

## THE EFFECT OF REACTION CONDITIONS ON SOLVENT LOSS DURING COAL LIQUEFACTION

Bruce R. Utz and Sidney Friedman

U.S. Department of Energy  
Pittsburgh Energy Technology Center  
P.O. Box 10940  
Pittsburgh, PA 15236

### INTRODUCTION

The fate of a coal-liquefaction recycle solvent during Integrated Two-Stage Liquefaction (ITSL) and other direct liquefaction processes is a major concern. If the solvent has an inadequate concentration of hydrogen donors or other solvent components that might enhance liquefaction, then the quality of the solvent will be degraded and conversion to liquid products will be adversely affected. Studies using the solvents phenol (1), tetrahydroquinoline (2-4), quinoline (5), and pyridine (6) have shown that these compounds are partially incorporated by covalent bonds, but a relatively large amount is hydrogen bonded to coal-derived products. In other studies using pure  $^{13}\text{C}$ - and  $^{14}\text{C}$ -labeled aromatic or hydroaromatic compounds as solvents (3,6-8), the amount of adduction was determined. Although adduction and hydrogen bonding of solvent components account for solvent loss, other degradative reactions also account for loss of original solvent and solvent quality. Ring contraction of tetralin (9), and octahydrophenanthrene (8,10) under coal-liquefaction conditions reduces the hydrogen-donor concentration and therefore the solvent quality.

The use of a one-component solvent system can be misleading because reactions with coal may be occurring that normally would not occur if other components of a solvent were present. The objective of this study was to examine a multicomponent synthetic solvent and determine if solvent components are preferentially lost or degraded during short-contact-time liquefaction (SCTL), and how solvent loss in SCTL compares with other liquefaction conditions that involve gradual heat-up.

### EXPERIMENTAL

Experiments were performed in a microreactor assembly (11) consisting of a 316 stainless steel 1/2-in. union tee with two end caps. Five grams of a synthetic solvent and one gram of moisture-free Western Kentucky 9/14 coal were added to the microreactor, which was assembled and pressurized to 1100 psig with  $\text{H}_2$ . The synthetic solvent consisted of 4% quinoline, 13% m-cresol, 20% tetralin, 33% 1-methylnaphthalene, 20% phenanthrene, and 10% pyrene. Experiments were conducted with one- and two-component solvents and coal in order to identify unique products from each of the simple solvent systems. The two-component solvent consisted of 20% pyrene and 80% tetralin, or 20% phenanthrene and 80% tetralin. One-component solvents of 1-methylnaphthalene, tetralin, and m-cresol were also used. The microreactor assembly was attached to a wrist-action shaker that moved the reactor through a small arc for adequate mixing of the reactor contents. The shaker was positioned above a vertically moving platform that supported a fluidized sand bath (11).

For SCTL experiments, the bath was heated to an initial temperature of 460°C. When the experiment was initiated, the temperature set point was changed to 425°C and the platform (with bath) was raised, immersing the microreactor. Heat-up to 425°C took approximately 1 min. Reaction time was 3 min at 425°C. For experiments conducted under traditional or severe conditions, the reactor was immersed in the sand bath, which was at room temperature, gradually heated (55 min) to 425°C, and held at reaction temperature for 30 min or 6 hours. At the end of the

reaction, the platform was lowered and the microreactor was cooled with a stream of room-temperature air. The outside of the cooled microreactor assembly was cleaned (to remove sand) with compressed air. Gases were vented, and the microreactor was disassembled.

The reacted suspension was pipetted into a 50-mL volumetric flask containing 0.100 gm durene and 0.100 gm fluorenone, which were the internal standards used for quantitative capillary gas chromatography. The remaining residue and synthetic solvent in the microreactor were removed with tetrahydrofuran (THF) and added to the flask. Aliquots were then analyzed using a 50-meter highly cross-linked phenylmethylsilicone capillary column. Flame ionization was used to detect individual components of the treated synthetic solvent, although in certain instances a mass-selective detector was also used to assist in the identification of products.

Solvent loss of each component was determined by calculating the difference between the original amount of the component and the recovered amount of the component and its reaction by-products. Solvent that was lost and unaccounted for represented adducted or polymerized material. All percentages will be discussed on an absolute basis; therefore, the loss of 10% tetralin would represent 10% of the synthetic solvent and not 10% of the 20% tetralin present in the synthetic solvent. The solvent losses would be five times larger if they were based on the weight of the coal sample, since the solvent:coal ratio was 5:1, i.e., loss of 3% of the solvent by adduction would represent a 15% addition to the weight of the coal.

