

## THE FATE OF NITROGENOUS MODEL PROCESS SOLVENTS IN COAL LIQUEFACTION

J. W. Hellgeth, P. G. Amateis and L. T. Taylor  
Department of Chemistry

Virginia Polytechnic Institute and State University  
Blacksburg, VA 24061

### INTRODUCTION

The nature and role of the liquefaction solvent are the keys to understanding liquefaction chemistry. Solvent apparently serves many purposes during the dissolution of coal but two of the most significant roles have been suggested to be as a hydrogen transfer mechanism and as a catalyst (1). In this regard recent work with 1,2,3,4-tetrahydroquinoline (THQ) as a model liquefaction solvent has demonstrated its ability to convert a variety of coals, both bituminous and subbituminous, to pyridine and toluene solubles in a rapid and nearly complete fashion (2-4). While high conversions to soluble products have been realized, the ultimate goal of conversion to distillate materials in high yields remains to be attained. It is now apparent that during liquefaction, significant portions of THQ are adducted to the dissolving coal to give a non-distillable yet toluene/pyridine soluble material. The purpose of the present work is to quantify this adduction with respect to product distribution and to discern the possible modes of solvent nitrogen loss either through adduction into the coal-derived product or through thermal cracking of the solvent. Products from an in-house tubing bomb reactor and from Kerr McGee Corp. are examined. In addition a series of THQ-related model solvents will be examined in order to ascertain the effect of slight changes in solvent basicity, nitrogen atom substituent and nitrogen atom ring position upon the extent of coal conversion to soluble and distillable material.

### EXPERIMENTAL

Liquefaction experiments on a Wyodak #3 western subbituminous coal were performed both in-house and at Kerr McGee Corp. (Crescent, OK). The in-house experiments involved preparation of the feed coal by drying at 293°K, 12 hours under a stream of dry nitrogen and then grinding to less than 60 mesh particle size. The Kerr McGee sample was prepared in a different manner which involved drying under vacuum at room temperature for 24 hours followed by grinding to 60 mesh particle size. The proximate and ultimate analysis (MF basis) for both samples are presented in Table I.

TABLE I

	Proximate Analyses		Ultimate Analyses		
	% Wt. <sup>a</sup>	% Wt. <sup>b</sup>	% Wt. <sup>a</sup>	% Wt. <sup>b</sup>	
			Carbon	56.1	57.2
			Hydrogen	3.2	4.6
			Nitrogen	0.8	0.8
			Oxygen	11.8	15.6
			Sulfur	7.6	3.02
Ash	17.5	18.7			
Volatiles	58.4	47.9			
Fixed Carbon	24.1	33.4			

<sup>a</sup>In-house Sample (19.2% H<sub>2</sub>O); <sup>b</sup>Kerr McGee Sample (24.1% H<sub>2</sub>O)

Liquefaction of the feed coal proceeded under the general conditions of 2:1 solvent:coal, 691°K reaction temperature, 30 minutes reaction time and 7.5 MPa hydrogen atmosphere (cold charge). Experiments performed in-house were conducted in 40 mL microautoclave vessels with 4 grams of coal. The Kerr McGee experiment involved a 1 liter autoclave vessel and 100 grams of coal. Sample workup for the in-house samples involved extraction with toluene and pyridine to obtain a conversion based on solubility and through distillation to a 1050°F endpoint (300°C, 1.3 Pa). The Kerr McGee product work-up involved distillation of the products to a 850°F endpoint at atmospheric pressure (400°F, 13.3 Pa). Nitrogen determinations of these products were obtained from Galbraith Laboratories (Knoxville, TN).

## RESULTS AND DISCUSSION

The model compounds used as process solvents in the liquefaction runs were 1-methylnaphthalene (MN), tetralin (TET), 1,2,3,4-THQ, 2,3-cyclohexenopyridine (CHP), 1,2,3,4-tetrahydroisoquinoline (THIQ), 1-methyl-2,3,4-trihydroquinoline (MTHQ) and quinoline (QU). We determined (1) the extent of conversion to both solvent soluble and distillate material and (2) the level of solvent incorporation into the residuum in terms of solvent basicity, position and presence of donatable hydrogen, substituent interference (MTHQ) and presence of nitrogen in the ring (THQ vs. CHP).

