

## Evaluation of the Donor Ability of Coal Liquefaction Solvents

Bradley C. Bockrath and Richard P. Noceti

United States Department of Energy  
Pittsburgh Energy Technology Center  
P. O. Box 10940  
Pittsburgh, Pennsylvania 15236

### INTRODUCTION

Hydrogen donor solvents are used in most processes for the direct liquefaction of coal. The overall performance of these solvents depends on several qualities, including the abilities to physically solvate coal and its liquefaction products, to hold coal particles in suspension, to assist transfer of hydrogen from the gas phase to coal by dissolving molecular hydrogen or undergoing hydrogenation/dehydrogenation cycles (hydrogen shuttling), and to donate hydrogen directly to coal. Unknown factors may also be involved. In addition, in the case of commercial application, the solvents must be derived from coal and be suitable for recycle operation as well. In order to fully understand the function and importance of liquefaction solvents, the influence of each property must be studied separately. As a step towards this goal, we have developed a method by which the relative hydrogen donor ability of liquefaction solvents may be evaluated.

Our method of evaluation is based on a generally accepted hypothesis of the mechanism of coal liquefaction that has been used to rationalize the kinetics of coal liquefaction (1,2) and has been discussed several times in recent reports (for example (3,4,5)). According to this mechanism, the initial act is rupture of the weaker covalent bonds in coal. This produces two free radicals in close proximity. These radicals may either abstract hydrogen from any available source (donor solvent, coal or molecular hydrogen), undergo rearrangement, or add to some other site on either coal or solvent. Recombination or addition may lead to production of insoluble or char-like residues that are clearly undesirable. One critical function of the donor solvent is to provide a source of hydrogen. Abstraction of hydrogen by coal-derived free radicals prevents retrogressive reactions that lead to higher molecular weight products, and it directs more coal along the desired pathways to lower molecular weight products. Thus, donors with high potential for hydrogen transfer are regarded as beneficial to increased liquefaction yields.

Our approach to evaluation of the donor property was to devise a test that embodies the main features of the free radical mechanism of coal liquefaction. The basic idea is shown in Figure 1. Benzyl radicals are generated by the thermolysis of a convenient precursor at relatively low temperatures. These radicals then behave like the free radicals generated by the thermolysis of coal at liquefaction temperatures. When benzyl radicals are generated in a donor solvent, the relative amounts of toluene and bibenzyl produced reflect the relative ability of the solvent to donate hydrogen and to prevent recombination. A variable amount of benzyl radical is also lost, which presumably represents that amount which adds to or combines with the solvent.

As precursors to benzyl radical, we have used both dibenzylidiazene and dibenzylmercury. Both decompose at convenient rates at moderate temperatures (130-170°C) (6,7). The initially formed reaction products were found to be stable at these relatively low temperatures. Thus their yields, determined after decomposition of the precursor, represent the actual quantities of products formed as a result of the primary reactions.

Other methods have been used in the past to provide a "solvent quality index." Notably, measurement of liquefaction yields produced under specified conditions and with a specified coal has been used to provide a direct empirical evaluation of solvent quality (8,9).

Various spectroscopic methods have also been used to estimate the relative amount of benzylic or hydroaromatic hydrogen available for transfer (10,11,12). These methods serve their intended purposes well. In the present work, we aim at developing a better understanding of the chemistry of liquefaction and the overall performance of liquefaction solvents by isolating the hydrogen donor ability and free radical scavenger ability for study.

## RESULTS AND DISCUSSION

Since many of the compounds to be tested as model hydrogen donors are solids at room temperature, it was worthwhile to use an inert liquid as a diluent. Tert-butylbenzene served this purpose well. It possesses only relatively inert aromatic and primary aliphatic hydrogen and sufficient solvent power to dissolve most of the donor solvents to be tested. Decomposition of either benzyl radical precursor in tert-butylbenzene solution produced only small yields of toluene.

Material balance studies showed that not all of the benzyl radical present in the precursor was recovered as either toluene or bibenzyl. A sizeable fraction is apparently removed by side reactions with the solvent. In pure t-butylbenzene, this accounted for 24% of the benzyl radical, while in a 50/50 wt mixture of t-butylbenzene and tetralin, it accounted for 32%. In the gas chromatograms of the decomposition products, new peaks appeared which were due to high boiling compounds. In the case of runs done in the presence of tetralin, GC/MS analyses indicated that three of these peaks had the correct molecular weights for benzyltetralins, benzylnaphthalene and bitetralyl. These products must arise from radical combination and addition reactions.

