazole, pyrene, and diphenyl ether). The effectiveness of 1-naphthol is not surprising because Orchin and Storch[6,19] found that both 2-ring solvents with a hydroxyl group attached to the aromatic ring and hydroaromatic rings were particularly effective in conversion of coal at about 380°C (720°F). They determined that with higher-ranked bituminous coal, 1- and 2-naphthols were effective solvents; but with subbituminous coals, 2-naphthol was less effective than phenanthrene, but 1-naphthol extracted about 83% of the coal. Orchin and Storch also determined that the solvent effectiveness of aromatic solvents for bituminous coal correlated well with the boiling point. Based on these tubing-bomb test results, the Wilsonville SRC-I solvent was moderately to highly effective, and the Lummus ITSL heavy oil solvent was highly effective.

8.2 Relative Effectiveness of Nondonor Solvents and a Process Solvent with Supplemental Hydrogen

The behavior of the set of nondonor solvents was evaluated at 427°C (800°F) and 10 min in the presence of a supplemental source of hydrogen, i.e., a coal conversion process solvent. Each was in turn mixed in a 30:70 wt% ratio with the Wilsonville SRC-I process solvent (V-131-A, SN71754). The solvents are ranked in Table 9 according to their relative conversion efficacy. The comparable conversion obtained with the 30 wt% Lummus ITSL and 70% Wilsonville V-131-A solvent is also given. Note that the determination of pyridine solubility was made in an inert atmosphere, thus the experimental results should represent an accurate assessment of the relative effectiveness at 427°C of the nondonors in the presence of supplemental hydrogen. Using the process solvent as a supplemental source of hydrogen apparently minimized the formation of pyridine-insoluble particulates in the range 0.5 to 25 μm for both pyrene and Lummus ITSL (compare particulate insolubles in Table 9 with those in Table 8). This decrease in

Table 9. Liquefaction performance of mixtures of nondonor solvents and a process solvent with Wilsonville process solvent (solvents ranked according to conversion efficacy[a])

	Pyridine solubility as determined by		
Solvent[b]	Soxhlet extraction[c,d] (% maf)	Soxhlet extraction and filtration[d,e] (% maf)	Pyridine insolubles: 0.5–25 μm particles (%)
1-Naphthol (run 40)	77	73	4
Lummus ITSL solvent (run 50)	74	73	1
Pyrene (run 43)	74	73	1
Carbazole (run 45)	72	72	0
Phenanthridine (run 46)	72	72	0
Quinoline (run 41)	66	66	0
Phenanthrene (run 42)	66	66	0
Naphthalene (run 44)	65	65	0
Wilsonville (run 49)[f]	61	61	0
Phenol (run 47)	59	59	0
Diphenyl ether (run 48)	55	55	0

[a] Test conditions: 5.0 g Kentucky No. 9 (Fies) coal (dried at 110°C and 28-in. vacuum for 1 h); 7.5 g of a 30:70 mixture of nondonor solvent and Wilsonville solvent; 19.5 mL tubing bomb; 427°C (800°F); 10 min; shaken at 3 strokes/s (3.8-cm stroke) with 2 SS balls.

[b] See Table 4 for run details.

[c] Pyridine solubility by Soxhlet extraction under N_2.

[d] Average of two runs.

[e] Pyridine solubility by Soxhlet extraction under N_2 followed by filtration through Whatman No. 42 filter paper under N_2.

[f] Wilsonville V-131-A solvent (SN71754) alone; 7.5 g total.

0.5- to 25-μm pyridine insolubles may be attributable to lower concentrations of 4- and 5-ring PAH constituents in tests with 70% Wilsonville process solvent.