A comparison of the toluene and pyridine conversions obtained for these runs is described in Figure 1. With respect to these conversions, the solubilities reported were obtained in the presence of the process solvent. Therefore, co-solvency effects may be involved. For example, as expected percent pyridine conversions are consistently higher than percent toluene conversions regardless of the model process solvent. For MN, TET and QU, the differences average more than 25%; whereas, with THQ, THIQ, MTHQ and CHP the differences are 6% or less. Co-solvency rather than depolymerization to smaller fragments may account for the relatively high toluene solubilities observed with most of the nitrogen-containing solvents. From these data conversion to pyridine solubles appears to be solely dependent upon the presence of readily donatable hydrogen as evidenced by comparing MN/TET (69.9% vs 96.8%) and QU/THQ (76.8% vs 95.5%). A dependence of toluene soluble conversion on the presence of nitrogen in the ring system is not very striking, MN/QU (51.1% vs 54.2%); whereas, if the nitrogen is accompanied by donatable hydrogen the dependence is great, TET/QU (71.4% vs 89.5%). Dependence of conversion to toluene or pyridine soluble products on the position of nitrogen in the ring, the basicity of the model solvent and the positional relationship of nitrogen to the donatable hydrogen in the ring structure was not found.

The product mass balances for the samples obtained through distillation are shown in Figure 2. Inspection of the figure demonstrates several points. First, the only run to demonstrate a net increase in distillate recovery was that of MN. In the TET case there was a net conversion of the insoluble MF coal. However, a recovery of volatile products demonstrated a conversion to light ends and gases rather than to slightly less volatile material. In all of the nitrogen heterocyclic cases, a net gain in residuum mass was found. In general, the distillate recoveries were greater than that in the tetralin case but they were still less than that predicted by the starting solvent mass. The reduction in distillate recovery correlates with incorporation of solvent into the residuum or a cracking of distillate to light ends of approximately 10-15% of the starting solvent mass. The exception found here was THIQ where even a larger amount of process solvent was lost to the light ends material.

The nitrogen content distributions for the products recovered in these runs are displayed in Figure 3. The nitrogen analyses were obtained from Galbraith Laboratories with use of the Kjeldahl method. In the cases of MN and tetralin, the sole source of nitrogen within the run was the coal itself. In both these products a shift of nitrogen content to the distillate mass was found. Under these conditions, approximately 20% of the nitrogen content in the coal is dynamic. When nitrogen heterocyclic compounds were employed a considerable amount of the nitrogen base was found to have adducted into the residuum or lost to the light ends. The percent nitrogen increase in the residuum reflects an incorporation of between 8 and 15% of the starting solvent mass. Steric interference was not found for MTHQ since the expected reduction in adduction did not occur. Distillate analysis via GC-FTIR demonstrated that a rapid dissociation of MTHQ to THQ had occurred resulting in a similar quantity of adduction.

To further delineate and quantify the coal-solvent interaction, nitrogen and mass balance data have been obtained on the products produced from a liquefaction run performed by Kerr McGee. The results of this investigation are presented in Table II. Upon inspection of these data, it is apparent that the nitrogen content of the initial solvent (THQ) is highly mobile. Approximately 8.0% of the original THQ material is lost to light ends, gas product and residuum material. The major portion of this loss was to the residuum (67.5% of N loss from solvent). This adduction was further found to be restricted to the solvent (THF) soluble material. The remainder of the loss was to ammonia and small chain alkyl amines located in the gas product and light end. See Figure 4.

It is apparent from these data that adduction of process solvent to non-distillate and high boiling distillate materials is significant. Though some breakdown of process solvent was found, its contribution to the loss of the dynamic nitrogen component is minimal in comparison to the problem of adduction.

#### REFERENCES

1. Atherton, L., EPRI Journal, Jan.-Feb., 1984, 37.
2. Atherton, L. and Kulik, C., Advanced Coal Liquefaction, AICHE Meeting Los Angeles, March, 1982.
3. Whitehurst, D. D.; Mitchell, T. D.; Farcasiu, M. and Dichert, J. J., "The Nature and Origin of Asphaltene in Processed Coal", EPRI Report AF-1298, Final Report under Project RP-410, December, 1979.
4. "Fundamental Studies in the Conversion of Coals to Fuels of Increased Hydrogen Content", Derbyshire, F. J.; Odoefer, G. A.; Rudnick, L. R.; Varghese, P. and Whitehurst, D. D., EPRI Report AP-2117, Volume 1, November, 1981.

Acknowledgments to EPRI for funding of this project and to Kerr McGee Corp. for sample preparation are gratefully extended.

