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INTRODUCTION

When the product gases from a coal gasification reactor are cooled, the excess steam condenses and forms a condensate water. This stream is highly buffered with ammonia and carbon dioxide to a pH of about 8.5 and contains many organic compounds. A commercial scale Lurgi gasification plant with a capacity of 3×10^5 standard m^3/h would produce an estimated 5×10^5 kg/h of condensate water (1). The management of this water is important for both environmental and economic reasons (2). Release of potential pollutants must be controlled, and reuse of the water is important because many coal deposits are located in arid regions. In this work chemical analyses and experimental tests of extraction solvents are discussed for condensate waters from a coal gasification pilot plant.

COMPOSITION OF CONDENSATE WATERS

Condensate water samples were obtained from a slagging fixed-bed gasifier which was operated by the U.S. Dept. of Energy at the Grand Forks Energy Technology Center (GFETC) in Grand Forks ND, U.S.A. The samples were protected from oxidation and were analyzed as rapidly as possible. Reversed-phase, gradient-elution, high performance liquid chromatography (HPLC) with variable-wavelength UV absorbance detection was employed to resolve and detect the compounds in the condensate water.

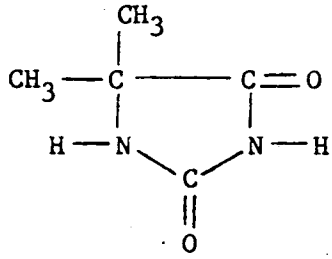
The identities of the compounds eluted from the HPLC were determined by either or both HPLC co-chromatography and gas chromatography-mass spectrometry (GC-MS). For GC-MS analysis, individual fractions were collected as they eluted from the HPLC. A batch azeotropic distillation with isopropanol concentrated the solute and removed water from the sample (3). Then the sample was analyzed by GC-MS (Finnigan model 4000), and the spectrum of an unknown solute was compared to a computerized library of known spectra. The advantage of this novel sample preparation technique is that it recovers very polar compounds which are not recovered by the methylene chloride extraction step in the standard GC-MS analytical technique (denoted MC/GC-MS). However,

these compounds must be less volatile than isopropanol.

Table 1 shows the analysis of one GFETC condensate water. The compounds are arranged in three groups. The first group is the hydroxybenzenes or simple phenols. These compounds are moderately polar and are easily detected by the standard MC/GC-MS technique. However, the precision of ±5% in Table 1 is an improvement over the MC/GC-MS technique because there are no losses associated with a preliminary solvent extraction step.

The second group of compounds is the dihydroxybenzenes which are more polar and much less volatile than phenol. It is important to have precise quantitative information about these compounds because they have lower distribution coefficients into many solvents (4). Since they are more difficult to extract, they have much lower recoveries in the standard MC/GC-MS technique.

The third group of compounds is the hydantoins. The major component is 5,5-dimethyl hydantoin:



The identification of this compound was confirmed by both co-chromatography and the isopropanol/GC-MS technique. This was the first report of hydantoins in condensate waters. These compounds are still more polar than dihydroxybenzenes. Hydantoins have very low distribution coefficients into methylene chloride, and therefore should be difficult or impossible to detect by the standard MC/GC-MS analytical technique.

Table 2 shows the analyses of four GFETC condensate water samples. Concentrations, expressed as fractions of the chemical oxygen demand (COD), are reported for the three groups of compounds described in Table 1. The results in Table 2 show significant differences in the proportion of simple phenols to COD for the four samples. There are also large differences in the proportions of dihydroxybenzenes and hydantoins to COD or simple phenols. Some increase in the concentration of dimethylhydantoin was observed as the samples aged, but this was not large enough to explain the composition differences among the samples (3). Samples were stored at 4°C in the dark. The sample-to-sample variability in Table 2 is probably due to changes in operating conditions for the gasifier despite the fact that the feed coal, steam/oxygen ratio, operating pressure, and oxygen rate were nearly constant. Changes in condensate-water composition introduce a large uncertainty into any general conclusions drawn from laboratory tests of a small number of condensate-water samples.

Finally, 23 to 31% of the COD remains unidentified in these four samples. Most analyses of condensate waters using the MC/GC-MS technique fail to identify an even greater fraction of the COD--see, e.g., (3).

SOLVENT EXTRACTION OF CONDENSATE WATERS

Distribution Coefficients: Table 3 shows the distribution coefficients of phenol and the three dihydroxybenzenes into three solvents. Diisopropyl ether (DIPE) and methyl isobutyl ketone (MIBK) have been proposed as solvents for commercial-scale treatment of condensate waters (4). Comparison of K_D values for these two solvents shows that MIBK has a significant advantage over DIPE, particularly for the dihydroxybenzenes. The third solvent in Table 3 is a mixture of 25% w/w trioctyl phosphine oxide in diisobutyl ketone (TOPO/DIBK). TOPO is non-volatile and as an extractant is a strong Lewis base. This solvent mixture provides very high K_D values, even for the dihydroxybenzenes.

