

## REACTIVITY OF SOME NITROGEN-CONTAINING COMPOUNDS AT SUPERCRITICAL WATER CONDITIONS

David M. Tiffany, Thomas J. Houser, Michael E. McCarville  
and Michael E. Houghton

Department of Chemistry, Western Michigan University  
Kalamazoo, MI 49008

### INTRODUCTION

The possible use of supercritical fluid extraction (SFE) of coal to produce liquids has been attracting significant interest recently. The temperatures at which SFE is generally carried out, about 400°C and above, will cause bond ruptures to occur in the coal structure. Thus, the extracting capability of the fluid is important in terms of both the intermediate products, usually involatile at these temperatures, as well as the original coal components. In addition, the fluid has the opportunity to participate as a reactant at process conditions, which may yield extracts of different compositions that will be dependent on the fluid used.

Thermodynamic consideration of SFE leads to the prediction that the enhanced solubility (volatility) of the solute has a very strong dependence on pressure (1). The enhancement may be as large as a factor of  $10^4$  under very favorable conditions (2). Thus, this method combines many of the advantages of distillation with those of extraction. The general advantages of SFE as applied to coal processing have been previously enumerated (1). Many of the reported studies in this area, using toluene as the fluid, have originated in Great Britain. The influence of residence time, temperature, and pressure on yield from the SFE of coal, using bench-scale and small pilot plant units has been reported (3). Economic (4) and energy efficiency (5) evaluations have indicated that SFE is competitive with most other coal conversion processes. However, despite the strong interest in SFE there has been very little reported on the basic chemistry that takes place during coal extraction by this technique.

One important function which coal processing can perform is the removal of heteroatoms to yield a cleaner product. In particular, the current program is concerned with nitrogen removal from model compounds thought to be representative structures found in coal. Studies have shown that quinoline type structures in coal liquefaction are among the most difficult to remove (6); more recent studies on catalytic hydrodenitrogenation of quinoline (7-9) have supported this assessment. Thus, experiments have concentrated on examining the reactivities of quinoline and isoquinoline; the reactivities of other compounds were studied briefly also. The selection of water as the fluid was based on several properties, in addition to solvent expense, which makes it suitable for the application of interest. Briefly, these properties are: (a) Critical temperature, 374.2°C. Theoretical considerations have shown that extract volatility enhancement is greatest when extraction is carried out near the fluid critical temperature (10). (b) Temperature and pressure dependence of the dielectric constant which will allow control of solvent properties (11). (c) High reactivity with cyanide wastes to form ammonia (12). (d) Molecular polarity since polar solvents exert a stronger depolymerizing action on coal than nonpolar ones and also increase extraction rate (1). Experimental verification of the effectiveness of water as an extracting fluid was indicated by the results reported in a study of solvent effects in supercritical extraction of coal (13); water was more effective than predicted from the theoretical calculations. The present paper discusses the results obtained to date of the treatment of several nitrogen-containing compounds and alkylbenzenes with supercritical water, including some treatments using acid catalysts to enhance reactivity. The expectation is to determine the least severe conditions at which nitrogen can be removed from several types of molecular structures.

## EXPERIMENTAL

The experiments were carried out in a small (47 cc) stainless steel, batch reactor which is not equipped with a pressure gauge or gas vent. The procedure was essentially the same for all experiments. The reactor was loaded with organic compounds (usually 2.00 mL for liquids, or 2.00 grams for solids, although a few quinoline experiments had different amounts), sufficient water was added to produce the desired pressure at reaction temperature as calculated from PVT data (14), catalyst was added as needed, the reactor purged with argon and bolted closed. The reactor was placed in the preheated furnace for the required reaction time. Initial experiments used an electric furnace but times to reach reaction temperature were found to be too long, which prompted a switch to a fluidized sand bath furnace, thus reducing heating times to reach critical temperature to about 15 minutes. Following reaction, the vessel was air cooled, opened, the reaction mixture removed and the water and organic layers filtered and separated. The reactor was washed with a portion of methylene chloride solvent and a second portion of solvent was used to extract the water layer. The organic layer was combined with the solvent portions and diluted to a standard volume of 25 mL with additional solvent.