8.2.1 Comparison with Wilsonville SRC-I process solvent

An incremental increase in conversion of greater than 10% was observed for 1-naphthol, pyrene, carbazole, and phenanthridine when compared with the Wilsonville solvent alone. As in the case of pure nondonor experiments, coal conversion was highest with the naphthol. The relative efficacy of the PAHs in the presence of a supplemental source of hydrogen correlates with the boiling point of the aromatic hydrocarbon in agreement with conclusions of Orchin et al.[19] Under these reaction conditions, the nitrogen-heterocycles, carbazole and phenthridine are more effective than quinoline in the presence of the process solvent. These results indicate that factors in addition to the basicity of the nitrogen-containing compound are important in determining the efficacy of a solvent. Note that the Lummus ITSL heavy oil solvent in 30% mixture with the Wilsonville SRC-I process solvent improved the conversion of the Wilsonville solvent by greater than 10%. The concentrations of 3-, 4-, and 5-ring PAH and hydroaromatic components and, also, molecular weight components is significantly higher in the Lummus ITSL solvent than in the Wilsonville process solvent (see Sect. 8.3). The improvement in conversion efficacy of the Wilsonville solvent is probably due to these added components; therefore, increasing the concentrations of 4- and 5-ring and higher molecular weight PAH and hydroaromatic components would improve the conversion efficacy of the Wilsonville solvent. This observation corroborates the observations of several other investigators that addition of high boiling and nondistillable components can improve coal conversion.[92,93]

A comparison of the conversion efficacies of the nondonor solvents (as ranked in Table 8) with that achieved in the 30:70 mixtures with the Wilsonville SRC-I process solvent shows large increases in conversion for all the nondonors except 1-naphthol. These data indicate that the presence of a supplemental hydrogen source in the form of the hydrogenated compounds present in the Wilsonville solvent (see Sect. 8.3) greatly improved the liquefaction effectiveness of the nondonors. We conclude that at 427°C (800°F), 10 min reaction, and a solvent/coal ratio of 1.5, only 1-naphthol (of the set of nondonors studied) gave coal liquefaction yields comparable to that achieved by the two process solvents that were used in this study. We also conclude that efficient liquefaction with the nondonor solvents evaluated in this study requires a supplemental source of hydrogen (e.g., H_2 or a donor solvent).

8.2.2 Comparison with weighted average of two components

In the presence of supplemental hydrogen (i.e., in a 30% nondonor—70% Wilsonville SRC-I solvent mixture) all nondonor solvents increased the effectiveness of Wilsonville solvent. This increase was greater than that predicted by the weighted average of the components for all nondonor solvents but especially for pyrene, carbazole, and phenthridine (Table 10). An incremental increase (above the weighted average) in conversion of greater than 18% was observed for pyrene, phenanthridine, and carbazole. The comparable incremental increase for

Table 10. Relative effectiveness of nondonor/process (Wilsonville SRC-I) solvent mixtures compared with calculated weighted average effectiveness (comparison values given for phenol and Lummus ITSL heavy oil in 30:70 mixture with the Wilsonville solvent; all values — except those designated — an average of two runs[a])

Solvent	Coal conversion of nondonor[b,c] pyridine solubility (% maf)	Calculated[d] coal conversion of nondonor-process solvent mixture, pyridine solubility (% maf)	Experimental coal conversion of nondonor-process solvent mixture[c,e]		
			Pyridine solubility (% maf)	Increase over weighted average (%)	Increase over pure nondonor (%)
Lummus ITSL	82	67	73	+7	-9
1-Naphthol	78[f]	66	73	+8	-5
Quinoline	50	58	66	+8	+16
Naphthalene	39	54	65	+11	+26
Phenanthridine	37	54	72	+18	+35
Phenanthrene	36	54	66	+12	+30
Phenol	36[g]	54	59	+5	+23
Carbazole	36	54	72	+18	+36
Pyrene	33	53	73	+20	+40
Diphenyl ether	32[g]	52	55	+3	+23
Wilsonville (SN71754)	61	--	--	--	--
Coal only	24[g]	--	--	--	--

[a] Test conditions: 19.5 mL tubing bombs; 5.0 g Kentucky No. 9 (Fies) coal (dried at 110°C and 28 in.vacuum for 1 h); 7.5 g solvent; 10-min reaction time; 427°C (800°F); mixing at 180 cpm (1.5-in. stroke) using two 0.64-cm diameter SS balls.

[b] Solvent was 100% nondonor, process solvent, or coal (see Table 8).

[c] Pyridine solubility was determined by Soxhlet extraction and filtration under N_2.