## RESULTS AND DISCUSSION

The effect of reaction conditions on solvent loss, and specifically on preferential loss of components of the solvent, was examined at three sets of reaction conditions. Experiments were conducted under SCTL conditions (rapid heat-up, 3 min at 425°C), traditional conditions (gradual heat-up, 30 min at 425°C), and severe conditions (gradual heat-up, 6 hours at 425°C). The advantages in using this synthetic solvent are that all components of the solvent are known, its elemental composition is similar to a coal-derived recycle solvent, and the multi-component solvent simulates a recycle solvent better than a one-component solvent does. The use of a synthetic solvent also allows the study of individual components in a more realistic environment.

The objective was to examine solvent recovery with increasing severity of coal-liquefaction reaction conditions. The SCTL stage of an ITS process involves rapid heat-up, followed by a short residence time at reaction temperature. During rapid heat-up, the rate of free-radical production should increase significantly in a SCTL stage. An increase in free-radical concentration was hypothesized, since the demand for hydrogen, with increased free-radical production, would increase and would be less likely satisfied by hydrogen donors and gaseous hydrogen. With an increase in free-radical concentration, a concomitant increase in solvent adduction was hypothesized, since free-radical addition, aromatic substitution, and polymerization reactions involving solvent and coal free-radicals would be likely.

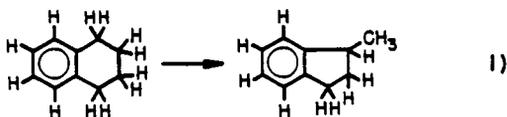
In comparing results obtained under SCTL conditions (Table 1) with results obtained from experiments conducted under traditional liquefaction conditions (gradual heat-up to 425°C, 30 min at 425°C), solvent loss due to adduction should also be occurring under traditional conditions. As the severity of the liquefaction conditions is increased, adducted solvent should undergo cleavage (cracking, hydrogenolysis, etc.) and re-form solvent-like products, resulting in improved solvent balance. While the original components may not be recovered, products having similar structures and chemical properties should be. For example, adduction of phenanthrene with a coal-derived benzylic radical may occur

and may ultimately form methyl-substituted phenanthrene (Figure 1). Based on this hypothesis, severe solvent loss was expected with a SCTL process compared to moderate solvent loss under traditional liquefaction conditions, and if the conditions were severe enough, solvent that was initially adducted, or solvent-like products, could be recovered.

Results from SCTL reactions demonstrated that components of the synthetic solvent were not adducted, degraded, or lost. While 75%-85% of the coal was converted to THF-soluble material, only 2.6% tetralin underwent dehydrogenation. No adduction of m-cresol or quinoline was observed. Results using a synthetic solvent demonstrate that SCTL is a favorable process because solvent balance with little solvent degradation can be achieved. These results were unexpected and suggest that an increased concentration of free radicals in a short period of time does not cause solvent loss or degradation when sufficient readily donable hydrogen is present. The results also imply that free radical production does not play an important role in solvent loss via adduction.

It should also be understood that little, if any, of the recovered, original solvent components are coal-derived. Based on coal experiments performed with one- and two-component solvents, negligible quantities of quinoline, m-cresol, and 1-methylnaphthalene could be considered coal-derived, while a maximum of 0.2% tetralin, 0.3% naphthalene, 0.2% pyrene, and 0.1% phenanthrene were coal-derived.

Experiments conducted using traditional coal liquefaction reaction conditions showed that solvent balance could still be achieved, but degradation of the solvent had started to occur. Results from experiments performed in the absence of coal showed that little, if any, demethylation and decomposition of 1-methylnaphthalene had occurred. Reactions in the presence of coal showed that approximately 3.2% 1-methylnaphthalene had undergone demethylation and decomposition. Some of the demethylated product (2.2%) could be accounted for by the increased amounts of naphthalene. Tetralin reactions included dehydrogenation to naphthalene (6.1%), rearrangement to 1-methylindane (0.5%), and decomposition to butylbenzene (0.1%). The total amount of tetralin and its reaction products is 22.2%; therefore, the additional amount (based on 20% tetralin in the synthetic solvent) could be accounted for by demethylation of 1-methylnaphthalene. It is possible that more than 2.2% 1-methylnaphthalene underwent demethylation to naphthalene if tetralin was being lost via unidentified reactions and not via dehydrogenation to naphthalene. If this occurred, then greater amounts of recovered naphthalene could be attributed to the demethylation of 1-methylnaphthalene and not to the dehydrogenation of tetralin. Methylation was also occurring, and 0.4% dimethylnaphthalene and 0.3% dimethylphenol were produced. Hydrogenation of the aromatic components was also occurring, producing 1.0% methyltetralin, 1.7% dihydrophenanthrene, 0.1% tetrahydrophenanthrene, 0.8% dihydropyrene, and 1.3% tetrahydroquinoline. The production of methyltetralin is most likely occurring via the hydrogenation of 1-methylnaphthalene, since no methylation of tetralin was observed when blank experiments using tetralin as a solvent were conducted. The major degradation reactions occurring were rearrangement of tetralin to 0.5% 1-methylindane (Equation 1) and cracking to butylbenzene (0.1%).