The appearance of solvent combination and addition products is in accord with some recently reported results from other groups. Collins et. al. (13) reported that after they heated coal with  $^{14}\text{C}$  labeled tetralin at  $400^\circ\text{C}$  for 1 hour, the pyridine solubles were 1.6 wt. percent tetralin and the residue 2.6 wt. percent tetralin. In another experiment (13),  $^{14}\text{C}$  labeled 1,3 - diphenylpropane was heated with tetralin at  $400^\circ\text{C}$  for 1 hour. Toluene and ethylbenzene were major products. In addition, methylnaphthalenes, methylidihydronaphthalenes, phenylethyltetralins, and phenylethyl-naphthalenes were found. A mechanism was proposed that involved combination of phenylethyl with tetralyl radical, followed by further thermolysis to produce methyl substituted tetralins and naphthalenes. Thus at higher temperatures, radical addition to solvent may be followed by subsequent thermolysis of the newly formed bridge. Evidence for the addition and subsequent dissociation of benzyl radical with tetralin at temperatures of  $400\text{--}450^\circ\text{C}$  has also been reported by workers at Gulf (14). Another piece of evidence showing the importance of addition reactions is the report (15) that negative solvent balances were found during preheater studies. These findings were interpreted to mean that during the initial phase of liquefaction ( $300^\circ\text{--}400^\circ\text{C}$ ), coal-derived solvent became bound to the coal so tightly that it could not be freed by either distillation or solvent extraction. Subsequent reaction after reaching  $450^\circ\text{C}$  changed the solvent balance to positive. Processes analogous to the addition/dissociation reactions described by Collins may be involved.

Taking this evidence together, it is apparent that an additional mode of action of donor solvent is that of free radical scavenger by combination and addition reactions. Accordingly, three indices were devised to compare donor solvents; the donor, the scavenger, and the combined index.

$$\text{Donor Index} = \frac{\text{Toluene}}{2 \text{ Precursor}}$$

$$\text{Scavenger Index} = \frac{2 \text{ Precursor} - (\text{Toluene} + 2 \text{ Bibenzyl})}{2 \text{ Precursor}}$$

$$\text{Combined Index} = \frac{\text{Precursor} - \text{Bibenzyl}}{\text{Precursor}}$$

These indices are based on mole ratios.

Since the combined index is merely the sum of the other two, we really have two independent measures of two different solvent qualities. The donor index may be taken as the relative amount of benzyl radical which abstracts hydrogen, and the scavenger index as the relative amount of benzyl radical which adds in some manner to the solvent. The scavenger index is determined by difference, being that fraction of benzyl which does not appear as toluene or dibenzyl.

Initial experiments were carried out with dibenzylidiazene and a series of model donor compounds. Although we were able to obtain satisfactory data with dibenzylidiazene, we have come to prefer using dibenzylmercury because it is far more stable in storage. We have found that dibenzylidiazene decomposes spontaneously over the course of several days by various pathways. This instability made it necessary to prepare the diazene immediately before use and to assay its purity by determination of the amount of nitrogen evolved upon decomposition of a known weight of crude material. By contrast, dibenzylmercury may be stored without significant decomposition for months. Thus with dibenzylmercury, the amount of benzyl added to each reaction mixture could be carefully controlled and was usually held constant at 0.87 wt. percent, based on the hydrocarbon portion of the precursor.

The three solvent indices were determined for the decomposition of dibenzylmercury for several solvent mixtures made from different amounts of tetralin in *t*-butylbenzene. The data contained in Figure 2 show that the donor index increases with increasing tetralin concentration. Also shown in this figure are data taken from reference (16) for conversion of a bituminous coal to pyridine soluble material after reaction for three minutes at 427°F in mixtures of tetralin with methylnaphthalene, cresol, and picoline. Conversion as well as the donor index goes up as the tetralin concentration in the solvent increases. This comparison is made only to point out the qualitative similarity between the two results since we assume that both coal conversion and toluene yield are related to the relative hydrogen donor ability of the solvent. In both cases the greatest increase in conversion or toluene yield comes at relatively low tetralin concentration.