[d] Calculated weighted average of the mixture (30% nondonor — 70% Wilsonville solvent) using conversion values given in column 1; for example, the calculated weighted average for coal conversion of the 30% 1-naphthol — 70% Wilsonville process solvent mixture is 0.30 x 78% + 0.70 x 61% = 66.1%.

[e] Solvent was 30% nondonor (or Lummus ITSL) and 70% Wilsonville (SN71754).

[f] Average of four runs.

[g] Single value.

naphthalene and phenanthrene was greater than 10%. Incremental increases for 1-naphthol, quinoline, diphenyl ether, and phenol were 3–8%. When the 30% Lummus ITSL heavy oil solvent and 70% Wilsonville SRC-I recycle solvent mixture was tested, the incremental increases in conversion above the weighted average was 7%. As in the case of the pure nondonor experiments, coal conversion was highest with 1-naphthol. This information tends to support the conclusion that increasing the concentration of pyrene, carbazole, phenanthridine, phenanthrene, naphthalene, quinoline, and 1-naphthol in the Wilsonville SRC-I solvent would improve coal liquefaction capability of that solvent. However, additional experimentation is necessary to determine optimum concentrations and liquefaction temperatures for each solvent, and also to determine solvent loss during liquefaction as well as the nature of the liquefaction product. It is significant that when Lummus ITSL solvent was added to the Wilsonville solvent, it increased coal conversion effectiveness of the Wilsonville solvent; and, on a molecular level, it depleted the Wilsonville solvent in quinoline, naphthalenes, and tetralins, but significantly enriched the Wilsonville solvent in carbazole, phenanthrene, pyrene, and multiring PAH and hydroaromatic constituents. A more fundamental understanding of the constituents responsible for improvement in coal conversion and the molecular reaction mechanisms involved would greatly facilitate development of more advanced coal liquefaction processes.

Our data corroborates the observation of Derbyshire et al.[77] that the presence of available hydrogen can increase coal conversion in solvents that have low donor capacity, and that the combination of a PAH (pyrene) and available hydrogen behaves synergistically with respect to coal conversion. Derbyshire et al. state that the relative effectiveness of pyrene is related to the formation of dihydropyrene during liquefaction.

The efficacy of 1-naphthol may be partially attributable to its condensation to binaphthol and the resulting availability of hydrogen.[115] Poutsma and Dyer estimated from data developed at 400°C that under the experimental conditions of the tubing-bomb experiments (i.e., 427°C and 10-min reaction) that approximately 5% of neat 1-naphthol would be converted to dinaphthofuran, binaphthol, and tetralone. Minor products would be tetrahydronaphthol, naphthalene, tetralin, and tetralol. With increasing reaction time, more dinaphthofuran product would be anticipated. In the presence of coal some of these compounds would be expected to be intermediates and would probably not be observed among the products because of the high density of free radicals occurring during the coal liquefaction process. In the thermolysis of 1-naphthol, the equivalent of hydrogen made available by conversion of two molecules of naphthol to a binaphthol is not released as molecular hydrogen but is somehow transferred to a third molecule of naphthol to effect its reduction to tetralone and to a lesser extent to tetrahydronaphthol. They postulate that the free radical and enolization reactions are rapid enough to serve as models for possible reactions of phenolic groups in coal liquefaction at 400-450°C. To the extent that naphthols are converted to arenes and the phenolic oxygen to water, the proposed reactions are beneficial for coal liquefaction. However, to the extent they form furans of larger molecular size which contain oxygen and are even more difficult to remove in later hydro treating, the reactions are undesirable.

Poutsma and Dyer determined that addition of benzophenone accelerated the condensation of the naphthol thermolysis and also eliminated the reduction portion in favor of almost exclusive formation of diphenylmethane. Thus thermolysis of naphthol in the presence of coal might be expected to decouple condensation from hydrogen transfer to another naphthol molecule and permit transfer to a coal hydrogen acceptor. To the extent that better hydrogen acceptors than naphthol exist in the coal, leaving naphthol playing only a hydrogen-donor role, then undesirable furans might be expected as major reaction products of naphthol-coal reactions. The major question in the utility of naphthol for improvement of coal liquefaction yields is whether good hydrogen donors present in the coal can reverse this scenario and maximize the dehydroxylation process, i.e., maximize the formation of arenes. Thus it is critically important to study the products from 1-naphthol and coal liquefaction reactions to determine the products and therefore the utility of increasing naphthol concentration as a method for improving yields.[115]

