

## THE FORMATION OF HYDANTOINS IN GASIFIER CONDENSATE WATER

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A number of 5,5-diakyl and 5-alkylhydantoin have been detected in the condensate water from the gasification of Indian Head (ND) lignite in the UNDERC slagging fixed bed gasifier (1, 2). These compounds were characterized by extensive GCMS studies (3) and quantitatively analyzed in samples of process water resulting from various stages in a pilot scale gasifier water treatment plant at UNDERC (4, 5). 5,5-Dimethylhydantoin and 5-ethyl-5-methylhydantoin constitute the major portion of the organic compounds remaining in the condensate water after extraction with diisopropyl ether and steam stripping (5). Because of their biological activity, they represent a potential health hazard in the effluents from a commercial gasifier. Although hydantoin can be adsorbed on activated carbon (3) and degraded by a bacterial nitrification system (6), the expense of removal from the water justifies an effort to gain a better understanding of the formation of hydantoin in the condensate water with the goal of predicting the extent to which the reaction will occur under various conditions.

The hydantoin does not form directly in the gasifier. They were shown to be either absent or present in low concentrations in water samples which were collected from a side stream sampler on the UNDERC gasifier and quickly frozen. When this side stream condensed water was heated in a constant temperature bath at 40°C, hydantoin concentrations increased in an approximately second-order manner. The formation is believed to proceed by the Bucherer-Berg reaction, the same reaction used in commercial hydantoin synthesis, from ammonia, carbonate, hydrogen cyanide and various ketones and aldehydes at a pH of 8.5.

A kinetic study was undertaken to obtain useful rate data for this reaction (7). Reliable and reproducible concentration data for acetone and cyanide were impossible to obtain for the raw gasifier condensate water because of the presence of reversible addition products of cyanide such as acetone cyanohydrin and 2-amino-2-methylpropanonitrile as well as large amounts of sulfide. Thus a model system was investigated where acetone cyanohydrin was reacted with excess ammonium carbonate at concentrations approaching those obtained in the condensate water, 0.020M and 0.25M, respectively. The reaction was studied at 50°, 70°, and 90°C using a capillary GC (OV351 phase) for the analysis of 5,5-dimethylhydantoin (DMH) using 4-methoxyphenol as the internal standard (4).

Linear second order plots were obtained for this reaction at the three temperatures. Table I gives the calculated pseudo second-order rate constants and linear regression fit.

Table I. Pseudo Second-Order Rate Constants and Least Squares Fit at Various Temperatures.

t(°C)	50	70	90
$k_2'$ & mole <sup>-1</sup> hr <sup>-1</sup>	1.86	3.60	4.62
r <sup>2</sup>	0.999	0.998	0.997

The initial concentrations of acetone and cyanide were varied in order to determine their effect on the rate of formation of DMH. When the acetone concentration was doubled, keeping the original cyanide, ammonia, and carbonate concentrations constant, the rate of the reaction doubled at 90°C. A decrease in cyanide concentration to one-half of its original value decreased the rate by one-half. Table II gives the values of the initial rates of formation of DMH at 90°C varying acetone and cyanide concentrations.

Table II. Initial Rate of DMH Formation at Varying Acetone and Cyanide Concentrations. Ammonia and Carbonate Concentrations Were Held Constant at 0.50M and 0.25M, Respectively.

<u>Initial Rate</u> (mmoles $\text{g}^{-1}\text{hr}^{-1}$ )	<u>Acetone</u> <u>Concentration (M)</u>	<u>Cyanide</u> <u>Concentration (M)</u>
123	0.02	0.02
220	0.04	0.02
60	0.02	0.01

In order to verify that the rate also depends on the concentrations of ammonia and carbonate, which were present in large excess in these experiments, the 90°C experiment was repeated using 0.02M acetone cyanohydrin and changing the concentration of ammonium carbonate to 0.20M. The expected pseudo second order behavior was again exhibited ( $r^2 = 0.998$ ) and the observed rate constant was 2.8 liters mole<sup>-1</sup>hr<sup>-1</sup>. The value expected for 0.8 times the concentration of ammonia and carbonate is 2.9 liters mole<sup>-1</sup>hr<sup>-1</sup>.

This established that the rate of formation of DMH was first order in all of the reactants as expressed by the following equation:

$$\text{Rate of formation of DMH} = k [\text{Acetone}] [\text{HCN}] [\text{NH}_3] [\text{CO}_2]$$

This kinetic data is valuable in predicting the rate of formation of DMH in coal gasification condensate water, provided the model is applicable. The pH of the model solution and the condensate water remained constant at around 8.4, but the effects of small changes in pH on the rate are not fully known.

In the earlier experiment with sidestream condensate water, it was noted that the concentration of acetone decreased by one-half at the endpoint when the hydantoin concentration no longer increased. This implies that the limiting species for formation of hydantoin in the UNDER gasifier water is cyanide. The hydrogen cyanide peak in the GC analysis had also disappeared. When condensate water was analyzed from initial runs of the Great Plains Gasification Plant which uses coal of the same Beulah-Zap seam as Indian Head coal, negligible hydantoin and HCN were found.

Similarly when Indian Head lignite was used in the METC gasifier, the condensate water contained negligible hydantoin and HCN. In both cases acetone and 2-butanone concentrations were significant.

Data on actual HCN concentrations in the raw gas and quenched gas are not available for these gasifiers. A thorough study was reported by Anastasia on the HYGAS gasifier using Illinois No. 6 coal (8). Although 10% of the nitrogen in the coal was converted to HCN, only 1% of the total HCN entered the condensate water. Most of the HCN (80%) remained in the gas phase (quenched gas) and the

rest dissolved in the oil-tar phase. We expect that significant amounts of HCN are also produced in the gasification of lignite and the factors which determine how much of the HCN ends up in the condensate water are of importance.

One major factor for determining the cyanide concentration in the condensate water is how long the aqueous phase is in contact with the gas phase and oil-tar phase. Diffusion of the HCN at the interface of the aqueous phase with the gas and oil phases and subsequent reaction with acetone and acetone imine over a long period of time will build up the concentration of cyanide addition products which reversibly interconvert and eventually proceed to hydantoin. The residence times for water in the UNDERC spray washer (quench water system) and tar-oil-water separator are several hours which can allow for considerable diffusion buildup of the cyanide conjugates which form significant amounts of hydantoin.

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