While some of the quinoline was undergoing hydrogenation to tetrahydroquinoline (1.3%), 0.3% could not be accounted for. Solvent balance under traditional liquefaction conditions was quite good. While methylation, demethylation, rearrangement, and cracking reactions have become apparent, 98.6% of the solvent can still be accounted for (less possible coal-derived products) and had not been lost because of adduction with coal-derived products.

Treatment of coal and solvent at more severe conditions resulted in greater rearrangement and degradation of the individual solvent components, although the solvent balance was approximately 97.5%. As much as 16.5% of 1-methylnaphthalene had undergone reaction. At least 12% 1-methylnaphthalene could be accounted for because of demethylation, methylation, and hydrogenation. Extensive dehydrogenation of tetralin was expected, and only 6.3% tetralin was recovered. Rearrangement reactions were significant and again were a major reason for the decrease in solvent quality. Approximately 2.1% tetralin had rearranged to 1-methylindane. Some loss of most components of the solvent had occurred. Methylation and demethylation of m-cresol was greater than observed under traditional liquefaction conditions, and approximately 11.1% was recovered. While quinoline represented the component that was present in the smallest amount, it was preferentially lost, and only 1.8% of quinoline and tetrahydroquinoline could be accounted for. While most of the solvent could be accounted for (approximately 97.5%), only 61.1% was recovered as original solvent and represented a solvent of much poorer quality.

Experiments conducted under these severe reaction conditions have shown that the synthetic solvent has undergone many reactions. Degradation reactions were evident; and greater, not lesser, quantities of solvent were lost. Even under these severe conditions, the overall solvent balance was better than expected.

#### SUMMARY

The effect of reaction conditions on solvent loss was determined. Solvent recovery and solvent balance were better than expected for SCTL and traditional liquefaction conditions. Surprisingly, very little adduction of solvent components was observed. Increased severity of reaction conditions caused an increase in degradation of the synthetic solvent and an increase in adduction (approximately 2.5%). From these results, the extent of solvent adduction under most liquefaction conditions is minimal, and the solvent quality is most affected because of increased degradation with increasing severity.

#### ACKNOWLEDGMENTS

The authors would like to thank John Siciliano, Katherine Lew, and Joseph Sharrow for their technical assistance in the laboratory. These individuals were part of the Oak Ridge Associated Universities (ORAU) Student Participation Program. The authors would also like to thank Tom Williams, whose meticulous efforts in the laboratory resulted in excellent precision.

#### REFERENCES

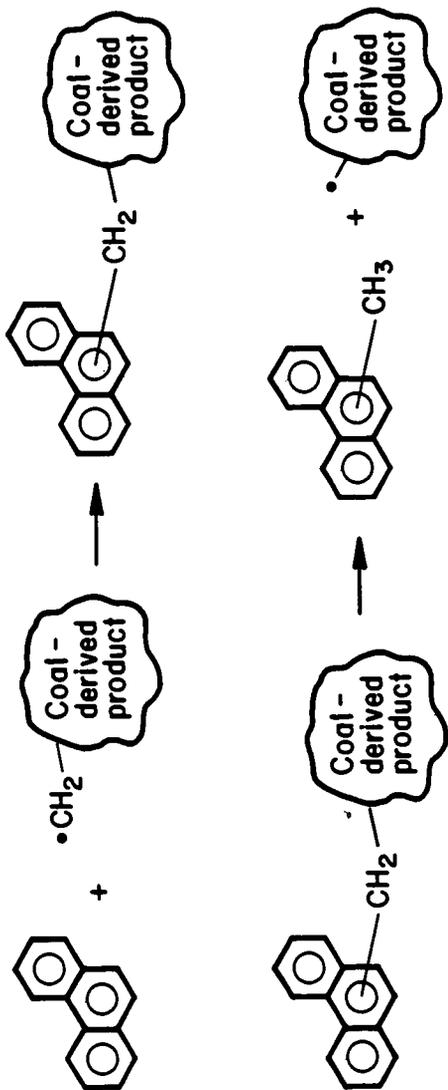
1. Larsen, J.W., Sams, T.L., and Rogers, B.R. Fuel 1981, 60, 335.
2. Bruecker, R., and Koelling, G. Brennstoff-Chemie 1965, 46, 41.
3. McNeil, R.I., Young, D.C., and Cronauer, D.C. Fuel 1983, 62, 806.
4. Hellgeth, J.W., Taylor, L.T., and Squires, A.M. Int. Conf. Coal Science 1983, 172.