Because the effectiveness of 1-naphthol was essentially the same with and without supplemental hydrogen (73%/78% conversion), we conclude that it solubilizes coal by a different mechanism than the other nondonor compounds studied. Our results correlate with the observations of Poutsma and Dyer that 1-naphthol dimerizes to a binaphthol, making hydrogen available for reduction of other materials (i.e., 1-naphthol functions as a weak hydrogen donor in coal liquefaction). However, the results do not rule out the possibility that it also functions as a hydrogen transfer or shuttling agent, although this mechanism must be of lesser importance because liquefaction yields were approximately the same with and without supplemental hydrogen.

The relative order of basicity and ionization constants (pK_a) of the three nitrogen-containing heterocycles in aqueous solution are: quinoline (pK_a 4.94 at 20°C), phenanthridine (pK_a 4.52 at 20°C), carbazole (pK_a estimated at -3.0 at 20°C).[132] The ionization constant for carbazole was estimated from that of pyrrole (pK_a -0.27 at 25°C) and also indole (pK_a -2.4 at 20°C).[132] Annelation of a benzene ring to pyrrole (i.e., formation of indole) decreased the basicity (pK_a from -0.27 to -2.4). Therefore annelation of another benzene ring to the indole should further decrease the basicity. Thus carbazole is a very weak base compared to either phenanthridine or quinoline; (in fact, it is essentially acidic).

The results from the current study indicate that at least for these three nitrogen-containing components, basicity may not be the significant factor in their coal conversion mechanisms. For the pure compounds, the most basic example, quinoline, is the most effective — giving conversion of 50% at 427°C and 10 min; whereas, phenanthridine and carbazole each gave 36% conversion. However, when mixed with supplemental hydrogen (i.e., Wilsonville solvent), both phenanthridine and carbazole (72% conversion each) were significantly more effective than quinoline (66% conversion). Since carbazole is a much weaker base than either quinoline or phenanthridine, it is concluded that basicity of the nitrogen-heterocycles under these test conditions was not the most important factor in their dissolution properties. Because their effectiveness increased significantly in the presence of a supplemental hydrogen source, their effectiveness may be related to their hydrogen shuttling or transfer properties. If their effectiveness were related simply to aromaticity or their solubility parameters, then they should have been equally effective either as pure compounds or in the presence of supplemental hydrogen. The comparable effectiveness of carbazole and phenanthridine is hard to understand and might be dependent upon the coal used.

8.3 Characterization of Coal Conversion Process Solvents

A detailed quantitative analysis was made of the Wilsonville SRC-I process solvent (V-131-A, SN71754) and the Lummus ITSL heavy oil solvent (Table 6). Over 100 gas chromatographable constituents were identified in each solvent. The concentrations of the nondonor solvents evaluated in this study are tabulated for each of the process solvents in Table 11. Note that the concentrations of each of the selected nondonor solvents in this study are quite low or not detected except for pyrene and phenanthrene in the Lummus ITSL heavy oil solvent and for diphenyl ether, phenanthrene, and naphthalene in the Wilsonville SRC-I solvent. A more detailed summary is given in Table 12. This quantitative comparison indicates that the major GC constituents in the Lummus ITSL solvent are polycyclic aromatic hydrocarbons, whereas the major GC constituents in the Wilsonville

Table 11. Concentrations of selected nondonor components in two coal liquefaction process solvents and comparative liquefaction yields

	Lummus ITSL (%)	Wilsonville SN/1/54 (%)
Liquefaction[a]	82	61
Concentration of nondonors[b]		
1-Naphthol	ND[c]	ND
Quinoline	ND	1.0
Pyrene	6.8	0.2
Phenanthrene	4.4	2.0
Naphthalene	1.2	1.7
Carbazole	1.4	ND
Phenanthridine	ND	0.3
Diphenyl ether	ND	3.3
Phenol	ND	0.1

[a] Solvent/Kentucky No. 9 coal ratio of 1.5; 427°C (800°F); 10 min; 3 strokes/s shaking; 19.5 mL tubing bomb; 12.5 g total charge.

