



Project Summary

Steam Stripping of Fixed-Bed Gasification Wastewaters

F. D. Skinner and B. J. Hayes

Laboratory- and bench-scale steam stripping tests were conducted using gas liquor from a fixed-bed coal gasifier at the Department of Energy's Morgantown Energy Technology Center. The gas liquor was pretreated by solvent extraction (for phenol removal) and filtered prior to stripping. This report presents the results of the wastewater stripping tests and provides engineering and environmental data for the design of steam strippers for fixed-bed gasification wastewaters. The laboratory tests were performed primarily to determine the effect of pH on contaminant removals. During the bench-scale tests, samples of influent, effluent, and overhead vapor and condensate were analyzed for a number of species of potential environmental concern (dissolved gases, sulfur and nitrogen species, trace metals, organics, and other water quality parameters). Mass transfer coefficients for ammonia, carbon dioxide, and hydrogen sulfide stripping were calculated.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The raw gas liquor resulting from fixed-bed coal gasification processes contains a number of contaminants, some of which are present in relatively high concentrations. These include tars and oils, dissolved organic (especially phenols), dissolved gases (e.g., NH_3 , HCN , H_2S , CO_2), and both suspended

and dissolved inorganics. Removal of these contaminants in a multiple step wastewater treatment system has been included in many proposed commercial coal gasification plant designs.

Steam stripping for the removal (and, in some cases, recovery) of dissolved ammonia and acid gases is a treatment process which is common to most of these designs. Capital and operating costs for steam stripping systems can account for a significant portion of the overall cost of wastewater treatment in coal gasification plants. There is a need, therefore, to develop design data that can be used to maximize the cost effectiveness of this process. In addition, the outlet streams need to be characterized to evaluate the effects of contaminants on downstream process performance.

This report presents the results of laboratory- and bench-scale stripping work, using wastewater obtained from a fixed-bed gasifier at the Department of Energy's Morgantown Energy Technology Center (DOE-METC).

Objectives and Approach

The principal objectives of the wastewater stripping study were:

- To provide data characterizing the various stripper outlet streams for species of environmental interest with respect to potential impacts on downstream process performance and environmental effects.
- To develop mass transfer data that could be used in the design of a steam stripper for wastewater from fixed-bed gasifiers following pretreatment by solvent extraction, filtration, and pH adjustment (if needed).

To meet these objectives, two series of tests were performed. First laboratory-scale screening tests were conducted to determine the effect of wastewater pH on the removal of dissolved ammonia, H₂S, CO₂, HCN, and the residual phenol remaining after pretreatment by solvent extraction using methyl isobutyl ketone (MIBK). These tests were conducted by heating a measured quantity of pH-adjusted wastewater to 95-100°C in a distillation flask. Gas (air or nitrogen) was sparged through the contents of the flask, and the ammonia concentration and pH of the wastewater were measured over a 270-minute period. After each run the contents of the flask were analyzed for pH, conductivity, total alkalinity, ammonia, cyanide (free and total), phenol, sulfide, sulfite, sulfate, and thiocyanate.

The results of the laboratory tests were used to determine the influent pH for the second series of tests, performed using a bench-scale steam stripping apparatus. The stripper was a 0.1 m (4 in.) diameter stainless steel column packed with 1.2 m (4 ft) of 0.6 mm (1/4-in.) ceramic Intalox saddles. Solvent-extracted wastewater was preheated to 90°C in an electric heater and pumped into the top of the column. Stripping steam entered below the packing and flowed countercurrent to the wastewater. Concentric tube heat exchangers were used to condense and cool the overhead vapor and to cool the stripped effluent. Samples were obtained periodically during each run of the various inlet and outlet streams for analysis of the environmental and performance parameters of interest. The principal independent variable during these tests was the steam to wastewater influent flow ratio.

Results and Conclusions

Laboratory-Scale Results

- Greater than 90% removals of dissolved ammonia and alkalinity (due to dissolved CO₂) were obtained by stripping the extracted METC wastewater at a pH of 8.6 (existing after solvent extraction) and higher. Ammonia removal increased from about 92% to over 99.9% as the initial wastewater pH was raised from 8.6 to 11.0. A decrease in CO₂ removal efficiency from over 99 to 96% was observed when increasing pH from 8.6 to 11.0.
- Dissolved H₂O removals decreased from 80 to 50% as the initial pH was

increased from 8.6 to 11.0. Cyanide removals were between 10 and 20%; most of the cyanide content of this wastewater was present as fixed (and therefore non-strippable) cyanide at the pHs evaluated. It is likely that some of the free cyanide initially in the wastewater had been converted to fixed cyanide and/or thiocyanate, and the removal may be higher for "fresh" wastewater.

- Removal of the small amount of phenol (total) remaining in the extracted wastewater was found to be less than 20%. No clear trends were observed as the pH was increased. Technical questions remain regarding phenol stripping for unextracted wastewater or wastewater having phenol levels closer to those expected from commercial gasifier systems.
- Because of its buffering capacity (due to HCO₃/CO₃ alkalinity), the wastewater required a significant quantity of lime to raise its pH from 8.6 to 11.0. In order to go from pH 8.6 to 9.5, 470 milliequivalents (meq) of lime per liter was required; to go from pH 8.5 to 11, nearly 1200 meq of lime per liter was needed. The buffering capacity of the wastewater is readily reduced by steam stripping of the dissolved CO₂.
- Two-stage stripping would likely be required to remove all (or nearly all) of the dissolved ammonia and acid gas species (especially H₂S and HCN) from this wastewater.
- Stripping the wastewater at a pH of 8.6 produced significant quantities of solids that collected on the surfaces of the equipment and led to plugging problems. Increasing the pH to 9.5 or higher by lime addition significantly reduced the plugging. The solids are likely ammonium salts, possibly ammonium carbonate or ammonium carbamate; however, the solids were not analyzed.