The series of model compounds in Table I were evaluated using dibenzylidiazene as the source of benzyl radical. In each case the donor was diluted to 50 wt. percent in *t*-butylbenzene. These data show that the donor ability as measured by this method is indeed variable. The relative order of donor ability of the hydrocarbons is mostly as expected. Both hydroaromatic compounds—tetralin and 9,10-dihydrophenanthrene—are distinctly better than either *t*-butylbenzene or 1-methylnaphthalene. Indan has the highest donor index of the hydrocarbons in Table I. This is noteworthy in view of the prejudice often voiced against indanyl structures. Rearrangement of hydroaromatic compounds in recycle solvents to indanyl structures is often said to be detrimental. However, indan seems to be a good rather than poor donor, although its capacity to shuttle hydrogen by dehydrogenation cycles is still open to question.

In the first case, the donors in Table I have been compared at equivalent weight percent concentrations. This relates more directly to their use in practice and is more convenient when making comparisons among actual coal-derived solvents. However, if the assumption is made that essentially all hydrogen donated comes from benzylic sites, the donor index may be expressed on the basis of the molal concentration of benzylic hydrogen. The molal donor indices shown in Table I should relate more directly to the reactivity of individual benzylic hydrogens than does the simple donor index. In this comparison, benzylic hydrogen on indan is ranked between those on dihydrophenanthrene and tetralin. An important factor contributing to indan's superior rank measured on a weight basis is that benzylic hydrogen accounts for a relatively larger fraction of its weight.

The heteroatomic substituted compounds in Table I are also found to be relatively good donors, with the exception of tetrahydroquinoline. A striking aspect of this data is that the heteroatomic compounds all have relatively high scavenger indices. Their combined indices are therefore distinctly higher than any of the hydrocarbon species. Said another way, the

yields of the product of recombination, bibenzyl, are found to be smaller in the presence of these heteroatomic compounds than in the hydrocarbons. Tetrahydroquinoline has been reported to be a superior solvent for coal liquefaction (17,18). Also, esr experiments have shown that the concentration of free radicals in mixtures of coal and solvent after treatment at liquefaction conditions was roughly a factor of six smaller in the case of tetrahydroquinoline (or tetralin) than naphthalene (19). Tetrahydroquinoline's superior quality has been attributed to a unique combination of readily donatable hydrogen with a heightened ability to solvate coal and its liquefaction products due to the presence of both aromatic and polar functionality. In view of its high scavenger index, an additional reason for the superior liquefaction performance of tetrahydroquinoline may be its ability to add to or combine with free radicals initially produced by the thermolytic reactions of coal.

Table 2 contains the donor indices obtained for several coal-derived liquefaction solvents selected to provide a range of quality from poor to satisfactory. In all of these cases, the scavenger index could not be obtained because the bibenzyl peak was buried within the broad envelope of unresolved peaks usually associated with gas chromatograms of coal-derived liquids. All of the donor indices in Table 2 were obtained using dibenzylmercury as the source of benzyl radical. Note that in this case the donor index for tetralin is somewhat different than that in Table 1. We attribute this to the change in precursor from diazene to mercurial. The precision of both determinations is about the same.

Anthracene oil, cresote oil, and Panasol are generally considered poor performers in coal liquefaction. They also have the lowest donor indices in Table 2. Panasol is not a coal-derived liquid, but it is largely made up of mono-, di-, and tri-methyl-naphthalenes, which are frequently also major components in coal-derived liquids. Its donor index is essentially the same as that found for methylnaphthalene. By comparison, the index determined for a distillate cut from a SRC-II recycle solvent is higher, although not as high as that for tetralin.

Comparison of the donor indices with other available quality criteria is made with two sets of solvents. The DCD series are recycle solvents derived from Blacksville coal under different processing conditions in the 1000 lb/day liquefaction unit at PETC. The values of IR were derived as recommended (10) from the ratio of absorbances at  $3040$  and  $2930\text{ cm}^{-1}$  due to aromatic and aliphatic hydrogen, respectively. Higher ratios reflect a greater degree of hydrogenation or relative aliphatic hydrogen content. In this comparison, there is a qualitative agreement between the two methods. That is, the donor index increases with the degree of hydrogenation of the recycle solvent.