TABLE II  
MASS BALANCE AND NITROGEN CONTENT DATA

<u>Starting Material</u>			
Mass		Total Wt. Nitrogen	21.66 g
THQ	200 g	% contribution	
Tetralin	--	by solvent	97.14%
Solvent	200 g		(21.06 g)
Coal	100 g	by coal	2.86%
MF Coal	75.9 g		(0.62 g)
<u>Recovered Products</u>			
Distillate Wt.	203.19 g	Residuum Wt.	55.23 g
%N	9.55%	%N	3.18%
Wt. N	19.40 g	Wt. N	1.74 g
% Total N	89.48%	% Total N	8.03%
Retained		Retained	
Net Gain or Loss		Net Gain or Loss	
From solvent		from Moisture free	
(initial weight)		Coal (initial weight)	
Mass	+3.19 g	Mass	-20.67 g
	(1.6%)		(-27.2%)
Nitrogen	-1.66 g	Nitrogen	+1.12 g
	(-7.88%)		(181%)
<u>Product Distributions</u>			
% Total Mass	86.14%	% Total Mass as	13.86%
Recovered as		Light Ends and Gas	
Distillate and		Product (by	
Residuum		difference)	
% Total Nitrogen	97.51%	% Total Nitrogen	2.49%
Retained in Residuum		in Gas Product	
and Distillate		and Light Ends	
		(by difference)	

# CONVERSION OF WYODAK #3 TO SOLUBLE PRODUCTS

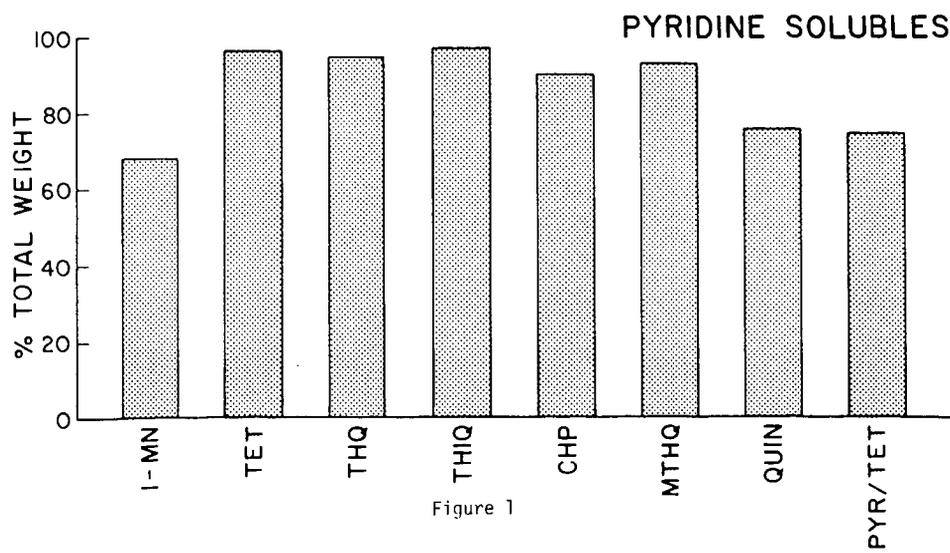
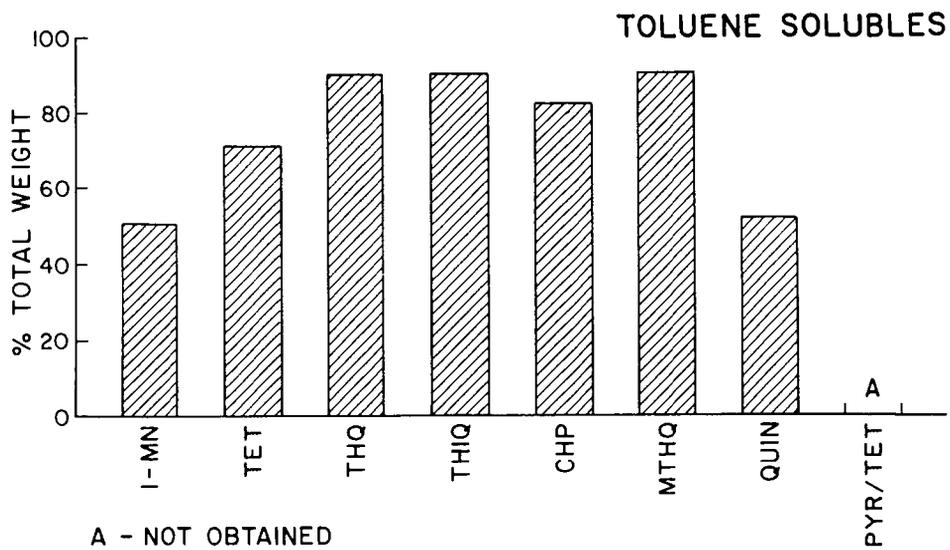