Dimethyl hydantoin is a very polar compound and is therefore difficult to extract from water. Tributyl phosphate (TBP) gives the highest value of K_D among the solvents listed in Table 4. Several of these solvents exhibit very low K_D values for this compound, including methylene chloride which is used in the MC/GC-MS analytical technique.

Removal of Chemical Oxygen Demand by Solvent Extraction: In Table 5 a condensate water sample from GFETC run No. 120 was contacted in batch equilibrations with several solvents at solvent-to-water ratios of 1:1 by volume. The COD of the raffinate was measured after residual dissolved solvent had been removed. MIBK was removed from the raffinates by stripping with 1.5 mole N_2/mole H_2O at 25 °C. The MIBK was purified before extraction by washing with 0.1 N NaOH and 0.1 N H_2SO_4 to remove impurities which would otherwise contribute to the COD.

A single extraction with MIBK removed nearly 90% of the COD and essentially all of the phenols and dihydroxybenzenes. A second extraction removed only a small increment of the remaining COD, indicating that most of the residual components have low values of K_D into MIBK. Lowering the pH of the condensate water from 8.5 to 3 did not significantly increase the removal of COD by MIBK. This indicates that ionizing weak acids do not compose a

substantial fraction of the residual COD. As the age of the sample increased, MIBK extraction removed less of the COD; however, concentrations of all of the compounds identified in Table 2 remained essentially constant over this time interval. This indicates the importance of conducting experimental tests of treatment processes on fresh condensate water samples.

As is also shown in Table 5, TBP removed a slightly greater fraction of the COD than did MIBK. The TOPO/MIBK mixture removed about the same fraction as did MIBK alone.

Table 6 shows the removal of COD and organic nitrogen from the same condensate water at a sample age of 190 days. Organic nitrogen is defined as the difference between Kjeldahl and ammonia nitrogen, both of which were measured after nitrogen stripping to remove most of the NH_3 (3). Comparison of the fourth and fifth extractions shows that 10% of the COD in this mixture has a vanishingly small K_D into MIBK. Also, the organic nitrogen has a low value of K_D into MIBK. Since the ratio of COD to organic N can be as high as 20 for a typical nitrogen-containing compound, these compounds could account for most of the unextracted COD. Since no increase in removal of the nitrogen compounds was observed at high pH with MIBK or with a Lewis-acid solvent (methylene chloride), these compounds are not simple organic bases. Other experiments with an MIBK raffinate showed that about half of the remaining COD was more volatile than water, all of the remaining nitrogen was non-volatile with respect to water, and all of the remaining COD had a molecular weight of less than 1000 as determined by ultrafiltration.

Capabilities of Solvent Extraction: There are two important questions in the design of a condensate water solvent extraction process. The first is whether a given solvent can remove enough of the organic solutes under any conditions to meet the treatment requirements. The second consideration is the reliability and economics of a particular process.

The data discussed above raise serious questions about the ability of current solvent extraction technology to remove organics from condensate waters to an acceptable level without further treatment. The COD of these condensate waters is so high that a 90% removal still leaves a highly contaminated raffinate. Some level of organics may be acceptable in a cooling-tower make-up stream, provided that the compounds are not volatile and do not excessively foul the heat exchange surfaces through biological growth. Then a small volume of cooling-tower blowdown could be treated by other techniques.

If the residual polar and hydrophilic compounds could be identified, then it might be possible to select chemically specific solvents to remove these compounds.

A number of additional factors are important in the selection of an economically viable solvent. A volatile solvent such as DIPE or MIBK must be regenerated as a distillate, and this requires a large amount of heat to vaporize the solvent. For a non-volatile solvent, such as TBP or TOPO in a non-volatile diluent, all of the solutes must be taken overhead. In a complex mixture such as these condensate waters, it is likely that non-volatile solutes would accumulate and possibly degrade the performance of the solvent. Acidic solutes could be removed from a solvent by extraction with aqueous base, but this could require an expensive consumption of chemicals. TOPO in an appropriate diluent provides high values of K_D for phenols and dihydroxybenzenes. This allows a low solvent flow rate, and therefore a regeneration process which is expensive per unit of solvent treated may still

be economically reasonable per unit of treated water.

A second factor which is important in the economics of a solvent extraction process is the amount of solvent which is lost in the raffinate. DIPE and MIBK are volatile solvents which can be removed to low levels by stripping the raffinate. Vacuum steam stripping is particularly attractive for removal of MIBK (4). Less polar solvents such as TOPO in isobutyl heptyl ketone have a sufficiently low equilibrium solubility in water that a solvent-recovery process may not be necessary. However, it is still necessary to account for losses by emulsification, micellarization, complexation into water-soluble forms, and losses due to irregular operation of the process, particulary for the more expensive solvents.