5. Narain, N.K., Utz, B.R., Appell, H.A., and Blaustein, B.D. *Fuel*, 1983, 62, 1417.
6. Collings, C.J., Haggman, E.W., Jones, R.M., and Raeen, V.F. *Fuel* 1981, 60, 359.
7. Cronauer, D.C., McNeil, R.I., Danner, D.A., Wieland, J.H., and Abichandani, J.S. *Prepr. Am. Chem. Soc. Div. Fuel Chem.*, 28(5), 40.
8. Cronauer, D.C., Jewell, D.M., Shah, Y.T., Modl, R.J., and Seshadri, K.S. *Ind. Eng. Chem., Fundam.* 1979, 18(4), 368.
9. Franz, J.A., and Camaioni, D.M. *Prepr. Am. Chem. Soc. Div. Fuel Chem.* 1981, 26(1), 105.
10. Ruberto, R.G. *Fuel Proc. Tech.* 1980, 3,7.
11. Utz, B.R., Appell, H.A., and Blaustein, B.D. Accepted for publication in *Fuel*.

TABLE 1. Solvent Recovery Values

Components and Percentages in Original Synthetic Solvent	Percentage of Components in Reacted Synthetic Solvent <sup>1</sup>							
	SCTL				Reaction Conditions			
	Solvent	Coal + Solvent	Solvent	Coal + Solvent	Solvent	Coal + Solvent	Solvent	Coal + Solvent
1-Methylnaphthalene	33	33.3	32.8	32.7	28.4	27.9	16.5	16.5
Dimethylnaphthalenes	--	--	--	--	0.4	--	0.6	0.6
Methyltetralins	--	--	--	0.1	1.0	1.2	2.0	2.0
Tetralin	20	20.1	17.5	19.6	15.5	16.6	6.3	6.3
Naphthalene	--	0.1	2.6	0.4	6.1	3.8	20.4	20.4
Ethylbenzene	--	--	--	--	--	--	0.1	0.1
Methylindane	--	--	--	0.2	0.5	1.7	2.1	2.1
Butylbenzene	--	--	--	0.1	0.1	0.2	0.4	0.4
Phenanthrene	20	20.1	19.8	19.4	18.1	17.3	17.3	17.3
Dihydrophenanthrene	--	0.1	0.5	0.8	1.7	2.4	0.8	0.8
Tetrahydrophenanthrene	--	--	--	--	0.7	0.3	0.5	0.5
m-Cresol	13	12.9	12.7	12.7	12.1	11.7	11.1	11.1
Dimethylphenol	--	--	--	--	0.3	--	0.7	0.7
Phenol	--	--	--	--	0.1	0.1	0.3	0.3
Pyrene	10	9.8	9.6	9.2	8.5	8.3	8.4	8.4
Dihdropyrene	--	0.1	0.1	0.7	0.8	1.4	0.5	0.5
Quinoline	4	4.1	4.0	3.3	2.4	1.6	1.5	1.5
Tetrahydroquinoline	--	0.1	0.1	0.8	1.3	1.6	0.3	0.3
Unidentified Solvent-Derived Products	--	--	0.1	0.3	1.2	2.7	4.9	4.9
Unidentified Solvent-Derived and/or Coal-Derived Products	--	--	--	--	1.5	--	2.8	2.8
Total Recoveries		100.7	99.8	100.3	100.1	98.8	97.5	97.5

<sup>1</sup> Values represent average of at least duplicate experiments.



**Figure 1. Methylation of Solvent by Coal**