SOLVATION OF SOME BITUMINOUS COALS IN QUINOLINE BY ULTRASONIC IRRADIATION

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INTRODUCTION

The first application of ultrasonic irradiation to disperse the α fraction of coal in pyridine was reported by Berkowitz.[1] Kirkby, Lakey, and Sarjant have investigated the ultrasonic solvation of coals of different ranks in pyridine.[2] In addition to an infrared study of the coal extracts, these authors have described the effects of irradiation time, coal rank, particle size, and charring temperature on the amount of coal solubilized. Littlewood, who also used pyridine as a solvent, studied the solubilization of coal as a function of the distance of the extraction vessel to the ultrasonic transducer, generator output power, and coal rank.[3] We have described the ultrasonic solvation of hvab coal at ambient temperature using quinoline, pyridine, formamide, N-N-dimethylformamide, and 1,2,3,4-tetrahydronaphthalene as solvents.[4] In our investigation the highest yield of extract was obtained with quinoline; after 4 hours of ultrasonic irradiation approximately half of the coal was solubilized, two and one-half times the yield with pyridine.

EXPERIMENTAL

The identification of the coals used in this investigation are given in table 1.

Table 1.- Identification of coals

Coal	Identification
1	Vitrain, high-volatile A bituminous Pittsburgh seam, Bruceton, Allegheny County, Pennsylvania
2	High-volatile A bituminous, Pittsburgh seam, Valley Camp No. 3, Ohio County, West Virginia
3	High-volatile A bituminous, bottom bench, Noon Mine, Ohio
4	High-volatile A bituminous, Kentucky No. 11 bed, Vogue Mine, Muhlenberg County, Kentucky
5	High-volatile B bituminous, Illinois No. 5 (c) Red Ember No. 2, Fulton County, Illinois

A commercial ultrasonic generator operating at a frequency of 80 Khz with a total power output of 80 watts was used. Samples of coal in 5 ml of solvent were ultrasonically irradiated at ambient temperature in an air atmosphere. The irradiation time used is given in each experiment. The coal-quinoline slurries were irradiated in flat bottomed glass vials (80 mm x 20 mm diameter). The vials were immersed in the ultrasonic generator tank (containing H_2O) to the position at which maximum agitation of the sample was observed. After irradiation, the solvent-extract mixture was removed from the coal residue by centrifugation. The

coal residue was then washed with two 5-ml portions of quinoline and two 5-ml portions of benzene. The residue was then air dried at 100° C to constant weight and used as the basis for determining the amount of solvation according to the method of Curran and co-workers;[5] the yields of extract determined by this method are on a maf basis.

RESULTS AND DISCUSSION OF RESULTS

Parameter Investigation

Carbon Content

One-half gram samples of various coals (-325 mesh) and 5 ml of quinoline were ultrasonically irradiated for 4 hours at ambient temperature. The results are given in table 2.

Table 2.- Amount of coal solvated versus carbon content

Sample	Rank	Weight percent solvated	Carbon content of starting coal, percent (maf)
Coal 1*	hvab	49.2	82.9
2	hvab	23.2	81.7
4	hvab	17.8	78.8
5	hvbb	17.6	76.9

* See table 1 for complete identification of samples

These data show that a correlation exists between carbon content and the amount of coal extracted with quinoline. Of the coals investigated, the amount of material solubilized decreased as the carbon content of the starting coal decreased. Kirkby and co-workers reported a definite relationship between carbon content and the amount of coal solubilized by pyridine.[2]

Irradiation Time--Coal

One-half gram samples of Pittsburgh seam hvab vitrain (-325 mesh) and 5.0 ml of quinoline were ultrasonically irradiated for periods ranging from 15 minutes to 24 hours at ambient temperature. A control was obtained by adding coal to the quinoline and then immediately removing the solvent using the standard procedure described earlier. The results are shown in figure 1. The amount of coal solvated varied from 16 percent for 15 minutes of irradiation to 77 percent for 24 hours. The largest increase in solubilized material occurred during the first 2 hours of irradiation. Littlewood has reported that the highest extraction rate for Brockwell 301 coal in pyridine occurred during the first hour of irradiation.[3]

Coal Chars

The chars used in these experiments were prepared by the following procedure: Pittsburgh seam hvab coal was heated to the desired temperature for 1 hour in a nitrogen atmosphere, air cooled, and then crushed to size. Chars were produced at temperatures of 275° C, 375° C, and 475° C. One-half gram samples of the starting coal (30 x 80 mesh) or char (30 x 80 mesh) were added to 5 ml of quinoline and ultrasonically irradiated for 4 hours. The results are shown in table 3.