CONCLUSIONS

MIBK provides much higher distribution coefficients than DIPE for phenol and dihydroxybenzenes. About 90% of the COD from one condensate water sample had a sufficiently high K_D into MIBK that it could be removed by this solvent in a counter-current extraction process at an economically reasonable solvent-to-water ratio. TOPO in a suitable diluent has high equilibrium distribution coefficients for phenols and dihydroxybenzenes, and therefore has the potential to remove these compounds at lower solvent-to-water ratios. However, this solvent may be difficult to regenerate in a continuous condensate-water extraction process.

Analytical techniques were discussed that provide higher recoveries for phenols and dihydroxybenzenes as compared to the standard MC/GC-MS technique. Hydantoins have been identified in four condensate water samples. About 20-30% of the COD remains unidentified in these four condensate water samples. Some of these unidentified compounds have very low values of K_D for extraction into MIBK. More information is required about these unidentified solutes before reliable solvent extraction processes can be designed.

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Table 1: Analysis of Condensate Water #RA-78 from the GFETC Slagging Fixed-Bed Gasifier

Compound	Conc. (mg/l)
Hydroxybenzenes:	
1. phenol	4,750
2. C_1-phenols	2,855
3. C_2-phenols*	450
4. o-methoxy phenol*	260
5. p-hydroxy acetophenone*	50
Dihydroxybenzenes:	
6. catechol	990
7. 4-methyl catechol	615
8. resorcinol	60
9. hydroquinone	35
Hydantoins:	
10. 5,5-dimethyl hydantoin	1,725
11. 5-methyl hydantoic acid	95
12. 5-methyl hydantoin	135

* These compounds were identified by the isopropanol/GC-MS technique. All of the compounds were identified by HPLC co-chromatography.

Table 2: Analyses of GFETC Condensate Waters Expressed as a Fraction of the COD

GFETC Run No.:	RA-78	RA-97	RA-106	RA-120
Hydroxybenzenes:	0.586	0.642	0.663	0.764
Dihydroxybenzenes:	0.095	0.059	0.006	0.0002
Hydantoins:	0.082	0.014	0.019	0.007
Total Fraction of COD Identified:	0.763	0.697	0.688	0.771
COD (mg/l):	34,870	46,670	22,920	23,390

Table 3: Distribution Coefficients (K_D) of Phenol and Dihydroxybenzenes

Solvent:	DIPE	MIBK	TOPO/DIBK*
Reference:	(4)	(4)	(5)
Phenol	36.5	100.	462.
Catechol	4.86	18.7	203.
Resorcinol	2.06	17.9	98.
Hydroquinone	1.03	9.9	35.

Solvents: DIPE: diisopropyl ether, MIBK: methyl isobutyl ketone, TOPO/DIBK: 25% w/w trioctyl phosphine oxide in diisobutyl ketone.

* The values reported here are for 2.5 moles TOPO/mole solute in the combined organic and aqueous phases. The value of K_D depends on this ratio (5).

Table 4: Equilibrium Distribution Coefficients for Dimethyl Hydantoin

Solvent	K_D
Methylene chloride	<0.05
Methyl isobutyl ketone (MIBK)	0.25
25% w/w trioctyl phosphine oxide in MIBK	1.2
25% w/w Adogen 363 (R_3N, Sherex Chemical Co.) in kerosene	<0.05
25% w/w di(2-ethyl hexyl) phosphoric acid in kerosene	<0.05
Tricresyl phosphate (TCP)	0.11
Tributyl phosphate (TBP)	2.6

Table 5: Fraction of COD Removed by Solvent Extraction from GFETC Run No. 120

Solvent	Number of Successive Batch Extractions	Sample Age (Days) 0.7	15	190
MIBK	1	0.897	0.883	0.856
MIBK	2	0.927	0.911	0.878
MIBK	1 and 1 @ pH 3	0.923	0.913	-
TBP	1	-	0.915	-
TBP	2	-	0.938	-
TBP	1 and 1 @ pH 3	-	0.945	-
25% w/w TOPO in MIBK	1	-	0.88	-
Same	1 and 1 @ pH 3	-	0.92	-

Table 6: Fraction of COD and Organic Nitrogen Removed by Extraction with MIBK. GFETC Run No. 120

COD = 23,390 mg/l
Organic Nitrogen = 220 mg/l

No. of MIBK Extractions	Fraction of COD Removed (±0.005)	Fraction of Organic N Removed (±0.10)
1	0.856	0.28
2	0.878	0.28
3	0.890	0.35
4	0.900	0.35
5	0.902	0.41
1 and 1 @ pH 12	0.878	0.23
1 and 1 with CH_2Cl_2 @ pH 12	0.880	0.10

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