The second set of solvents—F2, F14, and F16—provide a comparison of liquefaction yield versus donor index. In this case, liquefaction yield refers to benzene soluble yield from Wyodak coal after heating to  $440^\circ\text{C}$  and immediately cooling in a two liter autoclave under hydrogen pressure (2000 psi, cold) at a 2/1 solvent-to-coal ratio (20). F2-HV is the  $500^\circ\text{F}$  + distillation residue from a lightly hydrogenated recycle oil made in the Wilsonville SRC pilot plant from Wyodak coal. F-14 is a lightly hydrogenated recycle oil made in the Tacoma SRC pilot plant from Kentucky coal. F-16 is a coal gasification tar from an in situ gasification project near Hanna, Wyoming. These three solvents were selected because the liquefaction yields clearly distinguish the order  $F14 > F2 > F16$ . The donor indices are in the same order. However, the reported IR values (20) are not in this order. The relatively high IR values and results from other methods of characterization (20) indicate that all of these solvents, F16 in particular, are highly hydrogenated. In this case, the optimum hydrogen content may be closer to that of F14. Hydrogenation of solvents beyond certain limits has been shown to be detrimental because aliphatic structures begin to replace hydroaromatic structures (16,20).

Taken together, these data indicate that there is good qualitative agreement between liquefaction performance and the donor index. The ability of solvents to donate hydrogen to a free benzyl radical is an indication of how well they may donate to a typical free radical site formed on coal during liquefaction. We are now developing refined methods designed to yield more quantitative comparisons among hydrogen donor solvents.

## EXPERIMENTAL

**MATERIALS:** All compounds that were purchased were reagent grade or equivalent and were used as received except as noted. Tetrahydronaphthalene (Tetrafin, Fisher) was trickled through a dry-packed column of activated alumina immediately before use and stored under argon. This treatment removed and prevented reformation of tetralin hydroperoxide and tetralone, which had been found to be present in all tetralin samples received. Dibenzylmercury (ALFA) was recrystallized once from absolute ethanol (m.p. 109-110° uncorr) and vacuum dried before use.

**METHODS:** Bis (phenylmethyl) diazene was prepared according to established procedures by the oxidation of N,N'-dibenzylhydrazine with freshly prepared mercuric oxide. (21,22). The diazene decomposes in air at room temperature but could be stored over a period of weeks at -10°C under argon. It was necessary to assay it before each use. This was done by measuring the nitrogen evolution on thermolysis in t-butylbenzene at 170°C. A mercury filled gas buret and leveling bulb proved satisfactory and gave a precision of about 2% absolute. Benzyl radicals were generated by thermolysis of either dibenzylmercury (7) or bis (phenylmethyl) diazene in a reaction vessel at selected temperatures between 130 and 210°C. The radical precursor was present at concentrations of 1-2 wt.% in various mixtures of donor solvents and t-butylbenzene. Each vessel was assembled from a 1/2" 316SS swagelock union and two end plugs and had a capacity of about 2 mL. The vessels were sealed after loading and maintained at temperature in a convection oven for 12-16 hours to ensure complete decomposition of the radical precursors. Product analyses were carried out on a HP5830 gas chromatograph with a six foot carbowax 20M (10% on chromosorb W) column, using internal standards. Each sample was analyzed in duplicate. Several unknown peaks were identified on a DuPont 21-490 MS after separation by an attached Varian 3700 G.C.

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TABLE I. SOLVENT INDICES OF MODEL HYDROGEN DONOR SOLVENTS\*

COMPOUNDS	DONOR	SCAVENGER	COMBINED	DONOR/ $\alpha$ -CH**
	0.09	0.24	0.33	
	0.27	0.32	0.59	0.0178
	0.31	0.23	0.53	0.0279
	0.35	0.30	0.65	0.0207
	0.13	0.45	0.58	0.0123
	0.18	0.62	0.81	
	0.32	0.46	0.78	
	0.28	0.56	0.84	
	0.40	0.41	0.81	

\*Determined by decomposition of dibenzylidiazene in solvent mixtures composed of 50/50 wt/wt of t-butylbenzene and donor. Estimated precision is  $\pm 0.02$ , based on triplicate determinations for tetralin.

\*\*Donor index divided by molal concentration of benzylic hydrogen.

TABLE 2. DONOR INDICES OF COAL-DERIVED LIQUEFACTION SOLVENTS

<u>SOLVENT</u>	<u>DONOR INDEX*</u>	<u><math>\bar{I}R</math></u>	<u>LIQUEFACTION YIELD**</u>
Tetralin	0.41		
Anthracene Oil	0.21		
Creosote Oil	0.17		
Panasol	0.14		
SRC-II Distillate	0.31		
DCD 12/1	0.24	2.2	
DCD 12/26	0.28	2.7	
DCD 13/5	0.24	2.0	
F2-HV	0.32	9.2**	83.6
F14	0.45	6.1**	93.6
F16	0.29	12.7**	63.2

\*Obtained using dibenzylmercury in 50 wt. per cent solutions with t-butylbenzene.  
Precision ( $2\sigma$ ) estimated as  $\pm 0.03$  based on six replicates.