[b] Concentration of compound in solvent as determined by high-resolution gas chromatography using flame ionization detection (FID). The concentration is given as percentage of total FID signal.

[c] ND = not detected.

Table 12. Summary of coal liquefaction solvent constituents identified by GC/MS

	Lummus ITSL		Wilsonville V-131-A	
	Constituents identified	Area percent[a]	Constituents identified	Area percent[a]
Alkanes	10	3.01	22	10.95
Alkenes	3	0.13	2	0.21
Phenols	1	0	9	7.05
Pyridines	0	0	3	0.07
N-Heterocycles	4	2.03	9	5.01
O-Heterocycles	2	0.66	2	0.40
Ethers	2	1.63	2	3.34
Alicyclics	6	0.56	2	0.04
S-Compounds	1	0.50	0	0
Aromatic				
1-ring	12	2.17	7	1.66
2-ring	25	10.28	33	38.84
2-ring hydrogenated	16	3.41	14	14.19
3-ring	6	6.40	10	3.47
3-ring hydrogenated	4	3.01	3	0.60
4-ring	9	18.66	3	0.48
4-ring hydrogenated	12	8.99	0	0.28
5-ring	4	4.94	0	0
6-ring	2	0.90	0	0
	119	67.28	121	86.59

[a] Area percent of total FID signal during GC run; area percent approximates weight percent for FID detection.

solvent are naphthalenes, tetralins, alkanes (straight-chain hydrocarbons), and phenols. A calculation was made for the identified GC constituents of the hydrogen available in each solvent for donating to liquefaction reactions (Table 13). These estimates are minimum values to the extent that certain components in the solvents were not detected by GC. This calculation indicates approximately the same amount of donor hydrogen available in the GC constituents of each solvent — about 0.48 wt% in the Lummus ITSL solvent and about 0.45 wt% in the Wilsonville solvent. However, the concentration of the donatable hydrogen in the heavy multi-ring compounds in the Lummus solvent is interesting. It is estimated that 99% of the Wilsonville solvent (SN71754) but only 46% of the Lummus ITSL solvent were volatile enough to pass through the gas chromatograph and be analyzed (see Appendix A). Therefore, it is of interest to know the molecular composition of the nonvolatile, unchromatographed constituents in the Lummus solvent and the nature and amount of the hydrogen-donor constituents therein.

Comparative conversion yields with Kentucky No. 9 coal under SCT conditions were 82% for Lummus ITSL solvent and 61% for Wilsonville solvent. Thus, it appears that hydrogen donors in the Lummus solvent are relatively more effective than those in the Wilsonville solvent. That is, the larger molecular weight PAHs in their reduced forms appear to be more effective hydrogen donors than the smaller ones. However, other chemical factors, e.g., hydrogen transfer and solubilization (effectiveness as solvent), are probably involved. This is substantiated by the observation that 1-naphthol, pyrene,

Table 13. Comparison of GC-detectable available hydrogen in two coal liquefaction process solvents[a]

Donor type	Lummus ITSL percent[b]	Wilsonville V-131-A percent[b]
Tetralin	0.019 (4.0%)[c]	0.062 (13.7%)[c]
Alkyl-substituted tetralins	0.071 (14.9%)[c]	0.301 (66.4%)[c]
Decalin	0.022 (4.6%)[c]	ND
Tetrahydroquinoline	ND	0.052 (11.5%)[c]
Alkyl-substituted tetrahydro quinolines	ND	0.022 (4.9%)[c]
Hydro 3-ring compounds[d]	0.181 (38.0%)[c]	0.016 (3.5%)[c]
Hydro 4-ring compounds[e]	0.184 (38.6%)[c]	ND
Total available hydrogen	0.477	0.453

[a] Available hydrogen is defined as that hydrogen in reduced forms of compounds that would be available for reduction of other constituents, e.g., 4 hydrogen atoms per molecule of tetralin, 2 hydrogen atoms per molecule of dihydropyrene.