The various phases were then measured quantitatively. The remaining volume of water and the mass of the char (defined as filterable solids) were determined. A few elemental analyses of the char were obtained. The ammonia produced and dissolved in the water layer was determined for some of the experiments with an ion specific electrode. The methylene chloride solution was examined gas chromatographically for products and extents of reaction. When a component was identified, standard solutions were prepared for quantitative determinations. Some components were confirmed using GC/MS analyses. There still was a significant fraction of product that remained dissolved and/or suspended in the solvent that did not show up on the chromatograms. This was termed the tar portion. Currently, this tar is being examined more closely.

## RESULTS AND DISCUSSION

### Isoquinoline

The results of the reaction of isoquinoline at supercritical water conditions and with water at these conditions are summarized in Table 1. The extents of reaction are significant but their dependence on time and pressure are not entirely unequivocal. The extents appear to level off at longer times and two increases in water pressure increased reaction extents while a third gave a small decrease. However, as with quinoline, the extents of reaction and the products found are different than those from the inert pyrolysis (15). The addition of zinc chloride appears to increase extents somewhat, as does the addition of tetralin or dihydroanthracene. The hydrogen transfer agents were consumed to a large extent also, but DA did not yield products that interfered with the reactant product chromatogram and estimates from a tetralin experiment run later allowed adjustments in the product peaks to produce the yields reported.

The results which are encouraging in terms of nitrogen removal are: (a) about 35 to 55 molar % of the converted reactant is in the form of desirable aromatics, benzene and alkyl benzenes, (b) most of the converted nitrogen appears as ammonia in the water phase and (c) the char is significantly reduced in nitrogen content as compared to the reactant. Other results to note are: (a) a rise in temperature appears to produce a relative increase in lighter molecular weight products as well as increasing extents of reaction, (b) the identifiable products are formed from heterocyclic ring rupture exclusively, thus leaving the homocyclic ring primarily intact, (this may not be true for the reactions leading to the tar/char formation) and (c) the effect of the hydrogen transfer agents indicate that prerreduction, followed by water treatment may improve conversions.

It should also be noted that one experiment run at 450°C and for 48 hrs. without water showed less than 10% reaction (as compared to about 50% with water) and no mea-

surable product or char was found.

### Quinoline

The results of the reaction of quinoline at supercritical water conditions are summarized in Table 2. The following observations can be made when comparing these with those from isoquinoline: quinoline is significantly less reactive, thus would require a catalytic agent, except at 500°C., and the product distribution is very different yielding a smaller fraction of identifiable products which also are primarily aromatic amines, aniline, toluidine and a small amount of quinaldine. The elemental analysis of one char sample did show a reduction in nitrogen content, but it was not as large as that found for the isoquinoline sample. One interesting observation is that two catalytic experiments at 400°C. gave essentially quantitative yields of ammonia. This will be investigated further including elemental analyses of tar and char. It is evident that there is a very large fraction of product in the form of unidentified tar.

### Miscellaneous Compounds

The reactivities of several other compounds with supercritical water were examined and the results are summarized in Table 3. Benzonitrile and carbazole represent nitrogen-containing compounds with different functionalities than the quinolines and these exhibited the extremes in reactivity. Carbazole appears essentially unreacted at our conditions. Benzonitrile evidently hydrolyzed, followed by decarboxylation, very quickly and cleanly, no discoloration of the reaction mixture was observed.

Ethylbenzene and aniline were included because they were observed as products which may have further degradation. Ethylbenzene did react to a small extent, again very cleanly to predictable products, benzene and toluene. Aniline reacts to a larger extent yielding only two organic products in the chromatograms. The aniline results can be considered only qualitative at this point.

