United States
Environmental Protection
Agency
Research and Development

Air and Energy Engineering
Research Laboratory
Research Triangle Park NC 27711
EPA/600/S7-87/017 Aug. 1987

Project Summary

Regeneration of Refrigerated Methanol in Conditioning Gases from Coal

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The report gives results of an examination of various methods of solvent regeneration in an acid gas removal system (AGRS) coupled to a fluidized-bed coal gasifier. (Earlier research on acid gas removal using refrigerated methanol had shown that, when a high purity gas is desired as a product gas, the most critical step in the process is solvent regeneration.) The composition of the absorber exit gas stream (the sweet gas) obtained from each system configuration studied was used as a basis for comparing the various schemes.

For the systems studied, the ability of the acid gas removal system to produce a conditioned gas with low levels of H_2S and CO_2 was found to be governed primarily by the purity of the solvent entering the absorber, and thus by regeneration conditions. These results are believed to be general for refrigerated methanol systems and, together with mathematical models developed as a part of the project, can provide a basis for selecting an optimum configuration for an acid gas removal system. The fate of the various trace compounds produced in the gasifier was determined, and a design method for predicting the exit stream in which these compounds leave the AGRS was proposed.

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

Research on acid gas removal using refrigerated methanol carried out at North Carolina State University has shown that, when a high purity gas is desired as a product gas, the most critical step in the process is solvent regeneration. This research examined various methods of solvent regeneration in an acid gas removal system (AGRS) coupled to a fluidized-bed coal gasifier. The composition of the absorber exit gas stream (the sweet gas) obtained from each system configuration studied was used as a basis for comparing the various schemes.

Under conditions used in these studies, it was found that the absorption of acid gases in the AGRS was governed primarily by how well the solvent entering the absorber was stripped of dissolved gases. It is likely that solvent regeneration plays such a role in any acid gas removal system, especially one using a physical solvent and where the absorber packing height or number of stages is sufficient to cause the exit gas from the absorber to be near equilibrium with the entering solvent.

Objectives

As a consequence of this observation, a major objective of the research reported here was to evaluate various schemes for solvent regeneration. In particular, the AGRS was operated with and without multiple flash tanks between the absorber and stripper, and with stripping by nitrogen or heat supplied in a reboiler at the base of the stripper. The study was conducted using Texas lignite as the gasifier feed, and refrigerated methyl alcohol in the acid gas removal system.

The data were used to evaluate the effect of system configuration on the quality of the conditioned gas leaving the absorber of the AGRS.

Also examined was the effect of adding water to the methyl alcohol solvent. Operation with small amounts of water in the solvent is important since it can accumulate in the solvent in an industrial operation. The solubilities of the acid gases in water are much less than in methyl alcohol, and thus the presence of water could have a major effect on AGRS operation.

Results

Although a conditioned gas containing less than 1.5 mole % CO_2 and less than 5 ppm carbonyl sulfide (COS), was produced at all operating conditions and with all regeneration configurations used in this study, the concentration of H_2S in the product gas stream varied significantly. Specifically, a product gas essentially free of H_2S was obtained only with the use of high temperature regeneration (use of the reboiler methanol in the stripper), or a very high flow of N_2 stripping gas. The major results of the study are summarized in Table 1.

The experimental results of this study provided information on the relationship between absorber operation and regeneration. For all of the work reported here, the height of packing in the absorber was sufficient to bring the absorber exit gas nearly to equilibrium with the entering solvent. Absorption was thus controlled by equilibrium between the gas and liquid phases in the column rather than by mass transfer. The experimental results may be generalized by an understanding of the operation of an absorber under these conditions. Most industrial absorption and stripping columns operate in this mode as a result of the practice of oversizing packing heights in design.

Graphical methods are a convenient tool for understanding the mass balance relationships and equilibrium constraints in absorption and stripping operations. Consider the equilibrium and operating lines given in Figure 1 for absorption with a physical solvent. The operating line represents conditions as they actually exist in the column, while the equilibrium line represents conditions at equilibrium between the solvent and the gas. The slope of the operating line is directly related to the liquid-to-gas ratio, while the slope of the equilibrium line is the ratio of the Henry's Law constant to the column pressure. The separation between the two lines represents the driving force