Table 3.- Solvation as a function of charring temperature

Char	Weight percent solvated
Starting coal	18
275° C	6
375° C	37
475° C	17

Solvation of similar chars has been described by Walters and co-workers using Soxhlet extraction with chloroform as the solvent.[6] Chloroform solubilities of 0.6, 4.8, and 1.1 percent were reported for 300° C, 400° C, and 500° C chars, respectively. In both the ultrasonic and Soxhlet extractions, yields followed the same pattern. Walters has also concluded that maximum extraction occurs for chars prepared at the temperature of maximum fluidity. In contrast to this, Kirkby and co-workers reported that, for a vitrain-pyridine mixture, greatest ultrasonic solvation occurred with the original coal.[2]

Particle Size

A portion of the 375° C char (30 x 80 mesh) used in the experiments described previously was crushed to -325 mesh. One-half gram samples of the 30 x 80 mesh or -325 mesh chars and 5 ml of quinoline were ultrasonically irradiated for 4 and 24 hours. The results are shown in table 4.

Table 4.- Solvation versus particle size

Irradiation time (hours)	Mesh size	Weight percent solvated
4	-325	65
4	30 x 80	37
24	-325	82
24	30 x 80	77

For the shorter irradiation time, these data show that the particle size of the starting coal is an important factor for the ultrasonic solubilization of chars in quinoline. After extensive irradiation (24 hours) both sizes of char produced approximately the same amount of solvate. Littlewood, using coal-pyridine systems, has also reported that the amount of ultrasonic solubilization is dependent upon the particle size of the starting material.[3]

Irradiation Time--Char

Figure 1 also shows the percent solvation in quinoline versus irradiation time for a 375° C char (-325 mesh) produced from Pittsburgh seam coal. The amount of char solvated ranged from 46 percent for 2 hours to 82 percent for 24 hours. The solvation rate for the char is similar to that of the vitrain, the highest extraction rate occurring during the first 2 hours of irradiation for both materials.

Temperature

Ten percent slurries of Pittsburgh seam hvab coal (-325 mesh) in quinoline were ultrasonically irradiated for 4 hours at ambient temperature and 80° C. The results of these experiments are given in table 5.

Table 5.- Coal solvation as a function of temperature

Temperature	Weight percent solvated
Ambient (36° C)*	22
80° C	25

*Ultrasonic action increased the temperature of the water bath to 36° C

Littlewood found that extraction at 90° C did not increase the yield of solubilized coal in pyridine.3/ Littlewood also stated that this was contrary to the findings of Mertins, who reported that a temperature of 80° C gave a three-fold increase in solvation yield.7/ Our data appear to substantiate the findings of Littlewood; namely, a two-fold increase in temperature relative to ambient temperature has little effect on ultrasonic solubilization.

Sulfur Removal

One-half gram samples of various bituminous coals (-325 mesh) in quinoline were ultrasonically irradiated for 4 hours at ambient temperature. Total sulfur analyses were obtained for the extracts. The results of these analyses and the analyses of the starting coals are shown in table 6.

Table 6.- Sulfur analyses

Sample	Rank	Weight percent sulfur		Percent removed
		Extract	Starting coal	
Coal 1*	hvab	0.6	1.0	40
2	hvab	1.9	3.5	46
3	hvab	4.1	7.5	46
5	hvbb	2.1	3.9	45
375° C char, Pittsburgh seam coal		0.7	1.2	42

* See table 1 for complete identification of samples.

In these five samples the sulfur is 40 to 46 percent lower in the extracts than in the starting coal.

To determine the type of sulfur removed by ultrasonic solubilization of coal, sulfur forms analyses were obtained from a quinoline extract of a Kentucky No. 11 raw head coal sample. See Coal 4, Table 1, for complete identification of sample. The results of the extract together with data for the starting coal are given in table 7.

Table 7.- Sulfur forms analyses

	Weight percent			
	Total S	Pyrite S	Organic S	Sulfate S
Starting coal	5.5	3.7	1.8	0.12
Extract	1.9	0.03	1.8	0.04

These data show that removal of the pyritic sulfur accounts for the decrease in sulfur content of the extract.

Ash Removal

Ash determinations were made on the extracts prepared as described above. The results, together with the analyses of the starting coals, are given in table 8.