[b] Percent of total flame ionization signal for GC run. For example, in the case of tetralin: (4/132) x area percent tetralin = percent available hydrogen.

[c] Distribution of hydrogen, i.e., percent of total available hydrogen.

[d] For example, dihydrophenanthrene.

[e] For example, dihydropyrene.

carbazole, and phenthridine each in 30% mixture with Wilsonville solvent gave 72-73% conversion (Table 9), which was comparable with that obtained with the 30% Lummus ITSL–70% Wilsonville mixture (i.e., 73% conversion). The effectiveness of these four constituents, representing three different chemical families, underscores the complex nature of the coal liquefaction process. As previously discussed, the effectiveness of each may possibly be attributed to a different chemical mechanism. These findings suggest that the presence of such nondonor solvents contributes significantly to the liquefaction process.

8.4 Procedure Development and Initial Studies with Selected Nondonor Solvents

In the initial tubing-bomb experiments, the relative effectiveness of the selected nondonor solvents for converting coal to liquid (as determined by pyridine solubility via Soxhlet extraction without inert gas atmosphere) at 427°C (800°F) and 10-min reaction was: 1-naphthol, 56%; quinoline, 42%; phenanthrene, 41%; pyrene, 40%; naphthalene, 37%; carbazole, 37%; phenanthridine, 37%; and diphenyl ether, 32% (runs 20-27, Table 5). For comparison, using the same reaction conditions, the conversion of phenol was 36%; coal only, 24%; Wilsonville V-131-A (SN71754), 50%; and Lummus ITSL heavy oil solvent, 75% (runs 18, 19, 28, and 29; Table 5). As will be discussed later, some or all of these conversion values may be low due to possible variation in mixing speed (and consequent reaction mass transfer limitations); and also, the values for pyrene and the Lummus solvent may be low due to determination of pyridine solubilities without a protective, inert (N_2) atmosphere.

8.4.1 Constant mixing speed

The three most promising candidates were retested with the following average results: 1-naphthol, 46%; quinoline, 34%; phenanthrene, 36% (runs 30-32, Table 5). The decrease in conversion is not fully understood, although most of the reaction conditions and parameters compare relatively well with the previous runs; however, the decrease may have been attributable to less mixing (and consequent mass transfer limitations of reactions) due to variation in air supply to the mixing motor. In later experimentation, particular attention was given to monitoring and maintaining a constant air supply to the motor.

8.4.2 Pyridine extraction under inert atmosphere

In order to assist in understanding the significance of the pyridine solubility test procedure, the pyridine solutions from runs 18 through 27 were filtered at 100°C through Whatman No. 42 filter paper (0.5-μm pore size). The estimated pore size of the Soxhlet extraction thimbles is about 25 μm (ref. 133). Table 14 presents the data comparing conversion values as determined by weight of pyridine-insoluble residues in only the Soxhlet extraction thimbles with conversion values as determined by the total weight of pyridine insolubles in the thimbles and on the Whatman No. 42 filters. In most cases the residual material, apparently passing through the extraction thimble but trapped by the filter paper, amounted to only a few percent (except for pyrene and Lummus ITSL). This material may represent (1) insoluble material that passed through the extraction thimble (i.e., about 0.5-25 μm), (2) material resulting from retrograde

Table 14. Comparison of coal conversion (pyridine solubility) as determined by Soxhlet extraction and by Soxhlet extraction followed by filtration[a]

Run	Solvent	Pyridine solubility as determined by		Pyridine insolubles: 0.5–25 μm particles (%)
		Soxhlet extraction (% maf)	Soxhlet extraction and filtration[b] (% maf)	
18	Wilsonville V-131-A	50	48[c]	2
19	Lummus ITSL	75	26[c]	49
20	Pyrene	40	30[c]	10
21	Phenyl ether	32	32[c]	0
22	Quinoline	42	38[c]	4
23	Naphthalene	37	37[c]	0
24	1-Naphthol	56	56[c]	0
25	Phenanthrene	41	38[c]	3
26	Carbazole	37	34[c]	3
27	Phenanthridine	37	35[c]	2
L-1	Lummus[d]	97	94	3

[a] All liquefaction runs were made with Kentucky No. 9 (Fies) coal (dried 1 h at 110°C and 28 in. vacuum); 1.5:1 solvent/coal ratio; 427°C (800°F); 10-min reaction.