Table 1. *Acid Gas Removal Summary*

		Composition, mole %					
		Absorber Feed Gas Sour Gas			*Absorber Exit Gas Sweet Gas*		
Run No. AMIL-	*Regeneration Scheme*	*CO_2*	*H_2S*	*COS*	*CO_2*	*H_2S*	*COS*
1	*1 flash tank and strp N_2 flow 0.03 scm/min strp liq temp 20.7°C solvent rate 4.8 L/min (standard conditions)*	*27.73*	*0.243*	*0.0058*	*N.D.**	*0.0048*	*N.D.*
2	*1 flash tank and strp N_2 flow 0.03 scm/min strp liq temp 26.6°C solvent rate 4.8 L/min*	*25.47*	*0.258*	*0.0078*	*N.D.*	*0.0024*	*N.D.*
3	*1 flash tank and strp N_2 flow 0.06 scm/min strp liq temp 31.9°C solvent rate 4.8 L/min*	*27.51*	*0.304*	*0.0039*	*N.D.*	*0.0016*	*N.D.*
7	*1 flash tank and strp N_2 flow 0.06 scm/min strp liq temp 31.9°C solvent rate 3.3 L/min*	*28.67*	*0.214*	*0.0029*	*N.D.*	*N.D.*	*N.D.*
11	*2 flash tanks and strp N_2 flow 0.03 scm/min flash 2 liq temp 27.5°C strp liq temp 23.7°C*	*26.46*	*0.152*	*0.0038*	*N.D.*	*0.0016*	*N.D.*
14	*1 flash tank and strp reboiler steam 7.7 kg/hr strp temp 70°C*	*27.38*	*0.258*	*0.0034*	*N.D.*	*N.D.*	*N.D.*
16	*3 flash tanks, no strp flash 2 liq temp 24.9°C flash 3 liq temp 17.8°C*	*27.10*	*0.247*	*0.0041*	*0.63*	*0.0029*	*N.D.*
19	*3 flash tanks, no strp flash 2 liq temp -10.9°C flash 3 liq temp -1.60°C*	*25.56*	*0.179*	*0.0025*	*1.08*	*0.0026*	*N.D.*
21	*same as AMIL-2, 10% water, 90% methanol*	*25.4*	*0.234*	*0.0051*	*N.D.*	*0.0029*	*N.D.*

**N.D. (none detected) <0.5% for CO_2, <5 ppm (0.0005%) for H_2S and COS*

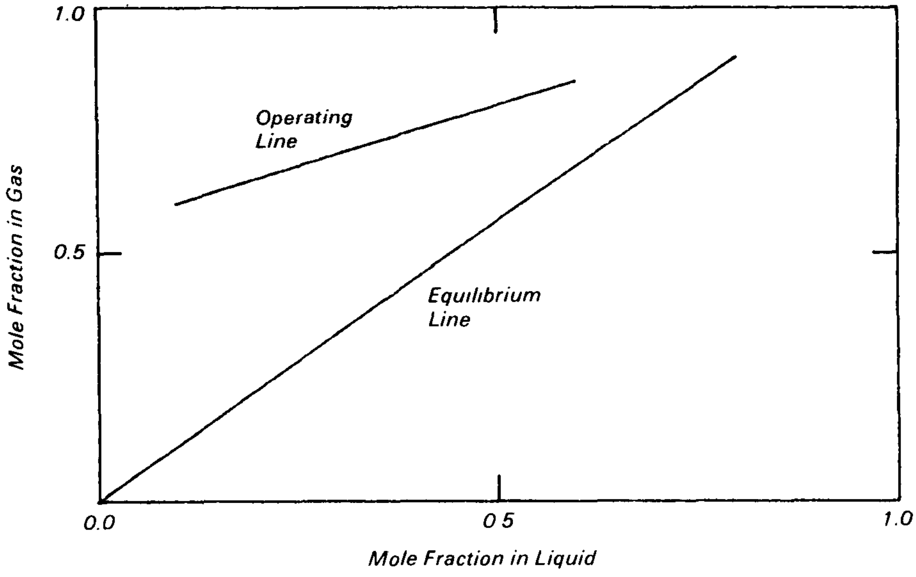

Figure 1. *Absorption with physical solvents.*

for mass transfer. Thus, when the operating line and the equilibrium line intersect, the two phases are in equilibrium and no mass transfer can take place. This condition is commonly referred to as a pinched condition in the column. If a pinch occurs, additional packing height will not result in improved separation of this species. For the experimental conditions of this study, the absorption of all major coal gas species was controlled by pinched conditions.

If the slope of the equilibrium line is greater than that of the operating line and an intersection occurs, it is clear from Figure 1 that the intersection will be at the top of the diagram, which represents the bottom of the column. If the slope of the operating line is greater, the intersection will occur at the bottom of the diagram (the top of the column). Since the slope of the equilibrium line decreases with increasing solubility, the absorption of species that have a high solubility in methyl alcohol will be controlled by equilibrium at the top of the absorber if a pinch occurs. Conversely, the absorption of species that are slightly soluble in methyl alcohol will be controlled by equilibrium at the bottom of the absorber.

When absorption is controlled by a pinch at the bottom of the column, the concentration of solute in the absorber exit gas is highly sensitive to its concentration in the absorber feed gas. If, however, absorption is controlled by a pinch at the top of the column, the concentration of solute in the absorber exit gas is governed primarily by its concentration in the liquid stream entering the absorber, or by the effectiveness of the solvent regeneration.

Table 2 gives the relative solubilities of the major coal gas species in methyl alcohol. As seen, the acid gas species CO_2, H_2S, and COS are highly soluble and their absorption is very sensitive to regeneration. Other major components are, however, only slightly soluble and are insensitive to regeneration.