Figure 1

### PRODUCT DISTRIBUTIONS

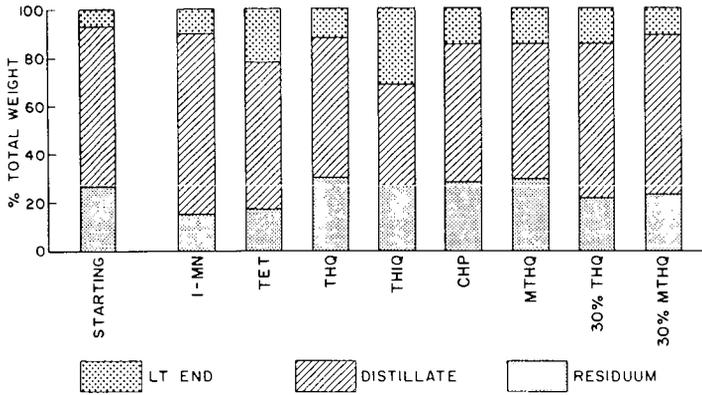


Figure 2

### PRODUCT DISTRIBUTIONS

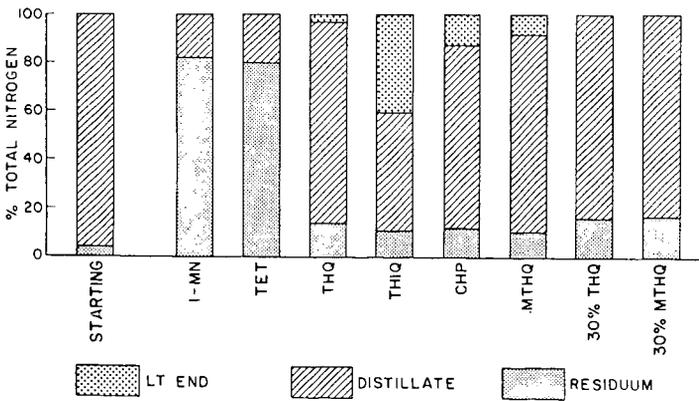


Figure 3

# KERR MCGEE RUN P-24 MASS AND NITROGEN DISTRIBUTIONS

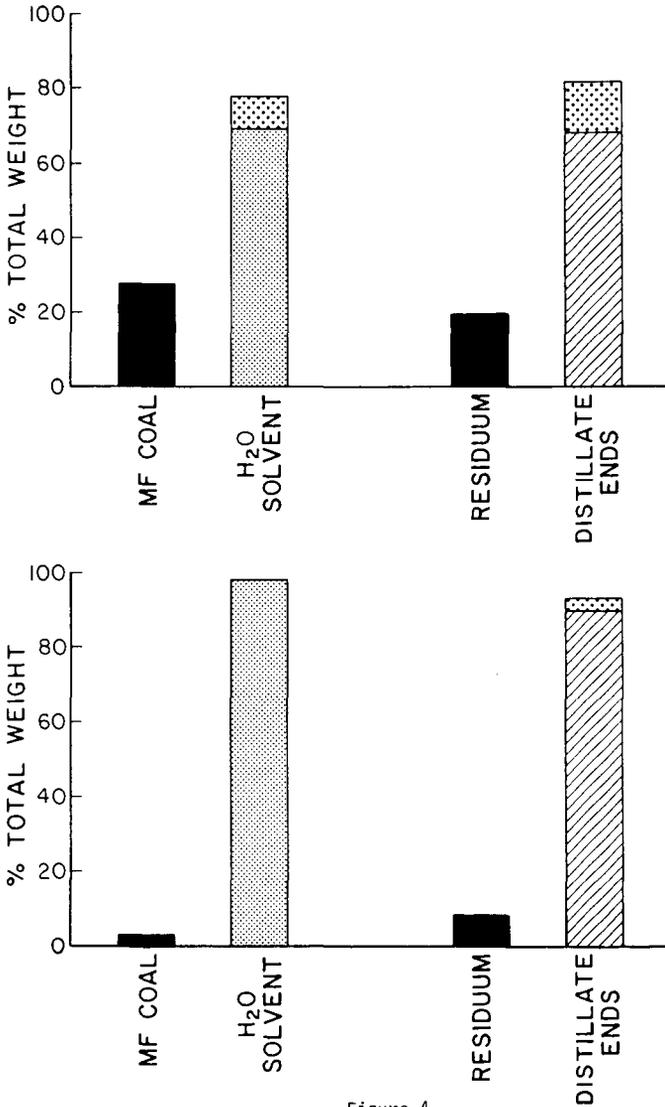


Figure 4