Table 8.- Ash analyses

Sample	Rank	Weight percent		Percent removed
		Extract	Starting coal	
Coal 1*	hvab	1.3	1.7	24
2	hvab	1.0	6.7	85
3	hvab	3.4	15.4	78
4	hvab	3.3	12.4	87
375° C char, Pittsburgh seam hvab		1.0	7.5	73

* See table 1 for sample identification

The lower ash values in the quinoline extracts can be attributed to ultrasonic grinding which causes submicron size particles to be formed; the ash particles are removed from the extracts by a washing procedure during the extract preparation described earlier. Evidence for this phenomenon was observed in the following experiment. The wash water from one of the extract preparations was saved and evaporated to dryness. The fluffy light-brown residue that remained was analyzed by emission spectroscopy and found to contain 20-30 percent Si, 10-20 percent Al, and 1-5 percent Fe. The concentrations of Si, Al, and Fe are similar to those found in coal ash.

Reuse of Quinoline

It has been observed in an investigation utilizing a high-boiling coal-tar fraction as a solvent that the solvating power of the recycle material decreased by several percent with each pass.8/ In order to determine if high molecular weight compounds produced by the sonolysis of quinoline or extracted during the

ultrasonic irradiation of coal-quinoline mixtures affect the efficiency of recycled quinoline, the following experiments were performed.

The fresh quinoline used in this investigation has a boiling range of 235°-237° C and contains approximately 0.1 percent methyl quinolines as determined by mass spectrometry. The distillate of the solvent from ultrasonically irradiated quinoline-coal extract mixtures contains a fraction boiling from 235°-239° C (primarily quinoline), Fraction 1, and a fraction boiling higher than 239° C, Fraction 2. Fraction 1 constitutes 98 percent of the distillable solvent and Fraction 2 constitutes the other 2 percent. The doped solvent used in this experiment consisted of 90 percent of Fraction 1 (b.p. 235°-239° C) and 10 percent of Fraction 2; the concentration of higher boiling material was, therefore, 5 times more than that found in ultrasonically irradiated quinoline-coal mixtures.

One-half gram samples of Pittsburgh seam hvab coal (-325 mesh) and 5 ml of doped quinoline or Fraction 1 (see above) were ultrasonically irradiated for 4 hours at ambient temperature. The results of these experiments, and of an extraction with "fresh" quinoline, are shown in table 9.

Table 9.- Solvation of coal in used quinoline

Solvent	Weight percent of coal solvated
Doped-reclaimed quinoline (10 percent boiling > 239° C)*	28
Fraction 1 (b.p. 235°-239° C)*	29
"Fresh" quinoline (b.p. 235°-237° C)	27

* See text for description

In another series of experiments, slurries consisting of 0.5 gm Pittsburgh seam hvab coal (-325 mesh) and 5.0 ml of solvent were ultrasonically irradiated for 4 hours at ambient temperature. After the coal residue was removed following each extraction, the quinoline and extracted material were used as the "solvent" for the next extraction of "fresh" coal. The results of these experiments are shown in table 10.

Table 10.- Recycled quinoline extract and fresh coal

Experiment	Solvent	Cumulative extract, weight percent	Weight percent solvated in 4 hours
I*	Fresh quinoline	26	26
II	Quinoline + extract from I**	52	26
III	Quinoline + extract from II**	88	28
IV	Quinoline + extract from III**	-	Not obtained, see text

* 0.5 gm Pittsburgh seam hvab coal (-325 mesh) used for all 4 experiments.

** Solvent (quinoline + extract) obtained from preceding experiment by removal of coal residue by centrifugation.

The mixture at the end of Experiment IV was so viscous that it could not be separated by centrifugation. Consequently, the percent of coal solvated could not be determined.

From these data it appears that high-boiling compounds extracted (or produced by the sonolysis of the solvent) during the ultrasonic irradiation of coal-quinoline slurries have little or no effect on the amount of coal solubilized by reused quinoline.

Crude Quinoline-Base Mixture

A 0.5 gm sample of Pittsburgh seam hvab vitrain (-325 mesh) and 5 ml of crude quinoline bases were ultrasonically irradiated for 4 hours at ambient temperature. The crude quinoline bases (obtained from a commercial high-temperature coking operation) had a boiling range of 99° C to 238° C and contained 50 percent quinoline. Only one percent of the coal was solubilized.

The crude quinoline-base fraction was found to contain 9 percent H_2O. To determine if H_2O inhibits ultrasonic extraction, 0.5 gm of the Pittsburgh seam vitrain (325 mesh) used above and 5.0 ml of a mixture containing 80 percent pure quinoline and 20 percent H_2O was irradiated for 4 hours. This experiment produced only 9.5 percent extract, compared with 49 percent using pure quinoline.