Bench-Scale Tests: Environmental

- Thiocyanate, sulfate, fluoride, and chloride are not removed by steam stripping. These contaminants will be found in the stripper effluent stream.
- Trace elements detected in stripper outlet streams appear to be largely system contaminants, possibly from the column, ceramic packing, and the lime added for pH adjust-

ment. It appears that some of the volatile trace elements (e.g., arsenic, selenium, and antimony) are stripped to some extent. This has implications for the potential environmental impacts of the stripper overheads and effluent streams. For example, it may be possible to reduce the amounts of some toxic trace elements that might otherwise concentrate in brines produced by downstream evaporators; however, this potential was not investigated.

- Phenols were the major organic species found in the wastewater. 2, 4-dimethyl phenol was largely stripped and was found principally in the overhead condensate. Other phenols (e.g., phenol, cresol, and other xylenols) were only partially stripped and are found in both the effluent and overhead condensate.
- Hydrocarbon analyses of the overhead vapor were hampered by the relatively high concentration of residual methyl isobutyl ketone (MIBK) from the solvent extraction process. Toluene and xylene were not detected in any of the samples, and benzene was detected (at 1.1 ppmv) in only one set of the samples collected on charcoal. The residual solubility of MIBK in water is significant (reportedly about 2% by weight). Some other organics may be present in the MIBK layer produced as a result of condensing the stripper overhead stream. The solvent layer was not analyzed in this work.
- The presence of significant quantities of solvent vapor in the stripper overhead vapor stream has potential impacts on the downstream processes that may be used to remove H₂S and other acid gas species from this stream. The residual solvent concentration after extraction/inert gas stripping seen in this study is probably not representative of commercial operations. In a commercial extraction system, solvent recovery would be more efficient, not only to reduce the possibility of problems with downstream processes, but also to reduce solvent makeup requirements. However, more efficient solvent stripping would likely produce additional streams containing species stripped from the raffinate (including ammonia and hydrogen sulfide).
- Carbonyl sulfide was detected in all

Table 1. Component Removal Summary for Bench-Scale Stripping Tests^a

Run Date	Steam/Influent kg/m ³	Influent pH	% Removal				
			NH ³	CO ₂	Sulfide	Total Cyanide	Total Phenols
9/25	133 ± 7	9.03 ± 0.05	83.6 ± 3.8	93.3 ± 0.5	30.9 ± 17.9	18.9 ± 4.2	-5.2 ± 5.4
9/27	298 ± 31	9.02 ± 0.15	94.3 ± 1.5	98.3 ± 0.6	17.7 ± 38.7	23.8 ± 13.6	44.9 ± 9.7
11/1	282 ± 44	9.14 ± 0.03	91.6 ± 4.5	98.6 ± 0.2	65.1 ± 9.1	59.7 ± 3.5	-72.8 ± 28.6
11/2	459 ± 49	9.17 ± 0.06	95.0 ± 1.7	99.0 ± 0.1	69.4 ± 16.6	16.6 ± 41.1	4.2 ± 31.8
11/5 ^b	297 ± 34	8.45 ± 0.04	31.0 ± 25.6	81.6 ± 5.1	-7.6 ± 51.8	23.7 ± 21.0	46.7 ± 12.4

^aValues shown are mean ± sample standard deviation. All runs performed using 1.2 m (4 ft) of packing.

^b11/5 run performed using effluent collected from previous stripping runs at similar steam/influent ratios.

overhead vapor samples at concentrations of about 0.04 ppmv in the two-pass stripper run and from 1 to 5 ppmv in the single-pass runs. Carbon disulfide was the only other sulfur species detected (1 to 32 ppmv).

Bench-Scale Tests: Performance

- Contaminant removals consistent with the results of the laboratory-scale tests were found for ammonia, CO₂, and H₂S. Data scatter precluded the development of meaningful correlations for HCN and phenol (total) removal as a function of the steam to influent ratio. The component removals are summarized in Table 1.
- Contaminant removals were found to increase with increasing steam to wastewater ratio up to 250-300 kg steam/m³ wastewater. Higher ratios produced no statistically significant improvement in contaminant removals. There would appear to be little incentive to operate at a steam to wastewater ratio higher than about 250 kg/m³.
- Overall volumetric mass transfer coefficients (K_La) were calculated for steam stripping of NH₃, CO₂, and H₂S for the wastewater. For ammonia, K_La increased from 1.8 to 6.6 hr⁻¹ as the liquid mass velocity increased from about 550 to 2000 kg/m²hr. Over this same range K_La for CO₂ increased from 2.2 to 4.5 hr⁻¹. K_La for H₂S was found to be approximately constant at 0.6 hr⁻¹ over this range of liquid flow rates.

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William J. Rhodes is the EPA Project Officer (see below).

The complete report, entitled "Steam Stripping of Fixed-Bed Gasification Wastewaters," (Order No. PB 85-247 450; Cost: \$16.95, subject to change) will be available only from:

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