Because tetralin and dihydroanthracene were consumed in the reaction with isoquinoline, they were also examined. The tetralin was completely consumed, about half of which formed naphthalene; the other half undergoes ring rupture to produce benzene and at least four alkylbenzenes. Calibrations have not been determined as yet for the two products with the longer retention times than o-xylene, but mass spectra of these are consistent with a C<sub>3</sub>-benzene and a C<sub>4</sub>-benzene. A tetralin experiment run for 48 hours at 450°C. without water gave only 26% reaction, 58% of which formed naphthalene. The next larger product peak had a retention time consistent with those of n-butyl- or o-diethylbenzenes (which were not present in the water reaction product). The dihydroanthracene results are only qualitative but it appears that about half is converted to anthracene. In addition, at least five other products are formed in small amounts and these have retention times between those of naphthalene and anthracene.

### CONCLUSIONS

It is evident from the results that supercritical water can be effective as an active reactant in the removal of nitrogen from several organic compounds as well as influencing the mechanism of hydrocarbon degradation. The effectiveness varies with molecular structure and there are indications that acidic catalysts, e.g., zinc chloride, can improve this effectiveness. Consideration of the extents of reaction shows that isoquinoline is much more susceptible to bond rupture than is quinoline. For isoquinoline, the product distribution shows a distinct preference to rupture the heterocyclic ring, but that rupture may occur with about equal probability between the 1-2 or 2-3 positions, followed by hydrolysis and decarboxylation. The 1-2 break would lead to o-xylene, the 2-3 to ethylbenzene, which are formed in about equal amounts. These products can then undergo further sidechain shortening or elimination.

Quinoline, on the other hand, does not react as readily and although the heterocyclic ring appears to be the preferential point of attack, the rupture is more probably between the 1-2 position than the 1-9 position. This fragment would not hydrolyze, but would produce alkyl anilines which could then further react. It was found that tar formation is far more probable with this reactant. It is interesting to note that supercritical water has a profound effect on both the extent of reaction (100 vs. 26%) and reaction mechanism of even the hydrocarbon, tetralin. Further mechanistic speculation will be deferred until additional data is obtained.

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Table 1. Reaction of Water with Isoquinoline<sup>a</sup>

Temperature (C)	400				450				500			
	350	3640	3870	3870	3870	3870	3580	4680	4680 <sup>c</sup>	4680	5200	4700
Pressure (psi)	2400	3640	3870	3870	3870	3870	3580	4680	4680 <sup>c</sup>	4680	5200	4700
Density (g/cc)	0.255	0.170	0.213	0.213	0.213	0.213	0.106	0.170	0.170	0.170	0.213	0.128
Time (hour)	72	48	48	96	144	96	48	48	48	120	48	48
Catalyst	ZnCl <sub>2</sub>	-	ZnCl <sub>2</sub>	-	-	ZnCl <sub>2</sub>	-	-	Tet	DA	-	-
(g)	(.08)	-	(.05)	-	-	(.05)	-	-	(1.22)	(.50)	-	-
% Converted	34	18	54	30	50	57	50	42	93	58	81	70

Products (% of Converted Reactant)<sup>b</sup>

Benzene	0	0	0	0	0	0.4	1.0	0.7	3.9	0	3.9	3.0	4.3
Toluene	0	5.0	6.3	10.7	8.8	14.2	17.0	24.0	16.7	9.0	21.3	21.1	16.6
Ethylbenzene	0.6	6.7	7.4	13.3	15.2	16.6	10.5	16.9	20.2	13.6	11.4	9.9	6.4
ϕ-Xylene	2.1	6.1	7.2	13.0	14.0	13.8	6.2	13.8	6.3	8.4	7.2	7.4	6.7
Ammonia	-	-	-	-	-	-	-	-	-	63	-	-	74
Water Recovered	-	99	92	98	98	98	90	99	99	90	84	90	87
Char	0	0	10.5	6.2	12.6	12.7	30.6	12.6	10.7	18.8	15.7	10.0	15.1 <sup>d</sup>

- An experiment run at 450C for 48 hours with no water gave greater than 90% reactant recovered and no products by GC or char.
- Compounds are given as mole %, char as weight %. The remainder of the sample is tar and a few minor products - small peaks which appear to be aniline and toluidine were found but not measured.
- These experiments were with added tetralin and dihydroanthracene. The extents of reaction are believed reliable but product distribution more uncertain because of consumption of hydrogen transfer agents.
- Elemental analysis of this char gave the atom ratio C21.7 H9.3 N1.0 O0.6.