Simulation

The regeneration of methyl alcohol may be simulated by flash tank and stripping algorithms developed as part of this project. An adiabatic flash tank algorithm for methyl alcohol and the major coal gas species was developed that gave predictions that were in good agreement with pilot plant data. In addition, an algorithm for the multicomponent stripping of major coal gas species from methyl alcohol was developed that also agreed well with pilot plant data. Trace components may be included in these algorithms if equilibrium and physical property data are available or may be predicted. These models may be used independently to predict the composition of methyl alcohol exiting a regeneration operation, or in conjunction with the absorpotion model to simulate a complete acid gas removal system. Although, these algorithms were developed for the methyl alcohol solvent, they may be modifed to simulate absorption and regeneration of coal gas species in other physical solvents as well.

Table 2. *Relative Solubilities in Methanol at -40° C*

Gas	*Solubility of Gas/Solubility of H_2*
H_2S	2540
COS	1555
CO_2	430
CH_4	12
CO	5
N_2	2
H_2	1

Table 3 shows the trace compounds produced by the gasifier and measured in this study, together with the lower detection limits for each species and the ranges of concentrations found in the AGRS feed gas. The relatively large variations in the concentrations of most trace components in the sour gas can probably be attributed to changes in reactor conditions and coal composition. Ten runs were selected for experiments to determine the effect of solvent regeneration conditions on the fate of trace components. For these runs the absorber was operated at conditions to give the maximum absorption possible.

For the compounds that did not accumulate in the methanol solvent and therefore have good mass balance closures, it should be possible to predict the concentration of the compound in the gas phase resulting from a flash operation. A simple flash model, using Henry's Law constant from the literature, was used to do this. The mass balance closures for the aliphatic hydrocarbons were usually good, and an example of the prediction for ethylene and ethane is shown in Figure 2. The agreement between predicted and observed is quite good for ethylene and ethane, and is reasonably good for the other hydrocarbons that were sufficiently volatile so that they did not accumulate in the solvent.

Table 3. *Trace Components In the AGRS Feed Gas*

Trace Component	*Lower Detection Limit, ppm*	*Range of Concentration in AGRS Feed Gas ppm*
Thiophene	3	11 - 26
CH_3SH	2	19 - 45
C_2H_5SH	2	ND - 2
CS_2	1	ND - 5
C_2H_4	20	1278 - 3729
C_2H_6	20	1809 - 5581
C_3H_6	20	331 - 1290
C_3H_8	20	125 - 595
C_4H_8	20	125 - 626
C_4H_{10}	20	44 - 186
Benzene	8	165 - 1040
Toluene	8	24 - 242
Ethylbenzene	3	ND - 21
P-Xylene	2	ND - 10
M-Xylene	2	ND - 21
O-Xylene	2	ND - 4

ND - None Detected

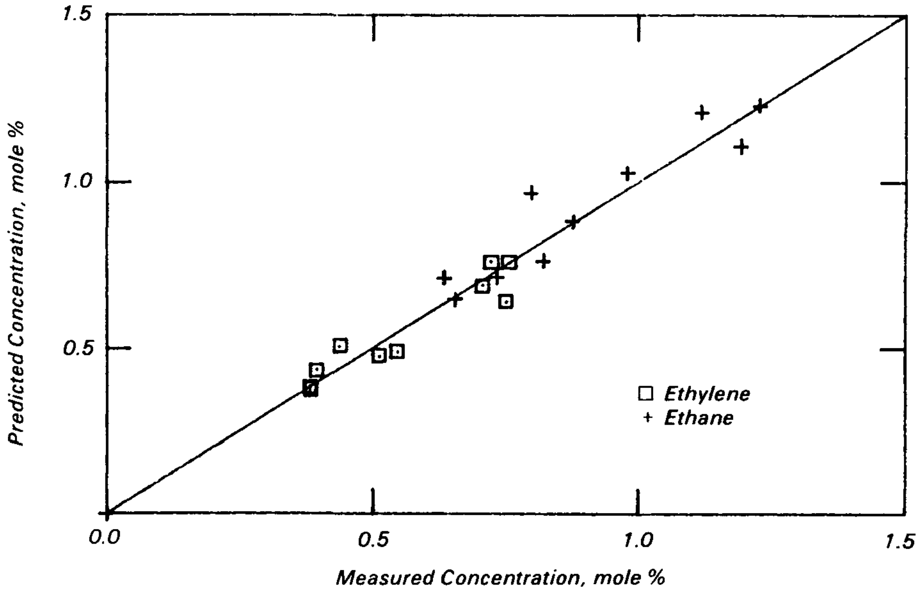

Figure 2. *Test of flash model.*

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***N. Dean Smith** is the EPA Project Officer (see below)*

The complete report, entitled "Regeneration of Refrigerated Methanol in Conditioning Gases from Coal," (Order No. PB 87-208 708/AS; Cost: $18.95, subject to change) will be available only from:

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