Water was distilled from the crude quinoline-base fraction, and the experiment was repeated. The water-free fraction (boiling range 220°-238° C) solvated 38 percent of the coal. These data indicate that the presence of water reduces the solvation power of the quinoline. Mertins also reported that the presence of water in pyridine reduced the extraction efficiency of the solvent.[7]

SUMMARY

This investigation of the ultrasonic irradiation of bituminous coal-quinoline mixtures has shown:

1. There is an apparent correlation between the carbon content of the bituminous coals investigated and the amount of material solubilized; that is, the amount of material solubilized decreased as the carbon content of the starting coal decreased.

2. The solvation rate for vitrain in quinoline is greatest during the first 2 hours of irradiation

3. A greater yield of extract can be obtained by first charring the coal at the temperature producing maximum fluidity

4. For shorter irradiation times the particle size of the starting coal is an important factor for increased solubilization

5. Increasing the temperature from 36° C to 80° C does not affect the yield of extract

6. The presence of water in quinoline reduces the extraction efficiency of the solvent

7. The solvates produced show marked decreases in sulfur content compared to the starting coal. The decrease in sulfur in the extracts is caused by removal of pyritic sulfur

8. There is a decrease in the ash content of the extracts.

9. Quinoline can be reused as a solvent with no impairment of solubilizing efficiency.

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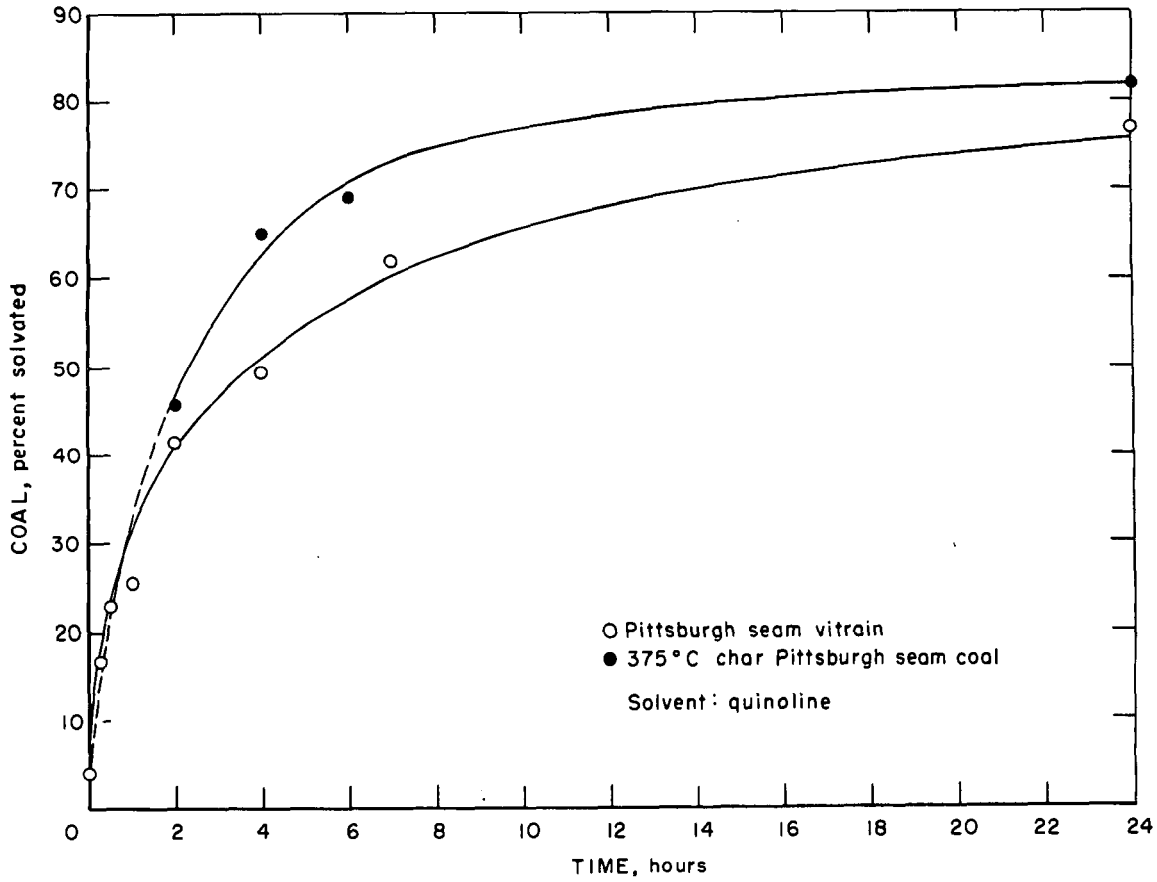

Figure 1.- Percent hvab vitrain and char solvated versus ultrasonic irradiation time.