Table 2. Reaction of Water with Quinoline

Temperature (C)	400			450			500
	3870	4020	4660	4680	4680	5200	
Pressure (psi)	0.213	0.255	0.426	0.170	0.170	0.213	0.213
Density (g/cc)	48	48	48	48	48	48	48
Time (hour)	ZnCl <sub>2</sub>	AlCl <sub>3</sub>	ZnCl <sub>2</sub>	-	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>	ZnCl <sub>2</sub>
Catalyst	(.05)	(.05)	(.05)	(.10)	(.01)	(.05)	(.08)
% Converted	22	60	53	28	81	7	15
			27			67	54

Products (% of Converted Reactant)<sup>a</sup>

Benzene	0	0	0	0	0.7	0	0.7	0	0.6	0.2	3.9
Toluene	0.9	0	0	3.6	2.6	8.6	2.7	2.5	1.5	1.5	5.3
Ethylbenzene	2.7	0	0	1.8	1.0	8.6	4.0	1.2	1.5	1.5	1.9
o-xylene	2.7	0	0	0.4	0.5	4.3	4.7	0.9	0.9	0.9	0.2
Aniline	2.3	1.2	1.7	4.3	6.0	14.3	4.7	7.0	9.3	9.3	8.2
Toluidene	3.2	1.2	1.5	5.4	3.3	8.6	4.7	3.0	4.8	4.8	3.2
Ammonia	-	96	115.	-	-	-	-	-	-	-	-
Char	7.2	13.3	5.9	0	6.1	0	0	13.7	-	-	27b

(a) Compounds are given as mole %, char as weight %. The remainder of the sample is unidentified minor products or tar. Quinaldine was found but not measured.

(b) Elemental analysis of this char gave the atom ratio of C<sub>13</sub>.9H<sub>6</sub>.9N<sub>1</sub>.000.6.

Table 3. Reaction of Water with Other Compounds

Compound	Benzonitrile	Ethylbenzene	Tetralin <sup>b</sup>	DAC	Carbazole <sup>d</sup>	Aniline <sup>e</sup>
Temperature (C)	400	450	450	450	450	450
Pressure (psi)	3640	5200	5200	5200	5200	5200
Density (g/cc)	0.170	0.213	0.213	0.213	0.213	0.213
Time (hour)	24	48	48	48	48	48
Catalyst	-	-	ZnCl <sub>2</sub>	-	ZnCl <sub>2</sub>	-
(g)	-	-	(.05)	-	(.05)	-
% Reacted	100	10	100	>50	<15	21
						74

  

Products <sup>a</sup>	Benzene	Toluene	Ethylbenzene	Naphthalene	Anthracene	Diphenylamine	Ammonia
Benzene	95	22	1.5	1.5	0	0	5
Toluene	-	78	10	7.0	0	0	0
Ethylbenzene	-	-	13	8.9	0	0	0
Naphthalene	-	-	52	45	0	0	0
Anthracene	-	-	-	-	∞	0	0
Diphenylamine	-	-	-	-	-	-	∞
Ammonia	-	-	-	-	-	-	66
							59

- Mole % of consumed reactant. No char found for any reactant.
- Two other chromatographic peaks with retention times consistent with indan and methylindan were found but calibrations have not been made for these yet. The largest after that of naphthalene was the indan peak.
- The dihydroanthracene chromatogram showed about six products, all having longer retention times than naphthalene but shorter than anthracene which was by far the largest, another was benzophenone but the others have not been identified as yet.
- Carbazole appeared close to zero % reacted.
- Due to chromatogram anomalies, the extents of these reactions are more uncertain. The only significant organic products in the chromatograms are the two reported in relatively small and large amounts. The s and ∞ indicate small and large product peaks respectively.