\*\*Values taken from Reference 20.

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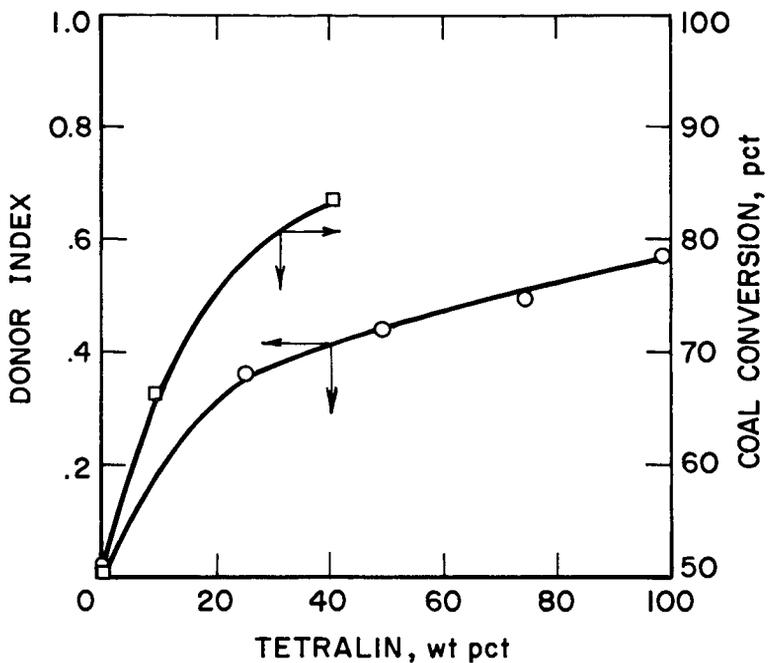


Figure 2.- Donor index of Tetralin/*t*-butylbenzene mixtures, ○, and coal conversion in synthetic solvents of different tetralin concentration, □, (from ref. 11).

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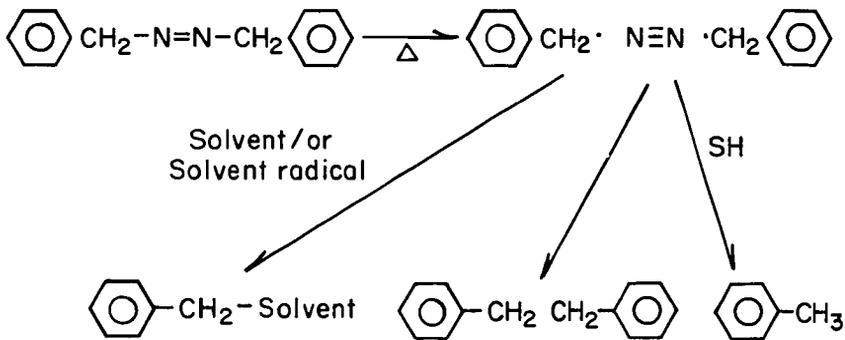
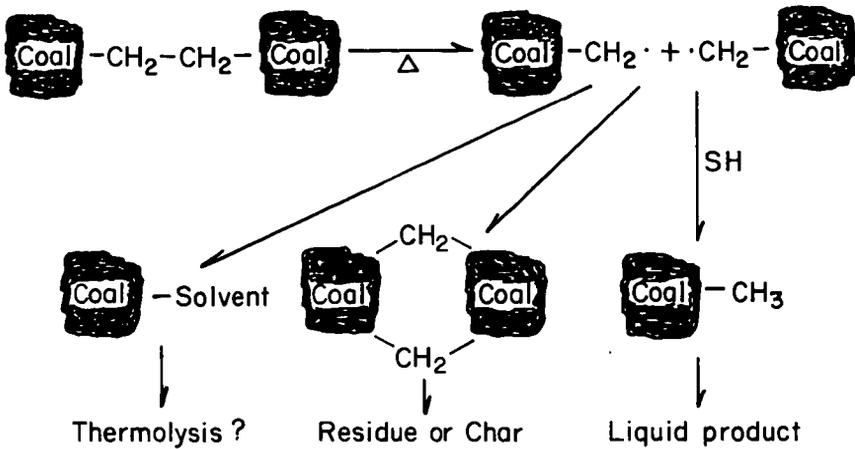


Figure 1.- Simplified hypothetical mechanism of coal liquefaction and its analog.

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