[b] Whatman No. 42 filter paper at 100°C.

[c] Pyridine solutions were stored at room temperature in the dark but without an inert gas atmosphere. They were filtered 4 to 8 weeks after the Soxhlet extraction.

[d] Not a liquefaction experiment, pyridine extraction of Lummus ITSL solvent only.

reactions occurring in the pyridine solvent in the several weeks time between Soxhlet extraction and filtration, or (3) oxidation products or polymer formation due to oxidation (protective nitrogen blankets were not used during Soxhlet extraction nor for the storage of the resulting pyridine solution for several weeks). To evaluate this phenomenon, subsequent Soxhlet extractions were made under inert atmosphere and the hot (~110°C) pyridine solutions were filtered under inert atmosphere immediately after extraction. This change made a difference in the yield, as will be explained later.

It was of interest to know whether the low conversion results previously attained with Lummus ITSL solvent at 427°C (800°F) (run 19, Table 5) might also be attributed to pyridine extraction under conditions favorable to oxidation and polymerization (i.e., without an inert atmosphere); therefore, the 427°C (800°F) run was repeated (run 39, Table 5). Coal liquefaction of 88% (pyridine solubility as determined by Soxhlet extraction under an inert atmosphere) and 82% (Soxhlet extraction followed by filtration under nitrogen atmosphere) were obtained. Thus the large amount of pyridine insolubles in the 0.5- to 25-μm range and low total conversion (26%) determined for run 19 is probably attributable to oxidation and polymerization reactions occurring during extraction and storage without an inert atmosphere. These results also tend to confirm that with the Lummus ITSL heavy oil solvent, coal liquefaction yields are high (greater than 80% in 10 min) at 427°C (800°F); that retrograde reactions may begin at 460°C (860°F); and that the liquefaction products, at least with Kentucky No. 9 (Fies) coal, are very reactive and subject to oxidation and polymerization in the presence of air. These conclusions must be considered tentative because a limited number of experiments were conducted.

8.4.3 Coke formation

Selected nondonor solvents were tested at 460°C (860°F) (previously determined to be the optimum temperature for conversion of Wyodak coal using phenol as the solvent)[1] with the following average results: 1-naphthol, 30%; phenanthrene, 30%; phenol, 34%; comparable value for Lummus ITSL, 30% (runs 33-36, Table 5). The lower conversion yields for the 460°C (860°F) runs [except for phenol, the value of which was within experimental error of that for the 427°C (800°F) run] may indicate beginning of coke formation. The insoluble residue from the pyridine extraction of the Lummus ITSL liquefaction test was found to contain about 60% coke (mesophase) and some unreacted coal.[134]

Because of the apparent coke formation during the 460°C (860°F) Lummus ITSL run (run 33, Table 5), we decided to (1) repeat the 460°C (860°F) Lummus ITSL/coal run and (2) determine the pyridine solubility of the Lummus ITSL heavy oil solvent. The ITSL solvent was subjected to pyridine extraction and a total of about 6% insolubles were determined (run L-1, Table 9). The 460°C (860°F) tubing-bomb experiment with Lummus ITSL heavy oil solvent and Kentucky No. 9 coal was repeated (run 37, Table 5), and the Soxhlet extraction and filtration was conducted under a nitrogen cover. The results were dramatically different — 62% after Soxhlet extraction as compared with 31% for the previous 460°C (860°F) run (run 33, Table 5) in which the Soxhlet extraction had not been conducted in an inert atmosphere.

However, considerable particulate matter (about 0.5- to 25-μm diam) was filtered from the hot pyridine extract of run 37, reducing the net conversion to 38% and indicating either retrograde reactions (coke formation) or production of colloid or semi-colloid with the Lummus solvent. Microscopic examination of the pyridine insolubles that passed through Soxhlet extraction thimbles, but were retained by Whatman No. 42 filters, revealed numerous small spheres of 3- to 5-μm diam; several spheres indicated the beginning of mesophase coke formation. Similar examination of the pyridine insolubles from the Lummus ITSL solvent itself revealed some particles — indicating possible mesophase coke formation. Although this phenomenon needs further study, it may indicate that the presence of higher molecular weight constituents (e.g., 4- and 5-ring PAHs) may contribute to the formation of higher molecular weight products, i.e., retrograde reactions resulting ultimately in coke formation. Despite the apparent coke formation, using an inert (N_2) atmosphere during the determination of pyridine solubility obviously increased the liquefaction yield. This indicates that oxidation or polymerization to pyridine insolubles occurs during pyridine extraction or storage without a protective inert atmosphere.

9. APPENDIXES

Appendix A: Relative Volatility of Two Process Solvents

This estimate is based upon vacuum distillation of the solvents at 0.02 mm and 200°C for 1 h. A plot of these points using the Cox method[135] indicated 200°C at 0.02 mm pressure was approximately equivalent to volatilization of $C_{36}H_{74}$ (detectable using the GC methodology used for analysis of the two solvents). A vapor pressure-temperature plot (log p versus log t) was made for a number of compounds according to the method of Cox. Data for chrysene, pyrene, phenanthrene, napthalene, napthol, phenol, quinoline, and carbazole indicated vapor pressure-temperature curves essentially parallel to those for aliphatic hydrocarbons; this result inspires confidence in the application of the Cox method to aromatic compounds and coal process solvents. After 6 h at 200°C and 0.02 mm pressure, 65% of the Lummus ITSL solvent had volatilized or sublimed.

Appendix B: Special Experiment — Effect of Quinoline Adsorption from Water Solution on Coal Conversion

Recent information[23] indicates that liquefaction yields may be higher using undried coal as compared with conventionally used dried coal. Also, adsorption of basic nitrogen compounds on the coal before coal slurry drying treatment prior to coal liquefaction may dramatically improve liquefaction yields and products. Theoretically, the improved liquefaction may result from replacement of hydrogen-bonded water by the basic nitrogen-containing compounds during the drying process, such that the basic nitrogen compounds are available for liquefaction reactions when reaction temperatures are achieved.

Consequently, an experiment was conducted in which the Kentucky No. 9 (Fies) coal, as received from the supplier (partially air dried, i.e., containing about 3.1% moisture), was soaked in an aqueous solution of quinoline. Five grams of coal rapidly (in less than 1 h) adsorbed 89.5% of the quinoline from 25 mL solution containing an initial 1-mg/mL concentration; total quinoline adsorbed was 4.5 mg per gram of coal. The liquefaction yield at 427°C and 10-min reaction using 7.5 g Wilsonville solvent and 5 g quinoline-adsorbed coal was 63.8%, whereas that with coal soaked in water only was 62.6% (run 54, Table 5). The yields are very similar to the 60.7% achieved with Wilsonville solvent and dried coal using the same test conditions (run 49, Table 5). However, the experiment is inconclusive because very little quinoline was adsorbed on the coal (less than 0.1% of the weight of the coal) and because the coal had been partially dried by the supplier (losing about 5–6% moisture). For definitive conclusions, further experimentation is required using undried coal and higher quinoline concentrations.

Appendix C: Special Experiment — Effect of Methanol Pretreatment on Coal Conversion

Because of the apparent importance of bound water in coal structure and the possible improvements in liquefaction yields if the bound water were replaced by hydrogen-containing solvents prior to liquefaction, an experiment was conducted in which the partially dried coal (as received from the supplier) was soaked in methanol before the liquefaction experiments took place. After soaking in methanol for several weeks, the coal approximately doubled in weight (i.e., 5 g coal increased in weight to approximately 10 g due to absorbed/adsorbed methanol). An average liquefaction yield of 75% was obtained in tubing-bomb tests at 427°C (800°F) and 10-min reaction time using 10 g methanol-soaked coal and 7.5 g Wilsonville (SN71754) process solvent (run 38, Table 5) compared with 61% with non-soaked coal (run 49, Table 5). The reaction yield is comparable to the 82% yield achieved with the Lummus ITSL heavy oil solvent (run 39, Table 5). This high conversion indicates that further experimentation is warranted to explore this phenomenon.

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